

Bernard Pajot

SPRINGER SERIES IN SOLID-STATE SCIENCES 158

# Optical Absorption of Impurities and Defects in Semiconducting Crystals

I. Hydrogen-like Centres



Springer



# Springer Series in **SOLID-STATE SCIENCES**

---

*Series Editors:*

M. Cardona P. Fulde K. von Klitzing R. Merlin H.-J. Queisser H. Störmer

The Springer Series in Solid-State Sciences consists of fundamental scientific books prepared by leading researchers in the field. They strive to communicate, in a systematic and comprehensive way, the basic principles as well as new developments in theoretical and experimental solid-state physics.

Please view available titles in *Springer Series in Solid-State Sciences*  
on series homepage <http://www.springer.com/series/682>

Bernard Pajot

# **Optical Absorption of Impurities and Defects in Semiconducting Crystals**

Hydrogen-like Centres

With 150 Figures

 Springer



Dr. Bernard Pajot  
Institut des NanoSciences de Paris, Campus Boucicaut  
rue de Lourmel 140, 75015 Paris, France  
E-mail: [bernard.pajot@insp.jussieu.fr](mailto:bernard.pajot@insp.jussieu.fr)

*Series Editors:*

Professor Dr., Dres. h. c. Manuel Cardona  
Professor Dr., Dres. h. c. Peter Fulde\*  
Professor Dr., Dres. h. c. Klaus von Klitzing  
Professor Dr., Dres. h. c. Hans-Joachim Queisser  
Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, 70569 Stuttgart, Germany  
\* Max-Planck-Institut für Physik komplexer Systeme, Nöthnitzer Strasse 38  
01187 Dresden, Germany

Professor Dr. Roberto Merlin  
Department of Physics, University of Michigan  
450 Church Street, Ann Arbor, MI 48109-1040, USA

Professor Dr. Horst Störmer  
Dept. Phys. and Dept. Appl. Physics, Columbia University, New York, NY 10027 and  
Bell Labs., Lucent Technologies, Murray Hill, NJ 07974, USA

Springer Series in Solid-State Sciences ISSN 0171-1873  
ISBN 978-3-540-95955-7 e-ISBN 978-3-540-95956-4  
DOI 10.1007/b135694  
Springer Heidelberg Dordrecht London New York

Library of Congress Control Number: 2009929171

© Springer-Verlag Berlin Heidelberg 2010

This work is subject to copyright. All rights are reserved, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilm or in any other way, and storage in data banks. Duplication of this publication or parts thereof is permitted only under the provisions of the German Copyright Law of September 9, 1965, in its current version, and permission for use must always be obtained from Springer. Violations are liable to prosecution under the German Copyright Law.

The use of general descriptive names, registered names, trademarks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

*Cover design:* eStudio Calamar Steinen

Printed on acid-free paper

Springer is part of Springer Science+Business Media ([www.springer.com](http://www.springer.com))

---

## Foreword

During World War II and in the years immediately following its end, the importance of silicon and germanium as semiconductors and their potential for solid state electronics became very apparent. The growth of bulk semiconductors, free from structural and chemical imperfections, followed by the deliberate introduction of specific impurities, were recognized as the strategy for solid state electronics, e.g. the transistor. It was established that when group V or III impurities were incorporated substitutionally in the elemental Si or Ge, free carriers were released in the host making it n-type or p-type. Simple arguments based on the tetrahedral bonding scheme showed that the group V and the III impurities, i. e., donors and acceptors, became Coulomb centres for the electrons and holes released, respectively. The large dielectric constant of the host and the effective mass of the charge carrier bound to the screened Coulomb potential of the donors or acceptors led to the important insight that the ionization energies of these centres will be small and that Lyman lines associated with them should be observed at low temperatures. These were experimentally observed in the middle infrared for Si and the far infrared for Ge. A complete understanding of the bound states of group V donors and group III acceptors followed after their relationship with the band structure of the host semiconductors was recognized.

In the past five decades, a number of donors, acceptors, and their complexes with excitons in semiconductors have been discovered and delineated. Isoelectronic impurities and their localized vibrational modes have also been extensively studied in infrared absorption and Raman and luminescence spectroscopies.

The present volume entitled “Optical Absorption of Impurities and Defects in Semiconducting Crystals – Hydrogen-like Centres” is by Dr. Bernard Pajot. He is an internationally recognized condensed matter experimenter. He has made numerous significant contributions to the field of donors and acceptors; local vibrations of oxygen related complexes in Si and Ge and magneto- and piezo-spectroscopy of donors and acceptors. This volume contains an authoritative and clear presentation of the theory of donors and acceptors. The

figures of apparatus and spectra, the tables, and the extensive bibliography will be significant resources for practicing scientists. Advanced graduate and postgraduate students will find it invaluable in their study of semiconductor physics.

The scientific community is indebted to Dr. Bernard Pajot for this comprehensive account of an important branch of the science of semiconductors.

West Lafayette  
June 2009

*Anant K. Ramdas*

---

## Preface

Most of the technological applications of semiconducting or insulating crystals come from the adjunction in these materials of foreign atoms which modify their electrical, optical, or optoelectrical properties. These dopant atoms can have to compete with foreign atoms or atomic complexes already present in the initial materials or arising from pollution during growth or technological processing. The properties of natural crystals, and, especially, their colour, are also modified by the presence of foreign impurity centres. From a general point of view, much has been learnt of the properties of these centres and on their mutual interaction by the methods of optical spectroscopy.

Spectroscopic measurements have shown that these centres, when electrically active, could be generally characterized by their electronic absorption, luminescence, and Raman scattering spectra, while vibrational absorption and Raman scattering are independent from the electrical activity.

From the coupling of the spectroscopic results with electrical measurements has emerged a classification of the electrically-active foreign centres into hydrogen-like (H-like) centres on the one side, opposed to deep centres on the other side. This classification is somewhat abrupt as there exist centres, like those related to the transition metals, which can display properties related to one or to the other category.

A H-like centre in a crystal can be visualized as a fixed ion (atom or complex) with a positive or negative elementary charge interacting through a screened Coulomb potential with a negative or positive elementary charge able to move in the crystal with the effective mass of a free electron or hole. The resulting entity resembles, *mutatis mutandis*, a H-like atom in atomic spectroscopy, hence its name. A consequence of the above structure is that the energies of its electronic excited states depend only on the effective mass of the charged particle and on the dielectric constant of the crystal, so that the H-like centres are also called effective-mass (EM) centres. This definition excludes from my presentation of the purely ionic insulators, in which no H-like centre of this kind can exist.

The fact that shallow p- and n-type dopants of germanium could be considered as H-like atoms emerged at the end of the 1940s to explain the electrical conductivity of this material, and this was clearly expressed by William Shockley in his monograph “Electrons and holes in semiconductors”, first published in 1950.

The absorption of H-like centres in semiconductors has been one of my main fields of research. In this volume, I provide a status of their electronic absorption, as known in 2009, and show its evolution from the mid-twentieth century and what this spectroscopy has brought to the understanding of the properties of semiconductors. This evolution has been marked by the improvement of the spectrometer–detector combinations, which have allowed an increase of the spectral resolution by nearly three orders of magnitude, and the production of semiconductor materials like the quasi-monoisotopic crystals, which bring new information on the H-like centres and on the role of isotopic disorder.

In an applied perspective, the interest in the spectroscopy of shallow impurities in semiconductors has been linked for a long time with the production of detectors for the medium and far infrared, but the possibility to produce terahertz lasers based on the transitions between discrete shallow levels has aroused a renewed interest in this spectroscopy in silicon. Another new potential field of application is the domain of quantum computing. A large part of the results presented in this book concerns silicon and this reflects the relative volume of investigations devoted to this material.

This book is the first of two books devoted to the optical absorption of impurities and defects in semiconducting and insulating crystals. The second one deals with the electronic absorption of deep centres like the native and irradiation defects or some transition metals, and with the vibrational absorption of impurity centres and defects.

Chapter 1 of the present volume provides the basic concepts related to the properties and characterization of the centres known as shallow dopants, the paradigm of the H-like centres. This is followed by a short history of semiconductors, which is intimately connected with these centres, and by a section outlining their electrical and spectroscopic activities. Because of the diversity in the notations, I have included in this chapter a short section on the different notations used to denote the centres and their optical transitions. An overview of the origin of the presence of H-related centres in crystals and guidelines on their structural properties is given in Chap. 2. To define the conditions under which the spectroscopic properties of impurities can be studied, Chap. 3 presents a summary of the bulk optical properties of semiconductor crystals. Chapter 4 describes the spectroscopic techniques and methods used to study the optical absorption of impurity and defect centres and the methods used to produce controlled perturbations of this absorption, which provide information on the structure of the impurity centres, and eventually on some properties of the host crystal. Chapter 5 is a presentation of the effective-mass theory of impurity centres, which is the basis for a quantitative interpretation

of the impurity spectra. Extensive sets of calculated energy levels obtained by variational or nonvariational methods are given in this chapter for EM donors and acceptors in silicon and germanium. For donors, it is shown how numerical values of the energy levels can be obtained for other cubic semiconductors of known band structures and dielectric constants. The implication of the degeneracy of the conduction band on the symmetry and eventual splitting of the donor states is discussed with application to silicon and diamond. A brief discussion is also given of the results of the calculations for the wurtzite form of SiC. For acceptors, I stress the importance of the value of the spin-orbit splitting of the valence band on the occurrence of EM impurity levels associated with the split-off valence band. This chapter ends with the calculation of the oscillator strengths of the main transitions of the donor and acceptor spectra. Experimental results on the absorption and photoconductive EM donor spectra in semiconductors can be found in Chap. 6. The main part is devoted to group-IV semiconductors, starting with the relatively well-known isolated single and double donors and pursuing with the donor complexes, with a large part devoted to thermal donors in silicon and germanium. Some results on EM-like spectra associated with interstitial iron and on donor-like properties of group-I atoms in silicon are also presented. It is also shown that isoelectronic-bound excitons in silicon can give, under appropriate conditions, absorption spectra similar to those of the EM donors. In the absorption of donors in compound semiconductors, we distinguish between the quasi-hydrogenic EM donors in direct-gap semiconductors and the donors in indirect-gap semiconductors with camel's back structure. As the quasi-hydrogenic donors in III-V compounds are characterized by rather small ionization energies, the widths of the lines of their spectra are broad and spectroscopic results obtained under a magnetic field, giving sharper lines are also presented. When possible, information on calibration coefficients relating the intensities of the absorption lines and the concentrations of the centres is provided. This chapter ends with a section dealing with the low-frequency excitations associated with the equivalent in semiconductors of the negative hydrogen ion in atomic physics, and to impurity absorption features due to hopping processes in heavily doped semiconductors. Chapter 7 is the equivalent of Chap. 6 for acceptors, and the spectroscopic properties of shallow acceptors in different semiconductors are described, showing the importance of the valence band structure and more specially of the spin-orbit interaction for the acceptor spectra in silicon and diamond. In Chap. 8, the effects of external and internal perturbations, including mechanical stress, magnetic, and electric fields on the absorption spectra of impurities are discussed. This allows also to discuss more synthetically of the line widths of the EM transitions observed in semiconductors and insulators as a function of the actual properties of different samples. To facilitate reading, appendices on energy units, energy-gap values, Bravais lattices, and group theory have been included.

This book, intended for students and scientists interested in the optical properties of semiconductors, should also be useful to scientists and engineers

interested or involved in the characterization of semiconductors. For the understanding of the principles underlying the experimental data, an elementary knowledge of quantum mechanics applied to spectroscopy and of solid-state physics is required.

I thank Michael Steger and Mike Thewalt for the communication of unpublished high-resolution absorption data on phosphorus in natural silicon and on boron and phosphorus in quasi-monoisotopic silicon. The spectrum of phosphorus in diamond displayed in Chap. 6 is the fruit of a collaboration with Etienne Gheeraert and Nicolas Casanova on a sample grown at the National Institute of Materials Science, at Tsukuba, Japan, by Satoshi Koizumi and Tokuyuki Teraji. I am grateful to Paul Clauws for providing synthetic data on thermal donors in germanium and to Kurt Lassmann for a clear formulation of the principles of phonon spectroscopy. Naomi Fujita, Ivan Ivanov, Vladimir Markevitch, Ben Murdin, and Sergey Pavlov are thanked for kindly sending information, reprints and figures. I am also indebted to Calvin Hamilton for a high-resolution image of the Hope diamond. Bernard Clerjaud is warmly thanked for a critical reading of the manuscript and for his suggestions and Anant Ramdas for having accepted to write the foreword. The help and the suggestions of Claude Naud for a substantial part of the spectroscopic results obtained at the Groupe de Physique des Solides-Laboratoire d'Optique des Solides (now Institut des NanoSciences de Paris, alias INSP) is gratefully acknowledged. I also thank Claudine Noguera, director of INSP, for allowing me to write this book in the frame of this Institute. Last, but not least I thank Claus Ascheron, for his patience during the preparation of the manuscript of this book and Adelheid Duhm for her support in the editing phase.

Paris  
12 June 2009

*Bernard Pajot*



---

## Notations and Symbols

Symbols in bold characters denote vectors. I have tried to comply with the IUPAC recommendations, but when the same letter is used too often, I have diverged (e.g.  $k_B$  for the Boltzmann constant). When confusion with chemical symbols is possible, the abbreviations are generally in italics.

### Acronyms

|           |                                          |
|-----------|------------------------------------------|
| <i>AB</i> | Antibonding or antibonded                |
| AM        | Average mass                             |
| amu       | Atomic mass unit                         |
| a.u.      | Atomic unit                              |
| <i>BC</i> | Bond-centred                             |
| BE        | Bound exciton                            |
| <i>BL</i> | Bravais lattice                          |
| BRN       | Background radiation noise               |
| BZ        | Brillouin zone                           |
| CAS       | Calorimetric absorption spectroscopy     |
| <i>CB</i> | Conduction band                          |
| CR        | Cyclotron resonance                      |
| CZ        | Czochralski                              |
| DAC       | Diamond anvil cell                       |
| DAP       | Donor-acceptor pair                      |
| DoS       | Density of states                        |
| DPA       | Deformation potential approximation      |
| EM(A)     | Effective mass (approximation)           |
| EMT       | Effective-mass theory                    |
| ENDOR     | Electron nuclear double resonance        |
| ESR       | Electron spin resonance                  |
| EXAFS     | Extended x-ray absorption fine structure |
| FE        | Free exciton                             |

|            |                                                   |
|------------|---------------------------------------------------|
| FEL        | Free-electron laser                               |
| FA         | Foreign atom                                      |
| FT(S)      | Fourier transform (spectrometer)                  |
| FWHM       | Full width at half maximum                        |
| FZ         | Float-zone or floating zone                       |
| h-e        | High-energy                                       |
| HB         | Horizontal Bridgman                               |
| HPHT       | High pressure, high temperature                   |
| HSL        | High-stress limit                                 |
| HVPE       | Hydride vapour phase epitaxy                      |
| IA         | Isoelectronic acceptor                            |
| <i>IA</i>  | Integrated absorption                             |
| IBE        | Isoelectronic bound exciton                       |
| ID         | Isoelectronic donor                               |
| IR         | Infrared                                          |
| <i>IR</i>  | Irreducible representation                        |
| IS         | Isotope shift                                     |
| JT         | Jahn-Teller                                       |
| LA         | Longitudinal acoustic                             |
| LEC        | Liquid encapsulated Czochralski                   |
| LHeT       | Liquid helium temperature                         |
| LNT        | Liquid nitrogen temperature                       |
| LO         | Longitudinal optic                                |
| LVM        | Localized vibrational mode                        |
| MBE        | Molecular beam epitaxy                            |
| MIT        | Metal-insulator transition                        |
| MOCVD      | Metal-organic chemical vapour deposition          |
| MOVPE      | Metal-organic vapour phase epitaxy                |
| NEP        | Noise equivalent power                            |
| <i>nn</i>  | Nearest neighbour                                 |
| <i>nnn</i> | Next nearest neighbour (second nearest neighbour) |
| NTD        | Neutron or nuclear-transmutation-doping or -doped |
| OS         | Oscillator strength                               |
| PAC        | Perturbed angular correlation                     |
| PL         | Photoluminescence                                 |
| PTI(S)     | Photo-thermal ionization (spectroscopy)           |
| QHD        | Quasi-hydrogenic donor                            |
| qmi        | Quasi-monoisotopic                                |
| RT         | Room temperature                                  |
| SHM        | Scaled hydrogen model                             |
| SIMS       | Secondary ion mass spectroscopy                   |
| s-o        | Spin-orbit                                        |
| SPL        | Selective photoluminescence                       |
| STD        | Shallow thermal donor                             |
| TA         | Transverse acoustic                               |

|           |                                   |
|-----------|-----------------------------------|
| TD        | Thermal donor                     |
| TDD       | Thermal double donor              |
| TEC       | Thermal equilibrium conditions    |
| TEM       | Transmission electron microscopy  |
| TM        | Transition metal                  |
| TPA       | Two-photon absorption             |
| TO        | Transverse optic                  |
| USTD      | Ultrashallow thermal donor        |
| <i>VB</i> | Valence band                      |
| ZPL       | Zero-phonon line (no-phonon line) |

## Symbols

|           |                                                                       |
|-----------|-----------------------------------------------------------------------|
| $a_0^*$   | Effective Bohr radius                                                 |
| <i>B</i>  | Magnetic field flux density                                           |
| <b>B</b>  | Magnetic field                                                        |
| Ch        | Chalcogen atom                                                        |
| <i>d</i>  | Sample thickness                                                      |
| <i>E</i>  | Electric field strength, doubly degenerate irreducible representation |
| <b>E</b>  | Electric field                                                        |
| <i>E</i>  | Energy, identity operation                                            |
| $E_g$     | Band gap energy                                                       |
| $E_i$     | Ionization energy                                                     |
| <i>g</i>  | <i>g</i> -factor                                                      |
| <i>I</i>  | Inversion operation                                                   |
| <b>I</b>  | Nuclear spin                                                          |
| <i>k</i>  | Extinction coefficient                                                |
| <b>k</b>  | Electron or photon wave vector                                        |
| <i>K</i>  | Compensation ratio                                                    |
| $K$       | Absorption coefficient                                                |
| $k_B$     | Boltzmann constant                                                    |
| $\bar{m}$ | Reduced effective mass or reduced mass                                |
| $m_e$     | Free electron mass                                                    |
| $m_n$     | Electron effective mass                                               |
| $m_h$     | Hole effective mass                                                   |
| <b>M</b>  | Metal atom                                                            |
| <i>n</i>  | Refractive index, principal quantum number, neutron, integer          |
| <i>n</i>  | Electron or free carrier concentration, occupation number             |
| <b>N</b>  | Interference order                                                    |
| $N_c$     | Conduction band density of state                                      |
| <i>N</i>  | Number per unit volume                                                |
| $N_c$     | Critical concentration                                                |
| <i>P</i>  | Polarization, parity                                                  |
| <i>p</i>  | Hole concentration                                                    |

#### XIV Notations and Symbols

|               |                                                                         |
|---------------|-------------------------------------------------------------------------|
| $\mathbf{q}$  | Phonon wave vector                                                      |
| $q$           | Effective charge                                                        |
| $R$           | Reflectance                                                             |
| $R$           | Reflectivity                                                            |
| $R_H$         | Hall coefficient                                                        |
| $R_\infty^*$  | Effective Rydberg constant                                              |
| $T$           | Transmittance                                                           |
| $T$           | Temperature, stress magnitude                                           |
| $\alpha$      | Polarisability                                                          |
| $\beta$       | Parameter                                                               |
| $\gamma$      | Ratio of transverse and longitudinal effective masses, damping constant |
| $\gamma_B$    | Effective magnetic field parameter $\hbar\omega_c/2R_\infty^*$          |
| $\Delta_{so}$ | Spin-orbit splitting or energy                                          |
| $\Delta_{CF}$ | Crystal field energy                                                    |
| $\varepsilon$ | Dielectric constant                                                     |
| $\epsilon_s$  | Static dielectric constant                                              |
| $\epsilon$    | Strain                                                                  |
| $\lambda$     | Wavelength                                                              |
| $\mu$         | Mobility, chemical potential                                            |
| $\rho$        | Electrical resistivity                                                  |
| $\sigma$      | Electrical conductivity                                                 |
| $\sigma$      | Mechanical stress                                                       |
| $\tau$        | Lifetime                                                                |
| $\omega$      | Pulsation (angular frequency)                                           |
| $\omega_c$    | Cyclotron pulsation                                                     |
| $[X]$         | Concentration of centre X per $\text{cm}^3$                             |

---

# Contents

|          |                                                        |    |
|----------|--------------------------------------------------------|----|
| <b>1</b> | <b>Introduction</b>                                    | 1  |
| 1.1      | Basic Concepts                                         | 1  |
| 1.2      | A Short Historical Survey                              | 3  |
| 1.3      | General Properties of the Hydrogen-Like Centres        | 5  |
| 1.3.1    | What are the Hydrogen-Like Centres                     | 5  |
| 1.3.2    | Electrical Activity                                    | 6  |
| 1.3.2.1  | Compensation                                           | 8  |
| 1.3.2.2  | Passivation                                            | 11 |
| 1.3.3    | Optical Transitions                                    | 11 |
| 1.3.4    | Bound Excitons                                         | 14 |
| 1.3.5    | Spin Effects                                           | 16 |
| 1.4      | Notations for Centres and Optical Transitions          | 17 |
|          | References                                             | 18 |
| <b>2</b> | <b>Origins and Atomic Properties of H-Like Centres</b> | 21 |
| 2.1      | Origins                                                | 21 |
| 2.1.1    | Occurrence in Nature                                   | 21 |
| 2.1.2    | Contamination                                          | 22 |
| 2.1.3    | Doping                                                 | 25 |
| 2.1.4    | Thermal Treatments and Irradiation                     | 29 |
| 2.1.5    | Concentration Measurements                             | 30 |
| 2.2      | Structural Properties                                  | 31 |
| 2.2.1    | Global Atomic Configurations                           | 31 |
| 2.2.2    | Solubilities and Diffusion Coefficients                | 35 |
| 2.2.2.1  | Solubility                                             | 35 |
| 2.2.2.2  | Diffusion Coefficients                                 | 37 |
| 2.2.3    | Lattice Distortion and Metastability                   | 38 |
|          | References                                             | 42 |

|          |                                                                    |     |
|----------|--------------------------------------------------------------------|-----|
| <b>3</b> | <b>Bulk Optical Absorption</b>                                     | 45  |
| 3.1      | Refractive Index and Dielectric Constant                           | 45  |
| 3.2      | Intrinsic Lattice Absorption                                       | 50  |
| 3.2.1    | One-Phonon Effect                                                  | 50  |
| 3.2.2    | Multi-Phonon Absorption and Anharmonicity                          | 55  |
| 3.3      | Electronic Absorption                                              | 57  |
| 3.3.1    | Energy Gap and Fundamental Absorption                              | 57  |
| 3.3.2    | Excitons                                                           | 74  |
| 3.3.3    | Free-Carrier Effects                                               | 77  |
|          | References                                                         | 81  |
| <b>4</b> | <b>Methods and Techniques of Absorption Spectroscopy of Solids</b> | 85  |
| 4.1      | Introduction                                                       | 85  |
| 4.2      | Radiation Sources and Spectrometers                                | 89  |
| 4.2.1    | Tunable Sources                                                    | 89  |
| 4.2.2    | Broadband Sources                                                  | 90  |
| 4.2.3    | Spectrometers                                                      | 91  |
| 4.2.3.1  | Dispersive Monochromators                                          | 91  |
| 4.2.3.2  | Fourier Transform Spectrometers                                    | 94  |
| 4.3      | Filtering and Polarization                                         | 99  |
| 4.4      | Radiation Detection                                                | 100 |
| 4.4.1    | Thermal Detection                                                  | 100 |
| 4.4.2    | Photoconductive Detection                                          | 103 |
| 4.4.2.1  | Intrinsic Photoconductors                                          | 103 |
| 4.4.2.2  | Extrinsic Photoconductors                                          | 104 |
| 4.4.3    | Limits to Detectors Sensitivity                                    | 106 |
| 4.5      | Conditioning the Samples                                           | 110 |
| 4.6      | Cooling the Samples                                                | 111 |
| 4.7      | Compressing the Samples                                            | 115 |
| 4.7.1    | Uniaxial Stresses                                                  | 115 |
| 4.7.2    | Hydrostatic Stresses                                               | 116 |
| 4.8      | Magneto-optical Measurements                                       | 119 |
|          | References                                                         | 121 |
| <b>5</b> | <b>Effective-Mass Theory and its Use</b>                           | 125 |
| 5.1      | Initial Assumptions                                                | 125 |
| 5.1.1    | Selection Rules                                                    | 127 |
| 5.2      | Donor Centres                                                      | 128 |
| 5.2.1    | The One-Valley Approximation                                       | 128 |
| 5.2.2    | Conduction Band Degeneracy                                         | 140 |
| 5.2.3    | The Quasi-Hydrogenic Case                                          | 145 |
| 5.3      | Acceptor Centres                                                   | 148 |

|          |                                               |            |
|----------|-----------------------------------------------|------------|
| 5.4      | Oscillator Strengths                          | 159        |
| 5.4.1    | Donor Transitions                             | 160        |
| 5.4.2    | Acceptor Transitions                          | 163        |
|          | References                                    | 165        |
| <b>6</b> | <b>Donor and Donor-Like EM Spectra</b>        | <b>169</b> |
| 6.1      | Introduction                                  | 169        |
| 6.2      | Group-V and Li Donors in Group-IV Crystals    | 171        |
| 6.2.1    | Silicon                                       | 171        |
| 6.2.2    | Germanium                                     | 186        |
| 6.2.3    | Silicon Carbide                               | 193        |
| 6.2.4    | Diamond                                       | 196        |
| 6.3      | Group-VI- and Mg Donors in Group-IV Crystals  | 198        |
| 6.3.1    | Silicon                                       | 198        |
| 6.3.1.1  | The Neutral Charge State                      | 198        |
| 6.3.1.2  | The Singly-Ionized Charge State               | 208        |
| 6.3.1.3  | Other Chalcogen-Related Donors                | 215        |
| 6.3.2    | Germanium                                     | 218        |
| 6.4      | O-Related Donors in Group IV Crystals         | 220        |
| 6.4.1    | The Thermal Double Donors                     | 220        |
| 6.4.1.1  | Silicon                                       | 221        |
| 6.4.1.2  | Germanium                                     | 231        |
| 6.4.2    | The Shallow Thermal Donors in Silicon         | 236        |
| 6.4.3    | The Ultrashallow Thermal Donors in Silicon    | 241        |
| 6.5      | Other Shallow Donors Involving Hydrogen       | 242        |
| 6.6      | TMs, Group-I Elements and Pt in Silicon       | 243        |
| 6.6.1    | Interstitial Iron                             | 243        |
| 6.6.2    | Ag, Au, and Pt                                | 247        |
| 6.7      | Pseudo-Donors and Isoelectronic Donors        | 249        |
| 6.7.1    | The “C” and “P” Centres in Silicon            | 250        |
| 6.7.2    | The (S,Cu) Centre in Silicon                  | 253        |
| 6.7.3    | Pseudo-Donor BEs in Germanium                 | 254        |
| 6.8      | Donors in III-V and II-VI Compounds           | 255        |
| 6.8.1    | Quasi-Hydrogenic Effective-Mass Donors        | 257        |
| 6.8.1.1  | Cubic Semiconductors                          | 257        |
| 6.8.1.2  | Non-Cubic Semiconductors                      | 261        |
| 6.8.2    | Semiconductors with CB Degeneracy             | 263        |
| 6.9      | The $D^-$ Ion and Hopping Absorption          | 269        |
| 6.9.1    | The Donor Equivalent of $H^-$ : the $D^-$ Ion | 269        |
| 6.9.2    | Photon-Induced Hopping                        | 270        |
|          | References                                    | 272        |

|          |                                                                     |     |
|----------|---------------------------------------------------------------------|-----|
| <b>7</b> | <b>EM Acceptor Spectra</b>                                          | 281 |
| 7.1      | Introduction                                                        | 281 |
| 7.2      | Group-III Acceptors in Group-IV Crystals                            | 282 |
| 7.2.1    | Silicon                                                             | 282 |
| 7.2.1.1  | The $p_{3/2}$ Spectra                                               | 283 |
| 7.2.1.2  | The $p_{1/2}$ Spectra                                               | 298 |
| 7.2.2    | Germanium                                                           | 300 |
| 7.2.2.1  | Single Acceptor Complexes                                           | 304 |
| 7.2.3    | Diamond and SiC                                                     | 307 |
| 7.3      | Groups-II and -I Acceptors in Group-IV Crystals                     | 311 |
| 7.3.1    | Germanium                                                           | 312 |
| 7.3.1.1  | The $A^0$ Charge State                                              | 312 |
| 7.3.1.2  | The $A^-$ Charge State                                              | 315 |
| 7.3.2    | Silicon                                                             | 317 |
| 7.4      | An Isoelectronic Acceptor: the $\text{Be}_2$ Pair in Silicon        | 323 |
| 7.5      | An Acceptor Equivalent of $\text{H}^-$ : the $A^+$ Ion              | 327 |
| 7.6      | Acceptors in III-V and II-VI Semiconductors                         | 328 |
| 7.6.1    | Groups-II and -IV Acceptors in III-V Compounds                      | 328 |
| 7.6.2    | The $\text{B}_{\text{As}}$ (78-meV/203-meV) Double Acceptor in GaAs | 334 |
| 7.6.3    | TMs Acceptors in III-V Compounds                                    | 335 |
| 7.6.4    | Acceptors in II-VI Compounds                                        | 337 |
|          | References                                                          | 339 |
| <b>8</b> | <b>Effects of Perturbations</b>                                     | 347 |
| 8.1      | Introduction                                                        | 347 |
| 8.2      | Mechanical Stresses                                                 | 348 |
| 8.2.1    | Effects on Electronic Transitions                                   | 349 |
| 8.2.1.1  | EM Donors with CB Degeneracy                                        | 350 |
| 8.2.1.2  | EM Acceptors                                                        | 373 |
| 8.2.1.3  | Stress-Induced Inhomogeneous Broadening                             | 382 |
| 8.2.2    | Uniaxial Stress and Orientational Degeneracy                        | 384 |
| 8.3      | Effect of Magnetic Fields                                           | 388 |
| 8.3.1    | Shallow Donors in Multi-Valley Semiconductors                       | 389 |
| 8.3.1.1  | Silicon                                                             | 391 |
| 8.3.1.2  | Germanium                                                           | 394 |
| 8.3.1.3  | Diamond                                                             | 397 |
| 8.3.2    | Shallow Acceptors                                                   | 397 |
| 8.3.2.1  | Silicon                                                             | 402 |
| 8.3.2.2  | Germanium                                                           | 405 |
| 8.3.2.3  | Diamond                                                             | 409 |
| 8.3.2.4  | Compound Semiconductors                                             | 409 |
| 8.4      | Effect of Electric Fields                                           | 411 |
| 8.4.1    | Homogeneous Electric Fields                                         | 411 |
| 8.4.2    | Internal Electric Fields                                            | 415 |



|                                                                                                                |                                               |            |
|----------------------------------------------------------------------------------------------------------------|-----------------------------------------------|------------|
| 8.5                                                                                                            | Line Widths and Lifetimes . . . . .           | 418        |
| 8.5.1                                                                                                          | Phonon Broadening . . . . .                   | 419        |
| 8.5.2                                                                                                          | Concentration Broadening . . . . .            | 422        |
| 8.5.3                                                                                                          | Lifetimes . . . . .                           | 422        |
|                                                                                                                | References . . . . .                          | 424        |
| <b>Appendix A Energy Units Used in Spectroscopy<br/>and Solid-State Physics . . . . .</b>                      |                                               | <b>431</b> |
| <b>Appendix B Bravais Lattices, Symmetry and Crystals . . . . .</b>                                            |                                               | <b>433</b> |
| B.1                                                                                                            | The Reciprocal Lattice . . . . .              | 435        |
| B.2                                                                                                            | Lattice Planes and Miller Indices . . . . .   | 436        |
| B.3                                                                                                            | A Toolbox for Symmetry Groups . . . . .       | 437        |
| B.3.1                                                                                                          | The Abstract Groups . . . . .                 | 437        |
| B.3.2                                                                                                          | The Symmetry Point Groups . . . . .           | 438        |
| B.3.3                                                                                                          | Representations and Basis Functions . . . . . | 439        |
| B.3.4                                                                                                          | The Symmetry Space Groups . . . . .           | 442        |
| B.4                                                                                                            | Some Crystal Structures . . . . .             | 444        |
| B.4.1                                                                                                          | Cubic Structures . . . . .                    | 444        |
| B.4.2                                                                                                          | Hexagonal Structures . . . . .                | 445        |
| B.4.3                                                                                                          | Other Crystal Structures . . . . .            | 447        |
|                                                                                                                | References . . . . .                          | 448        |
| <b>Appendix C Optical Band Gaps and Crystal Structures<br/>of Some Insulators and Semiconductors . . . . .</b> |                                               | <b>449</b> |
| <b>Appendix D Table of Isotopes . . . . .</b>                                                                  |                                               | <b>451</b> |
| <b>Appendix E Some Tensor Properties . . . . .</b>                                                             |                                               | <b>461</b> |
|                                                                                                                | References . . . . .                          | 462        |
| <b>Index . . . . .</b>                                                                                         |                                               | <b>463</b> |



# Introduction

## 1.1 Basic Concepts

In this monograph, semiconductors and covalent or partially covalent insulators are considered. These materials differ from metals by the existence, at low temperature, of a fully occupied electronic band (the valence band or *VB*) separated by an energy gap or band gap ( $E_g$ ) from an empty higher energy band (the conduction band or *CB*). When  $E_g$  reduces to zero, like in mercury telluride, the materials are called semimetals. In metals, the highest occupied band is only partially filled with electrons such that the electrons in this band can be accelerated by an electric field, however small it is.

From a chemical viewpoint, most of these semiconducting and insulating crystals are elements or compounds in which all the valence electrons are used to form covalent or partially covalent chemical bonds, leaving no extra electron for electrical conduction. This is the case for the diamond form of carbon, for silicon and germanium, for many crystals resulting from the combination of group-II $B$  or -III $A$  elements of the periodic table with group-V or -VI elements (the II-VI or III-V compounds), or for the partially ionic IB-VII (e.g.,  $\text{CuCl}$ ) compounds. In purely ionic insulators, like sodium chloride, electron capture from the electropositive element by the electronegative element produces ions with closed shells.

From an optical viewpoint, on the other hand, the difference between semiconductors and insulators lies in the value of  $E_g$ . The admitted boundary is usually set at 3 eV (see Appendix A for the energy units) and materials with  $E_g$  below this value are categorized as semiconductors, but crystals considered as semiconductors like the wurtzite forms of silicon carbide and gallium nitride have band gaps larger than 3 eV, and this value is somewhat arbitrary. The translation into the electrical resistivity domain depends on the value of  $E_g$ , and also on the effective mass of the electrons and holes, and on their mobilities. The solution is not unique; moreover, the boundary is not clearly defined. “Semi-insulating” silicon carbide 4H polytype samples with reported room temperature resistivities of the order of  $10^{10} \Omega \text{ cm}$  could constitute the

electrical limit between semiconductors and insulators, but the definition of such a limit is of moderate significance. In the following, for simplification, the term “semiconductors and insulators” are replaced by “semiconductors”.

In a category of materials known as Mott insulators, like MnO, CoO or NiO, with band gaps of 4.8, 3.4, and 1.8 eV, respectively ([2], and references therein), the upper energy band made from 3d states is partially occupied resulting in metallic conduction. The insulating behaviour of these compounds is attributed to a strong intra-atomic Coulomb interaction, which results in the formation of a gap between the filled and empty 3d states [35].

In the covalent or partially covalent semiconductor crystals, a free electron is created in the *CB* once sufficient energy has been provided to a *VB* electron to overcome the energy gap  $E_g$ . This energy can be produced thermally under equilibrium at temperature  $T$ , by optical absorption of photons with energies  $h\nu \geq E_g$ , or by irradiation with electrons in the keV energy range. These processes leave in the *VB* a positively charged free “hole”, which has no equivalent in metals, and whose absolute electric charge is the elementary charge. When free carriers can only be produced by the above processes, the materials are said to be intrinsic. When molecules and solids are tightly bound, the value of  $E_g$  for covalent or partially covalent semiconductors with  $sp^3$  bonding has been related to a covalent energy of the bonds, modulated by the so-called metallic energy involving atomic states [19].

A consequence of the existence of an electronic band gap is that at sufficiently low temperature, intrinsic semiconductors or insulators show no absorption of photon related to electronic processes for energies below  $E_g$ . Inversely, the photons with energies above  $E_g$  are strongly absorbed by optical transitions between the valence and conduction bands, and this absorption is called fundamental or intrinsic.

Compound semiconductor crystals show strong infrared absorptions in certain specific spectral region at photon energies below  $E_g$ , due to the vibrations of the atoms of the crystal lattice. In these regions, the lattice absorption can be so strong that the crystals are opaque for the usual thicknesses. At energies below the lattice absorption region, the crystals become transparent again. In elemental crystals like diamond ( $C_{\text{diam}}$ ) or silicon, this first-order vibration of the lattice atoms is not infrared-active and hence, the pure crystals of this kind do not become opaque, but they show, however, weaker absorption bands due to combinations of vibration modes of the crystal lattice.

Extrinsic semiconductors are materials containing foreign atoms (FAs) or atomic impurity centres that can release electrons in the *CB* or trap an electron from the *VB* with energies smaller than  $E_g$  (from neutrality conservation, trapping an electron from the *VB* is equivalent to the release of a positive hole in the otherwise filled band). These centres can be inadvertently present in the material or introduced deliberately by doping, and, as intrinsic, the term extrinsic refers to the electrical conductivity of such materials. The electron-releasing entities are called donors and the electron-accepting ones acceptors. When a majority of the impurities or dopants in a material is of

the donor (acceptor) type, the material is termed n-type (p-type) and the electrical conduction comes from electrons (holes). In semiconductors with  $E_g \gtrsim 0.6$  eV, the intrinsic free-carrier concentration can usually be neglected at room temperature (RT) compared to the extrinsic one. In these semiconductors, when the energy required to release a free carrier from the dominant donor or acceptor (the ionization energy) is comparable to the RT thermal energy ( $\sim 26$  meV), a measurement of the RT resistivity  $\rho = (ne\mu)^{-1}$ , where  $\mu$  is the mobility of the free carrier, gives a representative value of the concentration  $n$  of the dominant donor or acceptor. Above a temperature depending on the value of  $E_g$ , the concentration of the electron-hole pairs produced thermally in extrinsic materials can become comparable to the extrinsic carrier concentration, and the semiconductor is said to move into the intrinsic regime. The presence of free electrons produces at RT a Drude-type continuous optical absorption, increasing as  $\lambda^2$ , where  $\lambda$  is the wavelength of the radiation. The wavelength dependence of the free-hole absorption is not as simple. For some values of the donor or acceptor concentrations depending on  $E_g$ , the free-carrier absorption can be so large that the material becomes opaque in the whole spectral range. For still higher dopant concentrations, a transition to a quasi-metallic state occurs, which will be discussed later.

When the temperature is reduced, the free carriers in the extrinsic materials are normally re-trapped by the donor or acceptor centres that had released them and the resistivity of the materials increases.

A large number of semiconductors, used in various technologies and in pure and applied research, are known, and most of them are grown artificially. It is difficult to grow intrinsic semiconductors because FA contamination affects the crystal growth; moreover, except for very special uses<sup>1</sup>, there are not many applications for truly intrinsic materials. The purest available crystals thus contain residual impurity atoms or more complex centres. Some of the residual impurities are not electrically active and they cannot be detected by electrical methods, and hence, the term intrinsic cannot be taken as a synonym for high purity.

## 1.2 A Short Historical Survey

The Italian term “*semicoibente*”, found in the presentation by Alessandro Volta before the Royal Society of London in 1782, could be translated into “semi-badly-conducting”, but eventually was translated to “semi-conducting” in English, and qualified nearly insulating substances [53]. The review by Busch [6] gives an interesting historical survey of the emergence of the semiconductor physics and chemistry, but a good account of the early work

---

<sup>1</sup> The fabrication of ionization bolometers used at very low temperatures ( $\sim 60$  mK) for the detection of weakly interacting massive particles (WIMPs) from outside of the solar system requires intrinsic silicon or germanium material.

on semiconductors can also be found in the first chapter of the book by Smith [46]. Near 1908, on the ground of measurements performed on different solids, Johann Königsberger, from the Albert-Ludwig University, in Freiburg in Brisgau, proposed that the mobile charge carriers in solids resulted from the thermal dissociation of the atoms of a “metallic” conductor into electrons and remaining positive ions. As a function of the value of a parameter  $Q$ , proportional to a dissociation energy, Königsberger classified the solids into insulators, with  $Q$  tending to infinity, metals, with  $Q$  tending to zero at high temperature, and “variable conductors” (*Variable Leiter*), for which  $Q$  was found to have a finite value. The consequence for “variable conductors” was that their electrical conductivity increased exponentially with temperature. These so-called variable conductors were iron oxides, and iron and lead sulfide polycrystalline minerals. In 1911, Weiss, a student of Königsberger, used for the first time the word “semiconductor” (*Halbleiter*) in his thesis “Experimental Contribution to the Electronic Theory in the Field of Thermoelectricity” (*Experimentelle Beiträge zur Elektronentheorie aus dem Gebiet der Thermoelektrizität*). In this work, he studied the thermoelectric effect of different metals, graphite, silicon, and metallic oxides and sulfides and compared the results with the existing electron theories. In the above context, the terms “variable conductors” and “semiconductors” had the same meaning. The term “semiconductor” is found again in a common publication [29]. The electrical properties of these early semiconductors were often irreproducible, partly due to inhomogeneities, impurities, structural imperfections and poor electrical contacts (silicon was not explicitly recognized as a semiconductor then). Some physicists were wary of these problems encountered in the study of semiconductors, which lasted till the end of the 1930s, when potential uses were conceived beyond their use as materials for photodetectors for the infrared.

A basis to the understanding of the electronic properties of semiconductors was provided in two papers by Wilson [56], where the concepts of intrinsic and extrinsic semiconductors were introduced. The fundamental nature of extrinsic semiconduction in relation to the atomic dopants in silicon was demonstrated [44] and it was presented in a very pedagogical manner with germanium as an example in the textbook of Shockley [45]. Around the same time, silicon was prepared with an acceptable purity allowing transmission measurements to be performed (see for instance [15]). Subsequently, optical spectroscopy, which was used for the study of insulators like diamond [42] became and is still a widely used tool for the study and characterization of semiconductors. This is acknowledged in several books devoted to the optical properties of semiconductors including the spectroscopy of impurity centres [28, 34, 37], but other contributions have been written on specialized topics, like the ones by Ramdas and Rodriguez [41] on the electronic absorption of hydrogen-like donor and acceptor atoms in semiconductors, by Davies [9] on the optical properties of the luminescent centres in silicon, or the book by Newmann [36] on the vibrational absorption of impurity centres.

### 1.3 General Properties of the Hydrogen-Like Centres

The spectroscopic absorption of impurities and defects in semiconductors is in itself a vast subject as it includes electronic and vibrational absorption. Moreover, two kinds of electronic absorptions can be roughly distinguished: the one related to the p- and n-type dopants, which proved to be related to a more general category of centres called hydrogen-like or effective-mass centres, and the other due to the deep centres. The spectroscopic properties of transition metals (TMs) are an intermediate category as the spectra of these atoms and of their complexes display in some cases hydrogen-like properties. The content of this book is limited to the absorption of hydrogen-like centres, including complex centres, and to facilitate the understanding of the subject, a general presentation of the properties of these centres is given.

#### 1.3.1 What are the Hydrogen-Like Centres

Either from natural or artificial origin, the semiconducting and insulating crystals contain impurity centres, doping atoms or defects. These centres can be either electrically active or not electrically active, and we consider here the electrically active ones. A centre is electrically active if it can display more than one electronic charge state; this is the case for donor and acceptor centres. In the neutral charge state, the electrically active centres can contain one or two electrons (holes) bound to an inner core, and these electrons (holes) can be ionized in the conduction (valence) band with well-defined ionization energies. When the contribution of the inner core can be considered as that of a global ion or pseudo-ion, the interaction between the lowest energy electron (hole) and the inner positive (negative) core, including eventually the second particles, is mainly Coulombic. This has led to compare these centres to hydrogen-like (H-like) pseudo-atoms with excited states comparable to those of the H atom. A main difference originates from the embedding of these centres in a crystal matrix with static dielectric constant  $\epsilon_s$ , which reduces the Coulomb energy by a factor  $\epsilon_s^{-2}$  when the particle is not too close from the charged core. The second difference comes from the mass of the particle (the outer electron or hole), which is different from the mass  $m_e$  of the free electron *in vacuo*. In a first step of the modelling of the properties of H-like centres, the relevant masses are replaced by scalar “effective” masses  $m_e^*$  or  $m_h^*$ , for electrons and holes, respectively. As will be seen later, this is an oversimplification, but scalar values of the effective masses can be obtained from a modelling of the RT electrical measurements. The scaling factor of the energy of these centres with the energy spectrum  $E_{0n} = R_\infty/n^2$  of H in vacuum is  $s = (m^*/m_e)/\epsilon_s^2$ , where  $m^*$  is the appropriate effective mass. The energy  $E_n$  of the effective-mass particle in the  $n$ th excited state is thus  $1.36 \times 10^4 s/n^2$  (meV), where  $n$  is the principal quantum number. This is the basis of the effective mass theory (EMT), which is discussed in more detail in Chap. 5. Within this approximation, the ground state energy or level for

a H-like acceptor in silicon ( $m^*_h \cong 0.6m_e$ ,  $\varepsilon_s = 11.7$ ) is separated from the *VB* continuum by 60 meV compared with  $E_g = 1170$  meV, and for the donors in GaAs ( $m^*_e \cong 0.07m_e$ ,  $\varepsilon_s = 12.9$ ) by 5.7 meV from the *CB* continuum, compared with  $E_g = 1519$  meV. These values are orders of magnitude of the ionization energies of the shallowest of these centres, known as shallow centres, and the crude assumptions made cannot account for the effect of the *VB* and *CB* structures on the effective masses, as well as for the effect of the chemical nature of the impurity on the ionization energies, which can be important for semiconductors like silicon.

The technological importance of the shallow donors or acceptors is that they bind the electrons or holes with energies comparable to the RT thermal energy and that the carriers released at RT by these shallow centres act as a reservoir to control the electrical conductivity of the crystals. Under equilibrium, this release is a thermal process and as the electrons and holes are particles with non-integer spins, their energy distributions follow Fermi-Dirac statistics. At a given temperature  $T$ , the concentration of electrons and holes in the continua can be expressed as a function of the chemical potential  $\mu$  of the semiconductor and of the density of states (DoS) in the *CB* and the *VB* (see [3]). In metal physics, the Fermi level  $E_F$  is the energy of the electron level whose occupancy probability is  $1/2$  and it has the same meaning as the more general chemical potential. The term “Fermi level” has been extrapolated from metal to semiconductor physics, despite the fact that in semiconductors,  $E_F$  lies in the band gap, with a limited number of discrete allowed states. To comply with the common use, we keep the “Fermi level” which is at best a quasi-Fermi level.

At very low temperature, the concentration of free carriers in the continuum is negligible as they are trapped by the ionized impurity centres of opposite charges and  $E_F$  is close to the energy level  $E_i$  of the dominant impurity. This level separates the band gap into two regions: one, between  $E_i$  and the relevant band continuum, taken as the energy origin and a second one for energies between  $E_i$  and the opposite band continuum. In energy diagrams for single donors (*D*) or acceptors (*A*), the zone contiguous to the opposite continuum is denoted “+” for donors and “−” for acceptors as, when  $E_F$  lies in this zone, the centre is ionized ( $D^+$  or  $A^-$ ). Similarly, the second zone is denoted “0” because when  $E_F$  lies in this zone, the centre is neutral at low temperature ( $D^0$  or  $A^0$ ).

### 1.3.2 Electrical Activity

From a chemical aspect, the electrical activity of substitutional impurities and dopants is determined by the presence or absence of electrons after bonding with the nearest neighbour crystal atoms. Thus, it usually depends on the chemical nature of the impurity or, more simply, on the column of the periodic table it belongs to, compared to the atom(s) of the crystal. For a



monoatomic semiconductor crystal, a FA from the column next to the column of the atom it replaces acts usually as a single donor<sup>2</sup>, and when from the preceding column, as a single acceptor. Similarly, substitutional FAs from the second next column or before the column of the atom(s) of the crystal are double donors or acceptors, respectively. When the crystal is made up of two kinds of atoms belonging to different columns of the periodic table, the electrical activity of a substitutional FA depends on the site occupied, and when behaving as an acceptor on one site, it can behave as a donor or be electrically inactive on the other site. Centres other than the isolated FAs can also be electrically active and give H-like levels in the band gap, like the substitutional chalcogen pairs, which are double donors in silicon, but there are more complicated centres like the complexes made from a shallow impurity and from an electrically inactive impurity, or the family of O-related thermal donors in silicon and germanium, which are relatively shallow donors, and where the origin of the weakly bound electrons is not as obvious as for substitutional donors. Besides substitutional impurities, interstitial FAs with  $ns$  or  $ns^2$  external atomic configuration like Li in silicon and germanium and Mg in silicon can display H-like donor behaviour, and there are also evidences that this is the case for sodium and potassium in silicon ([30] and references therein).

In a semiconductor, substitutional FAs from the same column of the periodic table as the one of the crystal atom they replace are usually electrically inactive and they are called isoelectronic with respect to the semiconductor. It can occur, however, that for some isoelectronic impurities or electrically-inactive complexes, the combination of the atomic potential at the impurity centre with the potential produced by the local lattice distortion produces an overall electron- or hole-attractive potential in a given semiconductor. This potential can bind an electron or a hole to the centre with energies much larger than those for shallow electrically-active acceptors or donors. The interaction of these isoelectronic impurities traps the free excitons producing isoelectronic bound excitons which display pseudo-donor or pseudo-acceptor properties. This is discussed later in this chapter in connection with the bound excitons, and examples of these centres are given in Chaps. 6 and 7.

At low temperature, the free carriers of a semiconducting crystal are trapped by donor or acceptor ions of the opposite sign. With increasing concentration of these neutralized impurities, the separation between the electronic clouds around each impurity centre decreases. To simplify, when these electronic clouds overlap in the ground state, an impurity band is formed at low temperature, in which electrons or holes have an appreciable electrical mobility. This is the limit of the concept of a semiconductor at low temperature and it goes through a transition to the metal-insulator transition or MIT [35], corresponding to a critical doping level  $N_c$  which depends on the ionization energy of the impurity considered: for P-doped silicon,  $N_c$  is  $3.5 \times 10^{18} \text{ cm}^{-3}$

---

<sup>2</sup> Nitrogen is a notable exception in silicon and in germanium [26].

and it is lowered to  $1.9 \times 10^{17} \text{ cm}^{-3}$  in Ga-doped germanium, but it rises to  $\sim 4 \times 10^{20} \text{ cm}^{-3}$  in B-doped diamond. The doping level for which the impurity band merges with the semiconductor continuum and for which the material becomes truly metallic occurs for doping levels significantly larger than  $N_c$ . Thus, for P-doped silicon, it is estimated to be  $3N_c$  [18].

### 1.3.2.1 Compensation

In a real semiconductor, more than one kind of donor and acceptor impurities are usually present at the same time, but to simplify, a material containing only one kind of FAs of each type is considered. The one with the highest concentration  $N_{\text{maj}}$  is the majority impurity, which determines the electrical type of the semiconductor and the other one is the minority impurity with concentration  $N_{\text{min}}$ . The net concentration of active centres able to contribute each a free carrier is  $N_{\text{maj}} - N_{\text{min}}$  and this evolves from the annihilation of a concentration  $N_{\text{min}}$  of electron-hole pairs. This situation is called compensation, and it can also arise from the presence of centres in concentration  $N_{\text{trap}}$  which can trap carriers from the majority impurity. The compensation ratio  $K$  is usually defined as the ratio  $N_{\text{min}}/N_{\text{maj}}$ . When one neglects the intrinsic concentration of electrons and holes, the net concentration is close to the free-carrier concentration measured when these active centres are thermally ionized, or to the number of neutral centres which can be spectroscopically detected at low temperature under thermal equilibrium. Between the low-temperature region where the electron concentration  $n$  in a n-type semiconductor is practically zero and the exhaustion region where it is  $N_{\text{maj}} - N_{\text{min}}$ , the temperature dependence of the electron concentration  $n$  released in the  $CB$  by the donor with ionization energy  $E_i$  is:

$$n = \frac{N_{\text{maj}} - N_{\text{min}}}{N_{\text{min}}} N_c e^{\frac{E_i}{k_B T}} \quad (1.1)$$

where  $N_c$  is the effective density of states (DoS) in the  $CB$ . A similar equation holds for the hole concentration  $p$  in the  $VB$  in a p-type semiconductor, by replacing  $N_c$  by the effective DoS  $N_v$  in the  $VB$ . Expression (1.1) shows that for shallow impurities,  $E_i$  can be derived from  $n(T)$  and it can be obtained, for instance, from the temperature dependence of the Hall coefficient  $R_H = -r/ne$  (the Hall factor  $r = \langle \tau^2 \rangle / \langle \tau \rangle^2$  depends on the electron or hole scattering process through their lifetime  $\tau$ , and in most semiconductors, it is close to  $3\pi/8$ ). An example of the temperature dependence of the free-carrier concentration deduced from Hall measurements is shown in Fig. 1.1. An alternative is a measurement of the energy absorption spectrum of the hydrogen-like impurities at low temperature, from which ionization energies can be extrapolated and this method is fully explained later in the book.

Compensation reduces the concentration of active majority impurities, but it also produces additional impurity ions of both charges. These ions are the

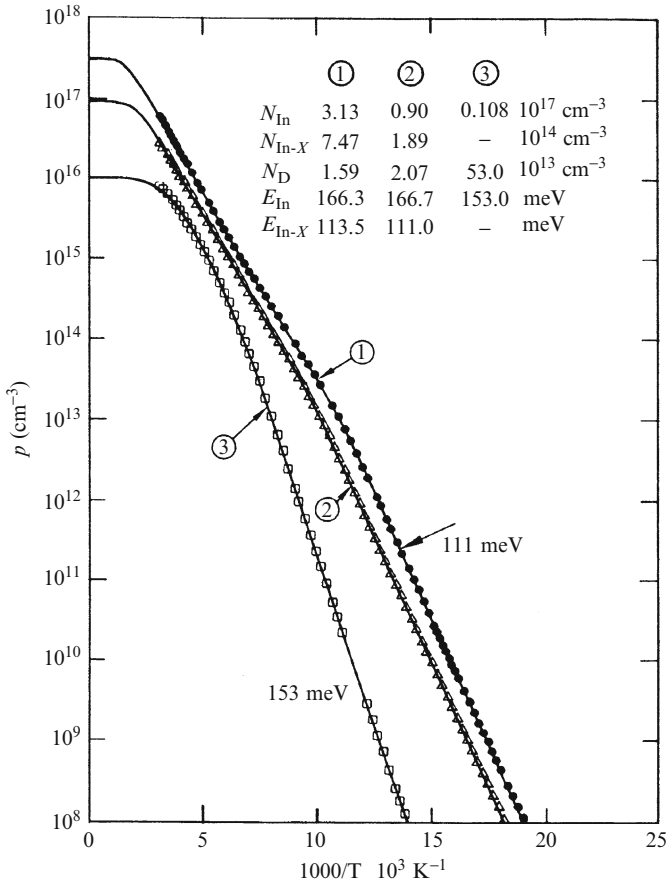


**Fig. 1.1.** Temperature-dependence of the free-hole concentrations  $p$  in three In-doped silicon samples measured by Hall effect. The fit of the curves shows that the dominant acceptor in sample 3 is isolated In ( $E_i = 153 \text{ meV}$ ) and the In-X centre ( $E_i = 111 \text{ meV}$ ) in samples 1 and 2. The compensating donor compensation  $N_{\text{D}}$  resulting from the fit is indicated (after [4]). Copyright 1977, American Institute of Physics

source of the so-called impurity scattering for the majority free carriers and it reduces their lifetime. The electrical conductivity of a crystal is proportional to the number of free carriers and to their electrical mobility, which in turn is proportional to their lifetime. As a consequence, in the extrinsic regime, a high resistivity (or a low value of the carrier concentration measured directly from Hall effect) does not necessarily mean a high purity of the material.

We have mentioned the situation of a dopant atom (Si in GaAs, for instance) that can be located on two different sites, where it behaves either like a donor or an acceptor. For some growth condition, this possibility can

produce what is known as self-compensation, and this can occur indeed for GaAs:Si. Another example of self-compensation is the doping of ZnO with Li: this results in a material with a relatively high resistivity and the reason for this is attributed to the occupancy with comparable probabilities by a Li atom of interstitial sites, where it acts as a donor, and of Zn sites, where it acts as an acceptor. In some cases, compensation is necessary to measure the properties associated with impurities: for instance, in an uncompensated crystal containing only a double donor DD, which can release in the *CB* two electrons with different energies, this donor is neutral at low temperature and its optical ionization is that of the neutral charge state (the electronic level corresponding to  $DD^0/DD^+$ ). To observe the optical ionization from the  $DD^+/DD^{++}$  electronic level and the optical spectrum of the  $DD^+$  charge state, it is necessary to ionize permanently the first electron to produce  $DD^+$ . This can be obtained by increasing the temperature to produce thermal ionization of  $DD^0$ , but the higher the temperature, the broader the spectral line widths. Another method is the counter-doping of the material with acceptor minority impurities or deep traps, which partially compensate the double donor and produce  $DD^+$ .

The compensation of impurities is an equilibrium process resulting from the minimization of the electronic energy in the crystals. Thus, under equilibrium conditions at low temperature, donors or acceptors can be either neutral ( $D^0$  or  $A^0$ ) or ionized ( $D^+$  or  $A^-$ ). In weakly-compensated materials, the out-of-equilibrium partial photoionization of donors in n-type materials or of acceptors in p-type materials produces photoelectrons or photoholes. At very low temperature, these photocarriers can then be trapped by neutral donors or acceptors to produce  $D^-$  or  $A^+$  ions. These centres are equivalents of the  $H^-$  ion and they are introduced in Sect. 1.3.3.

The actual compensation in a material is more complex than a simple balance between a majority impurity and a minority impurity as the material usually contains a combination of residual impurities, dopant and deep centres, whose concentrations must be estimated to determine the actual degree of compensation in the material. As mentioned before, compensation of the majority impurities by adding opposite type dopant leaves in the material charged ions, which reduce the lifetime of the free carriers. When the lifetime of the carriers in a given pure material is known, a lifetime measurement of an unknown sample of this material can determine the degree of compensation of the sample.

Correlations between the free-carrier concentration and the RT resistivity have been made for n- and p-type silicon by Irvin [22] as a function of the dopant concentration ( $\text{cm}^{-3}$ ) assuming no compensation. From these measurements, in n-type silicon with  $\rho \geq 1.4 \, \Omega \text{ cm}$ ,  $N_P$  or  $n$  is about  $5.0 \times 10^{15} \, \rho^{-1}$  and in p-type silicon with  $\rho \geq 0.9 \, \Omega \text{ cm}$ ,  $N_B$  or  $p$  is about  $1.3 \times 10^{16} \, \rho^{-1}$ . For a more extended range in P-doped silicon, see [52].

A very close compensation between donors and acceptors is sometimes required to obtain, for instance for epitaxial growth, substrates with a resistivity close to the intrinsic one. In the case of GaAs, this can be realized nearly

“naturally” as the GaAs crystals grown by the LEC method contain a native deep defect labelled EL2, whose main ingredient, if not the only one, is an As antisite ( $\text{As}_{\text{Ga}}$ ). This defect is a deep double donor with a level 0.75 eV below the  $CB$  and it traps the residual acceptors present in the crystal. By limiting the C acceptor doping of the crystal in the  $10^{15} - 10^{16} \text{ at/cm}^3$  region, it is possible to obtain semi-insulating GaAs LEC crystals with electrical resistivities of the order of the intrinsic resistivity of the material ( $\sim 10^8 \Omega \text{ cm}$ ). In GaAs containing residual donors, this result is obtained by doping with chromium.

### 1.3.2.2 Passivation

In the compensation process, there is only a change in the charge state of the impurity or dopant atom and it is temporarily reversible, for instance by illumination of the crystal with band-gap or above-band-gap radiation, which produces electrons and holes that are trapped by the ionized centres. This is a non-equilibrium condition, which exists only during illumination.

When studying the interaction of hydrogen plasmas with crystalline silicon surfaces, it was discovered that hydrogen could penetrate in the bulk of the material and decrease its electrical conductivity [38, 43]. What could have been due to a compensation effect revealed itself as a passivation effect where hydrogen interacted chemically with the shallow acceptors in silicon to form a complex. This was reminiscent of older studies which showed that hydrogen played a role in the passivation of deep centres at the Si/SiO<sub>2</sub> interfaces and later on the bulk and interface defects in crystalline silicon, not to mention the role of hydrogen in amorphous silicon. An evidence of this interaction with shallow acceptors in silicon was the observation of IR vibrational modes related to hydrogen-acceptor complexes. These complexes were electrically inactive and hence, they did not contribute to the ionized impurity scattering. This process has been naturally called passivation and it has been observed for many donors and acceptors in semiconductors (for a review, see for instance [8]). The stability of hydrogen passivation is limited by the thermal dissociation of the electrically-inactive complexes, which produces the reactivation of the dopant atoms, and for an annealing time of about 30 min, this usually takes place in the 350 – 500°C range. However, the interaction of hydrogen with impurities in semiconductor crystals is complex and in some cases, it can turn electrically inactive impurities into electrically active complexes. Moreover, for double donors or acceptors, it can passivate partially the centre and turn a deep impurity into a shallow donor or acceptor complex.

### 1.3.3 Optical Transitions

Atomic hydrogen excited in a discharge tube gives an emission spectrum originating from transitions between excited states and the  $1S$  ground state [32]. This discrete spectrum extends, in the UV, from 121.57 nm to the ionization limit of 91.13 nm corresponding to the Rydberg energy  $R_\infty$ . When the

above-described H-like donor or acceptor centres are neutral, i.e., when they are not electrically compensated and when temperature is low enough for the ground state to be populated, a discrete electronic absorption spectrum from the ground state to the excited states is observed. By analogy with the case for hydrogen, such a spectrum is often referred to as a Lyman spectrum. The exact spectral region of observation depends on the ground state energy, which is the ionization energy of the centre, but it is located in the IR region of the electromagnetic spectrum. This absorption, determined by the electric-dipole selection rules, is best observed at LHeT; it is relatively intense and allows the detection of shallow impurities down to concentrations in the  $10^{11} - 10^{12} \text{ cm}^{-3}$  range when the absorption lines are sharp and when high resolution is used. This limit of detection can even be lowered to the  $10^7 - 10^9 \text{ cm}^{-3}$  range using the photoconductivity-based techniques described in Sect. 4.4.2.2. In compensated crystals containing donors and acceptors, one observes under equilibrium the absorption spectrum of the active uncompensated majority impurities. The randomly distributed positive and negative ions due to compensation produce statistical electric fields which interact with the weakly bound electrons or holes whose transitions are observed. The resultant inhomogeneous Stark effect broadens the spectral lines of the EM spectra of the majority centres with respect to their standard values and this broadening is generally the signature of compensated samples. When the compensated samples are illuminated during the absorption measurement with band-gap or above-band-gap radiation, photoelectrons and photoholes trapped by the compensated ions of both types convert them into neutral atoms that participate in the optical absorption. It thus reveals the absorption spectra of both the majority and minority centres. When the absorption spectra have been previously calibrated, this even allows a determination of the compensation ratio  $K$ . Examples of this method are given in Chaps. 6 and 7. At energies above the ionization energy, the electronic absorption of the neutral centres is continuous and is called the photoionization spectrum. The spectral dependence of this continuous spectrum has been actively investigated in silicon and germanium in relation with the production of extrinsic photodetectors.

Population inversion between discrete hydrogenic states of impurities can in principle be produced by optical pumping in the photoionization spectrum of the impurities. When the population of the state with the lowest energy ( $E_{\text{low}}$ ), i.e., the one nearest from the continuum, is higher than the one of the state with higher energy ( $E_{\text{high}}$ ), emission at energy  $E_{\text{high}} - E_{\text{low}}$ , can take place, and ultimately, for sufficiently high pumping power, stimulated emission or laser effect occurs. At the end of the 1990s, stimulated emission between excited levels of phosphorus donors in silicon has indeed been reported [39].

Some of the possible transitions are forbidden by the electric-dipole selection rules, but they can be allowed by the polarizability selection rules and can subsequently be observed in Raman scattering experiments [24, 57].

Electronic absorption of impurities can couple with phonon modes of the host crystal and a photon is absorbed at an energy corresponding to the sum of the electronic excitation and the phonon mode, and such features, resonant with the photoionization absorption spectrum of the impurities are often observed. For indirect-band-gap semiconductors, the phonon energy can correspond to that of a phonon promoting the scattering of a bond electron from a *CB* minimum to another minimum, and its momentum is well-defined. For acceptor impurity transitions, corresponding to degenerate electronic states at the maximum of the *VB* at  $k = 0$  (the usual situation), the phonon coupling takes place with zone-centre optical phonons. In covalent semiconductors, the resonance of these coupled excitations with the photoionization spectrum of the impurity can be strong and it results in what is known as a Fano resonance, after the theoretical explanation by Fano [16] of similar resonances of atomic auto-ionizing states. For smaller couplings, generally encountered in crystals with significant ionicity, one observes phonon replicas which can involve several optical phonons.

In an indirect-gap semiconductor containing neutral H-like donors or acceptors, illumination with RT thermal radiation of a sample held at LHeT is sufficient to partially ionize the neutral impurities. Coulomb interaction implies that the recombination mainly takes place on the photoionized impurities, but as has been mentioned in Sect. 1.3.2.1, these photocarriers can also be trapped by the neutral impurities giving  $A^+$  acceptor ions and  $D^-$  donor ions. These ions are the equivalents of the  $H^-$  ion, studied first by Chandrasekhar in relation with astrophysics (for an early review, see [7]). The ionization energy of  $H^-$  calculated by Pekeris [40] is  $6083.1 \text{ cm}^{-1}$  or  $0.7542 \text{ eV}$  ( $0.0554 \text{ Rydberg}$ ), close to the experimental value of  $0.75 \text{ eV}$ . The existence of such ions in semiconductors was predicted by [31]. Their absorption spectra have been observed at very low temperature for several donor impurities in silicon, germanium and compound semiconductors, and also for acceptors in silicon and germanium. The binding energies of these equivalents of the  $H^-$  ion are small, but evidence for their absorption (and photoconductivity) in the very far IR has been given; it is presented and discussed in Sects. 7.5 and 6.9.

Under strong band-gap excitation, the photo-neutralized ions can de-excite thermally, but in direct-band-gap semiconductors, they can also de-excite efficiently by radiative recombination of the bound electrons with the bound holes. Such photoluminescence (PL) lines are known as donor-acceptor pair (DAP) spectra. In a semiconductor with dielectric constant  $\epsilon$ , the energy of the photon emitted by a pair whose constituents, with ionization energies  $E_D$  and  $E_A$ , are both in the ground state and at a distance  $R$  is:

$$h\nu(R) = E_g - (E_D + E_A) \frac{e^2}{4\pi\epsilon_0\epsilon R} + J(R) \quad (1.2)$$

The term  $J(R)$ , which depends on the donor-acceptor interaction, becomes important when the distance  $R$  becomes comparable with the largest effective

Bohr radius of the two constituents. The DAP spectrum consists of many lines whose energies differ by the Coulomb term, resulting in a continuum for large values of  $R$  (see for instance [13]). It is also possible to create a pair separated by  $R$  with the acceptor in an excited state  $A^*$ . The energy required, which is larger than  $h\nu(R)$ , is:

$$h\nu_x = h\nu^*(R) = E_g - (E_D + E_A^*) + \frac{e^2}{4\pi\epsilon_0\epsilon R} + J^*(R) \quad (1.3)$$

As the lifetime of the hole in the excited state is much shorter than that of the DAP, the radiative recombination occurs at  $h\nu(R)$ . Thus, by scanning energies  $h\nu_x > h\nu(R)$  and detecting at  $h\nu(R)$ , one obtains an excitation spectrum of the acceptor excited states from which the energies of these states can be derived. One chooses for  $h\nu(R)$  a plausible energy value, provided it is large enough for neglecting  $J(R)$  and  $J^*(R)$ . This method has been proposed by Street and Senske [48], who applied it to the study of the shallow acceptors in GaP and it is known as selected pair luminescence (SPL). Nevertheless, sharp PL lines due to DAPs have also been reported in indirect-gap semiconductors [58].

Free electrons and holes produced by photoexcitation with energies above  $E_g$  can form free exciton (see Sect. 3.3.2), but a free electron (hole) can also recombine with a hole (electron) of a neutral acceptor (donor). The energy of the photon produced by this  $e$ - $A^0$  or  $h$ - $D^0$  recombination is  $E_g - E_i + k_B T/2$  where  $E_i$  is the ionization energy of the acceptor or of the donor and  $T$  the electron or hole temperature, which is close to the lattice temperature for moderate excitations close to  $E_g$ . In high-purity samples and at very low temperature, these lines can be sharp and when identified, they allow a good estimation of the impurity ionization energies when the value of  $E_g$  is known accurately.

When band-gap excitation is obtained by irradiation of the sample with electrons with energies in the keV range, the resulting PL is known as electroluminescence or cathodoluminescence.

### 1.3.4 Bound Excitons

Excitons are electron-hole pairs weakly coupled through the band gap by Coulomb interaction. When they are free to propagate in the crystal, they are logically called free excitons (FEs) and are characterized by a binding energy  $E_{ex}$ . Their properties are described in Sect. 3.3.2.

The FEs can bind to neutral shallow impurities and become bound excitons (BEs), with a value of  $E_{ex}$  slightly larger than the one of the FE. The difference is called the localization energy  $E_{loc}$  of the BE. For the P donor, it is  $\sim 4$  meV in silicon, but 75 meV in diamond.  $E_{loc}$  is given approximately by Haynes' empirical rule [20] as  $0.1 E_i$ , where  $E_i$  is the ionization energy of the impurity. BEs are created by laser illumination of a semiconductor sample at an energy larger than  $E_g$  and the study of their radiative recombination by PL



has been and is still an active field of the optical spectroscopy of semiconductors [9, 12, 33, 50]. The excitons can recombine radiatively by emitting a photon at energy  $E_{\text{gx}} = E_{\text{g}} - E_{\text{ex}}$ , but in indirect-gap semiconductors, the conservation of the momentum of the weakly-bound electron, comparable to the one of a free electron, implies the creation of a lattice phonon of opposite momentum so that a part of the recombination energy is used to produce a phonon. The energy of the photon emitted is then  $E_{\text{gx}} - E_{\text{phon}}$  where  $E_{\text{phon}}$  is the energy of the momentum-conserving phonon, and such transitions are called phonon-assisted transitions, or phonon replicas. For BEs in the indirect-gap semiconductors, however, zero-phonon-lines (ZPLs) at energies  $E_{\text{gx}}$  are also observed, but their intensities are smaller than those of the phonon-assisted recombination lines. Besides the phonon-assisted replicas, the recombination of excitons bound to complexes with internal vibration modes can take place with the excitation of some of these modes, producing what is known as vibronic sidebands. To obtain the emission of a momentum-conserving phonon, in the absorption measurements of BE, the absorption takes place at energy  $E_{\text{gx}} + E_{\text{phon}}$ , but for PL measurements, ZPLs can also be observed.

Radiative recombination of an exciton bound to a shallow impurity generally leaves this impurity in the electronic ground state, resulting in the principal BE (PBE) line, but weaker PL lines can also be observed at lower energies, where the impurity is left in an electronic excited state. These so-called two-electron or two-hole PL spectra are usually observed in their phonon-assisted form, and they mainly involve *s*-like excited states whose detection escapes the absorption experiments. These PL experiments are, therefore, valuable complements to absorption spectroscopy, which involves mainly the *p*-like excited states, and examples will be given when appropriate.

PL evidence for the binding of more than one exciton to a shallow impurity exists, starting with the excitonic molecule was first reported in silicon [20]. A model for the bound multi-exciton complexes in silicon (the shell model) has been elaborated by Kirczenow [27] to explain the experimental results of these centres. For a review on these centres, see [49].

In doped uncompensated semiconductors, very weak absorption lines due to the direct creation of excitons bound to neutral donors or acceptors can be observed at low temperature (typically 2 K) at energies close to  $E_{\text{g}}$  [11, 14, 21].

The optical properties of an exciton bound to a neutral donor or acceptor depend on the interaction of the exciton constituents with the neutral entity. When, for instance, the hole part interacts more strongly than the electron part with the neutral atom, the binding between the two exciton components decreases and the electron part can be considered as an electron bound to a pseudo-negative ion, forming some kind of pseudo-acceptor.

In semiconductors containing isoelectronic centres with an attracting potential for electrons or holes mentioned in Sect. 1.3.2, free excitons can be trapped because of the preferential interaction of these centres with the electron (or hole) part of the exciton. The hole (resp. electron) part of the exciton is then comparable to a hole (resp. electron) bound to a neg-

actively (resp. positively) charged acceptor (resp. donor) ion, and a pseudo-acceptor (pseudo-donor) results. This process is somewhat similar to the one presented above for excitons bound to neutral donors and acceptors. The spectroscopy of excitons bound to isoelectronic centres in silicon and compound semiconductors (isoelectronic bound excitons or IBE) has been actively investigated in the 1980s. In compound semiconductors, one of the best-studied electron-attracting centre (pseudo-acceptor) is probably  $N_P$  in GaP [51]. Isoelectronic oxygen can also play this role in some II–VI compounds ([1] and references therein). Bi at a P site in GaP and InP seems to be the best documented hole-attracting centre [10,55]. In silicon, the potential near a C or Ge atom cannot bind an electron or a hole, but isoelectronic centres with pseudo-donor properties like the Be pair at a Si site or some (C,O) complexes in irradiated or annealed CZ silicon have been identified, and they are discussed in Sect. 6.7.

### 1.3.5 Spin Effects

Electron spin effects are observed for electrically active centres with an odd number of electrons. In charge states with an even number of electrons, the spins are generally paired. There are, however, a few cases where a 2-electron centre gives a resultant spin  $S = 1$  [23]. A centre in a charge state with non-zero spin is said to be paramagnetic. Such a centre interacts with an external magnetic field  $\mathbf{B}$  through the magnetic dipole moment of the electron arising from the electron spin and the angular momentum. For many centres, the angular momentum of the electron is quenched in the ground state so that one can only consider the spin. In a solid, the Zeeman term can then be expressed as [54]:

$$H_{Zee} = \mu_B g S B$$

where  $\mu_B$  is the Bohr magneton and  $\mathbf{g}$  a symmetric tensor whose values  $g_1$ ,  $g_2$ , and  $g_3$  with respect to the principal axes of the  $\mathbf{g}$  tensor are close to 2. The ground state of a centre with spin  $S = 1/2$  is split by the magnetic field into a doublet with  $M_S = +1/2$  and  $-1/2$  separated by  $\mu_B g B$  (for a magnetic field of 1 T and  $g \sim 2$ , this separation is  $\sim 30$  GHz ( $\sim 0.12$  meV)) and a magnetic dipole transition can take place between the two components. Non-cubic centres with different equivalent orientations in a cubic crystal present an orientational degeneracy. When these centres are paramagnetic, the doublet separation depends on the angle between the magnetic field and the main axis of the centres. In classical electron spin resonance (ESR) experiments, the transition between the two levels is induced by the magnetic field of a fixed microwave frequency for a critical value of  $\mathbf{B}$ . Practically,  $\mathbf{B}$  oriented along a high-symmetry axis of the crystal ( $\langle 100 \rangle$ ,  $\langle 111 \rangle$  or  $\langle 110 \rangle$ ) is tuned in order to make the splitting of the centres with different orientations to coincide with the microwave frequency and this is repeated for different orientations. The variation of the number of resonances for different orientations of  $\mathbf{B}$  allows then to determine the orientational degeneracy of the centre.

A paramagnetic atom with  $T_d$  symmetry should give only one resonance line, but when this atom has a nuclear spin, the electron and nuclear spins can couple by hyperfine interaction, and for a nuclear spin  $I$ , each electronic spin component splits into  $2I + 1$  components giving the same number of  $\Delta m_I = 0$  resonances. For instance, the ESR spectrum of tetrahedral interstitial Al ( $I = 5/2$ ) produced by electron irradiation of Al-doped silicon is an isotropic sextuplet due to transitions between the six nuclear sublevels of each electronic-spin component ([54], and references therein). The electron spin of a centre can also interact with the nuclear spins of neighbouring atoms to give additional structures and this is clearly shown for  $^{29}\text{Si}$  atoms ( $I = 1/2$ ) in Fig. 4 of [54]. The ESR spectrum can thus also determine the atomic structure of the centre. This can also occur for non-cubic centres and the hyperfine structure is superimposed on the orientational structure.

For a given value of  $\mathbf{B}$ , the energies of  $\Delta m_I = 1$  transitions between the nuclear sublevels of a given electronic spin state are much lower than those between the electronic spin components. Information on the amplitude of the wave function of the electron whose spin is responsible for the ESR spectrum at different lattice sites in the vicinity of the centre was obtained by Feher [17] by monitoring the ESR spectrum as a function of the frequencies in the nuclear frequency range, and this technique was called electron nuclear double resonance (ENDOR). Improvements in the sensitivity of ESR can be obtained using optical or electrical detection methods [47].

All the neutral single donors without  $d$  or  $f$  electrons have spin  $1/2$  while the double donors and acceptors have spin 0 in the ground state, but in some excited states, they have spin 1 and optically forbidden transitions between the singlet and triplet states have been observed. The spins of the neutral acceptors in the ground state depend on the electronic degeneracy of the  $VB$  at its maximum. For silicon, the threefold degeneracy of the valence band results in a quasi spin  $3/2$  of the acceptor ground state.

## 1.4 Notations for Centres and Optical Transitions

We are faced with two interconnected problems related to the intelligibility of the presentation. The first one concerns the nomenclature of the centres other than isolated atoms and the second the labelling of the optical transitions. These problems are not trivial, [5], but not as severe for H-like centres as for deep centres. The different notations for the shallow thermal donor complexes in silicon, discussed in Sect. 6.4.2, are however, a counter-example of this statement. In this book, on the basis of the present knowledge, names of centres, in direct relation with their atomic structure, have been privileged, but the usual label has however been indicated. When the exact structure is not simple and when there exist an acronym, like TDD for “thermal double donor”, it has been used. The labelling by their excited states of the transitions of the shallow donor centres and of similar species, whose spectra

are experimentally and theoretically well identified, is a generally accepted rule. There are a few exceptions, as for some lines of transition metals and isoelectronic bound exciton spectra in silicon discussed in Chap. 6. From the beginning, the transitions of the shallow acceptors in silicon, whose direct attribution was much more difficult than for donors, were denoted by integers in order of increasing energies and there have been several labelling changes with the improvement in the resolution of the spectra. These labellings have to be related to “physical” ones by correlation between the experimental data and the calculated acceptor energy levels discussed in Sect. 5.3, assuming that the comparison is significant. There is an exception for the Au and Pt transitions in silicon, denoted  $I_N$ , where  $N$  is the number of corresponding acceptor lines in silicon. The label of the acceptor lines in other semiconductors (except for diamond) is based on the notation used for germanium in [25]: the lowest-energy transition is denoted  $G$  and the other ones denoted in inverse alphabetical order, with the resurgence, for the more recent spectra, of indexed  $I$  lines near from the photoionization continuum, to cope with the observation of additional transitions. The different notations in the case of the acceptors and the spectroscopic attributions are discussed in detail in Chap. 7.

In the labelling of defects, the ESR family is a world of its own and when an unidentified ESR spectrum was first observed in a given material, it has been the rule to label it by the initials of the laboratory, city or country and by an integer corresponding to the order of discovery (an indication of the nature of the centre is sometimes added). There are, however, exceptions to this labelling, where the atomic nature of the centre is indicated.

## References

1. K. Akimoto, H. Okuyama, M. Ikeda, Y. Mori, Appl. Phys. Lett. **60**, 91 (1992)
2. V.I. Anisimov, M.A. Korotin, E.Z. Kurmaev, J. Phys. Condens. Matter **2**, 3973 (1990)
3. M. Balkanski, R.F. Wallis, *Semiconductor Physics and Applications* (Oxford University Press, 2000) p. 101
4. R. Baron, M.H. Young, J.K. Neeland, O.J. Marsh, Appl. Phys. Lett. **30**, 594 (1977)
5. F. Bridges, G. Davies, J. Robertson, A.M. Stoneham, J. Phys.: Cond. Matt. **2**, 2875 (1990)
6. G. Busch, Eur. J. Phys. **10**, 254 (1989)
7. S. Chandrasekhar, Rev. Mod. Phys. **16**, 301 (1944)
8. J. Chevallier, B. Pajot, *Interaction of Hydrogen with Impurities and Defects in Semiconductors*. Solid State Phenomena 85–86:203–284. (Scitec Publications, Switzerland, 2002)
9. G. Davies, Phys. Rep. **176**, 83 (1989)
10. P.J. Dean, R.A. Faulkner, Phys. Rev. **185**, 1064 (1969)
11. P.J. Dean, W.F. Flood, G. Kaminsky, Phys. Rev. **163**, 721 (1967)
12. P.J. Dean, J.R. Haynes, W.F. Flood, Phys. Rev. **161**, 711 (1967)
13. P.J. Dean, E.G. Schönher, R.B. Zetterstrom, J. Appl. Phys. **41**, 3475 (1970)

14. K.R. Elliot, G.C. Osbourn, D.L. Smith, T.C. McGill, Phys. Rev. B **17**, 1808 (1978)
15. H.Y. Fan, M. Becker, Phys. Rev. **78**, 178 (1950)
16. U. Fano, Phys. Rev. **124**, 1866 (1961)
17. G. Feher, Phys. Rev. **114**, 1219 (1959)
18. A. Gaymann, H.P. Geserich, H.v. Löhneysen, Phys. Rev. B **52**, 16486 (1995)
19. W.A. Harrison, Pure Appl. Chem. **61**, 2161 (1989)
20. J.R. Haynes, Phys. Rev. Lett. **4**, 361 (1960)
21. M.O. Henry, E.C. Lightowers, J. Phys. C **10**, L601 (1977)
22. J.C. Irvin, Bell Sys. Tech. J. **41**, 387 (1962)
23. D. Israël, F. Callens, P. Clauws, P. Matthys, Solid State Commun. **82**, 215 (1992)
24. K. Jain, S. Lai, L.V. Klein, Phys. Rev B **13**, 5448 (1976)
25. R.L. Jones, P. Fisher, J. Phys. Chem. Solids **26**, 1125 (1965)
26. R. Jones, S. Öberg, F. Berg Rasmussen, B. Bech Nielsen, Phys. Rev. Lett. **72**, 1882 (1994)
27. G. Kirczenow, Can. J. Phys. **55**, 1787 (1977)
28. C.F. Klingshirn, *Semiconductor Optics* (Springer, Berlin, 1997)
29. J. Königsberger, J. Weiss, Ann. Phys., Leipzig **35**, 1 (1911)
30. V.M. Korol', A.V. Zastavnyi, Sov. Phys. Semicond. **11**, 926 (1977)
31. M.A. Lampert, Phys. Rev. Lett. **1**, 450 (1958)
32. T. Lyman, Phys. Rev. **3**, 504 (1914)
33. B. Monemar, U. Lindefelt, W.M. Chen, Physica B + C **146**, 256 (1987)
34. T.S. Moss, *Optical Properties of Semi-conductors* (Butterworths, London, 1961)
35. N.F. Mott, *Metal-Insulators Transitions* (Taylor and Francis, London, 1974)
36. R.C. Newman, *Infrared Studies of Crystal Defects* (Taylor and Francis, London, 1973)
37. J.I. Pankove, *Optical Processes in Semiconductors* (Electronic Engineering Series, ed. by N. Holonyak, Jr., Prentice Hall, Englewood Cliff, NJ, 1971)
38. J.I. Pankove, D.E. Carlson, J.E. Berkeyheiser, R.O. Wance, Phys. Rev. Lett. **51**, 2224 (1983)
39. S.G. Pavlov, R. Kh. Zhukavin, E.E. Orlova, V.N. Shastin, A.V. Kirsanov, H.-W. Hübers, K. Auen, H. Riemann, Phys. Rev. Lett. **84**, 5220 (2000)
40. C.L. Pekeris, Phys. Rev. **126**, 1470 (1962)
41. A.K. Ramdas, S. Rodriguez, Rep. Prog. Phys. **44**, 1297 (1981)
42. R. Robertson, J.J. Fox, A.E. Martin, Phil. Trans. Roy. Soc. London Ser. A **232**, 463 (1934)
43. C.-T. Sah, J.Y.-C. Sun, J.J.-T. Tzou, Appl. Phys. Lett. **43**, 204 (1983)
44. J.H. Scaff, H.C. Theuerer, E.E. Schumacher, J. Metals **1**, 383 (1949)
45. W. Shockley, *Electron and Holes in Semiconductors* (Van Nostrand, Princeton, 1950)
46. R.A. Smith, *Semiconductors*, (Cambridge University Press, 1964)
47. J. -M. Spaeth, in *Identification of Defects in Semiconductors*, vol. 51A, ed. by M. Stavola (Academic, San Diego, 1998), p. 45
48. R.A. Street, W. Senske, Phys. Rev. Lett. **37**, 1292 (1976)
49. M.L.W. Thewalt, in *Excitons*, ed. by M.D. Sturge, E.I. Rashba (North Holland, 1982), p. 393
50. M.L.W. Thewalt, Solid State Commun. **133**, 715 (2005)
51. D.G. Thomas, J.J. Hopfield, Phys. Rev. **150**, 680 (1966)

- 52. W.R. Thurber, R.L. Mattis, Y.M. Liu, Filliben, J. Electrochem. Soc. **127**, 1807 (1980)
- 53. A. Volta, Phil. Trans. R. Soc. **72**, 237 (1782) (*in Italian*) *Ibid.* 72: vii-xxxiii (*in English*)
- 54. G. Watkins, (1998) in *Identification of Defects in Semiconductors*, vol. 51A, ed. by M. Stavola (Academic, San Diego, 1998), pp. 1–43
- 55. A.M. White, P.J. Dean, K.M. Fairhurst, W. Bardsley, B. Day, J. Phys. C **7**, L35, (1974)
- 56. A.H. Wilson, Proc. R. Soc. A **133**, 458; *Ibid.* **134**, 277 (1931)
- 57. G.B. Wright, A. Mooradian, Phys. Rev. Lett. **18**, 608 (1967)
- 58. U.O. Ziemelis, R.R. Parsons, Can. J. Phys. **59**, 784 (1981)

## Origins and Atomic Properties of H-Like Centres

Many of the H-like centres are isolated atoms, with a few known cases of pairing. These pairs are the simplest of a variety of complexes, whose atomic structures have been elucidated in many cases. In this chapter, we discuss the occurrence of H-like centres in semiconductors, and attempt to qualitatively relate the diffusion coefficient and solubility of the simplest pair to their atomic parameters.

### 2.1 Origins

#### 2.1.1 Occurrence in Nature

Several insulators and a very few semiconductors are found in the native state. The existence of natural diamonds with a significant electrical conductivity was first reported in 1954 [14], and this category was classified as type IIb diamonds, also known as blue diamonds because of a more or less intense blue colour (Fig. 2.1). This rare variety of natural diamonds, with resistivity as low as  $5\ \Omega\ \text{cm}$ , contains boron in variable amounts, and it is a p-type semiconductor [9]. This is attributed to the substitutional B atom, an acceptor with a moderate ionization energy (0.37 eV) with respect to the diamond band gap ( $\sim 5.5\ \text{eV}$ ). The presence of B-containing minerals in the earth's zone where the blue diamonds are formed explains the presence of boron in these diamonds. The origin of their blue colour is explained in Sect. 7.2.3. The purest natural diamond crystals, classified as type IIa diamonds, are colourless in the absence of plastic deformation. The type II diamonds contrast with type I diamonds that contain varying nitrogen concentrations in different complexes.

Although the above distinction between type I and type II diamonds is useful, there exists type IIb diamonds containing both boron and a small nitrogen content.

Blue-grey insulating diamonds were extracted from the Argyle mine in Australia and their colour attributed to high concentrations of hydrogen, defects containing two and four N atoms, and to a small concentration of three-N-atom defects [36].



**Fig. 2.1.** The Hope diamond (central gem), weighing 45.52 carats (9.10 g). The original stone was discovered before 1668 in India and cut several times before deriving the above stone. This IIb diamond belongs to the Smithsonian Institute and its absorption spectrum confirms the presence of substitutional boron. The smaller diamonds of the mounting are of IIa type and they are assumed to have a very small impurity concentration. Copyright Calvin J Hamilton (2004)

The colour of many natural diamonds is also affected by the plastic deformation they underwent during their growth and rise to the surface of Earth.

Other FAs can be present in natural diamonds and in other native crystals, but they give deep levels whose spectroscopic properties are not discussed in the present volume.

From a physical aspect, the colour changes in a crystal can be attributed to the selective absorption of light by impurities or defects in the crystal at the corresponding energies, or to the absence of a spectral domain in the energy spectrum reflected by the crystal, which is absorbed by the crystal (see for instance [53]).

### 2.1.2 Contamination

Artificially-grown materials can be contaminated by FAs for several reasons. The first one is the initial purity of the starting material: for instance, the LHeT spectra of high-purity intrinsic silicon samples with RT resistivities  $\sim 10^4 \Omega \text{ cm}$  show the presence of residual boron and phosphorus at concentrations  $\sim 2 \times 10^{12} \text{ cm}^{-3}$  (see Fig. 7.7). Polycrystalline silicon also contains carbon as a residual impurity, which is transferred into the single crystal [45]. In bulk crystal growth, the impurities can come from the growth atmosphere,



and when a crucible is used to contain the melt, from chemical elements and impurities of the crucible. To illustrate this, most of the silicon crystals used in the electronic industry are grown by the Czochralski (CZ) method, from a melt contained in a silica crucible by dipping a monocrystalline silicon seed just below the melt, and slowly pulling it while the silicon solidifies as a crystal at the seed bottom. With this method, named after the Polish metallurgist Czochralski [15] and applied to germanium by Teal and Little [78], a rather large concentration ( $\sim 10^{18} \text{ cm}^{-3}$ ) of electrically-inactive oxygen originating from the partial dissolution or etching of silica by molten silicon is introduced in the crystal (see [47] and references therein). If this pollution has a detrimental effect on the electrical properties of silicon after being subjected to thermal treatments in the 300–500°C range because of the production of O-related thermal donors (see Sect. 6.4.1), it can be used after specific thermal treatments for the internal gettering (trapping) of harmful metallic impurities introduced in silicon during its processing [71]. The purest crucible-grown crystals are probably the undoped Ge crystals, grown from a silica crucible in a hydrogen atmosphere by the CZ method, with an overall bulk impurities concentration (mainly Si, O and H) in the  $10^{14} \text{ cm}^{-3}$  range ( $\sim 2.3$  atomic parts per billion (ppb)). A much lower O contamination in germanium is attributed to its melting point (937°C) compared to silicon (1414°C), and to the lower affinity of O for germanium. Severe O contamination ( $\sim 0.02\%$ ) is also observed in the high-pressure growth of GaN from a gallium solution containing dissolved nitrogen. When crystals containing an element with a high vapour pressure, like P or As, are grown by the CZ method, they form an indirect source of contamination: to prevent evaporation of the volatile element, a compound with a low vapour pressure is placed at the top of the polycrystalline charge to be melted. Once molten, this encapsulant makes a tight seal between the molten material and the atmosphere of the furnace (usually nitrogen), and this growth method is known as the Liquid Encapsulation Czochralski (LEC) method. Consequently, the impurities contained in the molten encapsulant are introduced in the crystals grown by this method: to grow GaAs and InP crystals, the encapsulant used is wetted boron oxide ( $\text{B}_2\text{O}_3$ ). In addition to the introduction of B and O impurities at high temperature, water is added to  $\text{B}_2\text{O}_3$  to prevent sticking between the encapsulant and the crystal, and its dissociation introduces hydrogen in the crystal [81].

The contamination introduced by melting polycrystalline charges in a crucible at high temperature has, for some crystals like silicon requiring a low O content for specific applications, led to the development of crucibleless growth methods. In this method, a monocrystalline seed is mounted at the bottom or at the top of a polycrystalline charge, and the polycrystalline region in contact with the seed is melted by a contactless technique (a RF field or a halogen lamp furnace). The melted region is prevented to flow from capillarity forces alone, and it is displaced upward or downward by moving the RF coil, leaving a monocrystalline region. This float zone (FZ) method was invented

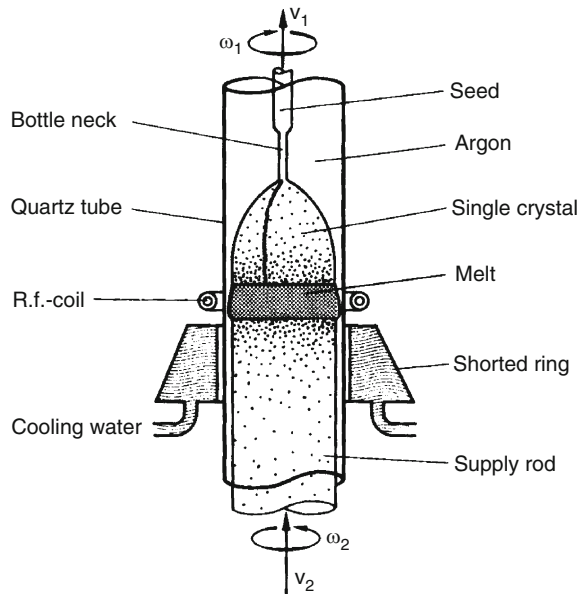


**Fig. 2.2.** Schematic set-up of a top-seeded FZ apparatus. A float zone of the polycrystalline silicon supply rod is locally melted by the RF field of the coil located outside of the quartz tube. In this particular set-up, at the beginning of the process, the diameter of the single crystal is reduced to a few mm to prevent dislocations to propagate in the monocrystalline part continuing the monocrystalline seed [44]

independently by several scientists ([44], and references therein). A schematic FZ setup for silicon crystal growth is shown in Fig. 2.2.

A down-seeded FZ apparatus is shown in Fig. 1 of Chap. 2 of [47]. The growth of crystals, with lower melting points and low reactivity, was obtained by the Bridgman method in an elongated crucible held horizontally, with the monocrystalline seed at one end of the crucible (horizontal Bridgman (HB) method). The principle of the monocrystalline growth is to displace the molten zone from the seed region along the crucible length. The Bridgman method is also used as a variant when a sealed crucible is displaced vertically in a temperature gradient (vertical gradient freeze (VGF) method), for instance in the growth of CdTe monocrystals [67]. The contamination of crystals often occurs from the ambient gas in these methods.

Besides the nitrogen contamination due to pollution of the carrier gas, the diamond films obtained by chemical vapour deposition (CVD) are usually contaminated with silicon. This contamination originates from the plasma etching of the silica walls of the reactor and of the commonly used silicon substrates [37].

The semiconductor layers grown by the metal-organic vapour-phase epitaxy (MOVPE) generally contain hydrogen pairs or complexes originat-

ing from the thermal dissociation of the organic part of the metal–organic precursor [13].

Metallic contamination by transition metals (TMs) and copper is found in many semiconductors because of the high diffusion coefficients of these elements. It has many origins, including the initial purity of the materials, chemical etching, electrical contacts, mechanical contacts with metallic parts or metallic constituents, or heating resistance in thermal treatments. For technological reasons, this contamination has been widely studied in silicon CZ wafers and also in germanium, in relation with nuclear radiation detectors. Generally, it remains at a low level, but can be detected by sensitive methods like deep level transient spectroscopy (DLTS) when deep centres are produced or photo-thermal ionization spectroscopy (PTIS) when the TMs form EM complexes.

### 2.1.3 Doping

The main objective for doping semiconductors and insulators is to control their electrical properties by introducing donors or acceptors in these crystals, which subsequently introduce well-defined concentrations of free carriers. Standard doping of bulk semiconductor crystals is achieved by adding to the solid charge or directly to the melt a particular amount of the dopant element or a crystal–dopant alloy. This method works for many dopants in group-IV and in III–V semiconductors. This is the principle; but the actual process can be more intricate because the final objective, which is usually the homogeneous doping of a crystal at a given level, depends on several physical factors that must be carefully controlled. For instance, in the CZ method, when the dopant is added to the melt, one must consider the segregation (or distribution) coefficient of the impurities, which is the ratio of the concentrations of a given impurity in the solid and liquid phases. It is usually smaller than unity; therefore, the dopant concentration in the melt increases as a function of the fraction of the melt already solidified. Subsequently, there is a steady increase of the impurity concentration in the crystal with the solidified fraction. Incidentally, the fact that the segregation coefficients of many electrically active impurities are less than unity has been used in the zone-melting process to purify a large region of semiconductor crystals grown by the Bridgman method: one extremity of the crystal, contained in an elongated “boat,” is melted and the molten zone is translated along the crystal, concentrating the impurities at the other end of the crystal and the process is repeated as long as is necessary.

Different techniques have been developed to produce CZ doped crystals with a good longitudinal homogeneity [65]. Radial fluctuations of the dopant concentration in the melt are also related to the convection current in the molten phase and to the speed of rotation of the crystal, and this can be troublesome for some technological applications. This problem has been solved in the n-type silicon by neutron transmutation doping (NTD), as shown in

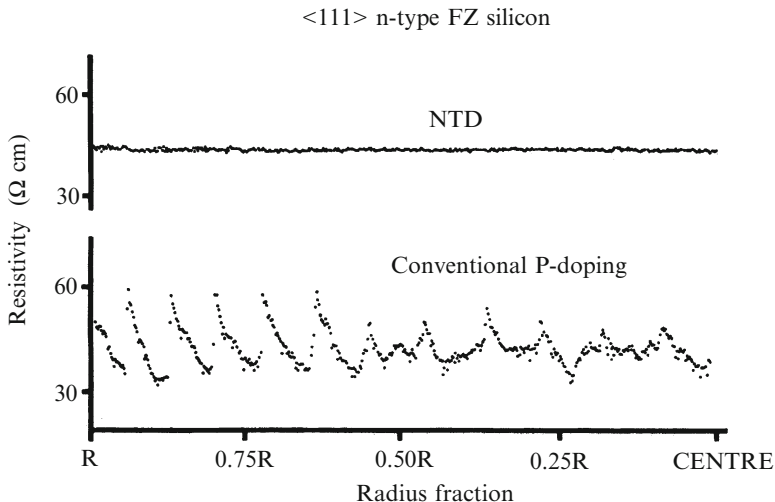
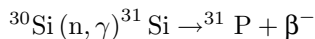


**Fig. 2.3.** Comparison of the radial distribution of phosphorus from the centre to the rim of two 3-in. ( $\sim 76$ -mm) silicon slices cut from a crystal doped in the melt (*bottom*) and from a NTD crystal (*top*). The local resistivity, proportional to the inverse of  $[P]$ , is measured by spreading resistance (after [31])

Fig. 2.3. A brief account of this method and of the results derived are given in this chapter.

The principle of NTD is to use a nuclear reaction involving first the absorption of a thermal neutron, of energy in the 25 meV range, by one isotope of a chemical element of a semiconductor crystal. The second step is the conversion of the radioactive nucleus thus formed, by emission of a high-energy (h-e) electron ( $\beta^-$ ), into a dopant atom. This method was first used with germanium by Cleland et al. [12], and is illustrated here for silicon with three natural isotopes (see the isotope table of Appendix D): nuclei of isotope  $^{30}\text{Si}$  (3.1% natural abundance) can absorb thermal neutrons with an absorption cross-section  $\sigma_n$  of 0.11 barn (1 barn is  $10^{-24} \text{ cm}^2$ ) to produce the radioactive  $^{31}\text{Si}$  nuclei in an excited state, which immediately relaxes into the ground state by the emission of a h-e photon ( $\gamma$ -ray). The  $^{31}\text{Si}$  nuclei then convert into a stable  $^{31}\text{P}$  nuclei (100% natural abundance) with a characteristic lifetime of 2.5 h by  $\beta^-$  emission. The above nuclear reactions are written synthetically as:



The concentration of P is proportional to  $[^{30}\text{Si}]$  in  $^{\text{nat}}\text{Si}$  ( $\sim 1.55 \times 10^{21} \text{ cm}^{-3}$ ), to the cross section  $\sigma_n$ , and to the thermal neutron fluence (integrated flux per  $\text{cm}^2$ )  $f_n$ . For a thermal neutron fluence of  $1 \times 10^{18} \text{ cm}^{-2}$ ,  $[^{31}\text{P}] \sim 1.7 \times 10^{14} \text{ cm}^{-3}$ . Besides homogeneous doping, another advantage of NTD is the control of doping level when  $f_n$  is accurately known. However, due to technological constraint, NTD is not suitable for the production of very low-

resistivity silicon material within reasonable irradiation times. The application of NTD to silicon doping was started in 1973 and presently, NTD silicon wafers with a  $5\ \Omega\text{ cm}$  resistivity, corresponding to  $[P] \sim 10^{15}\text{ cm}^{-3}$ , are commercially available. Most of the high-power silicon devices and thyristors are fabricated with NTD material because of the improvement of doping homogeneity. Thermal neutrons can also be absorbed by  $^{31}\text{P}$  with a cross-section of  $\sim 0.2$  barn to give radioactive  $^{32}\text{P}$ , that decays with  $\beta^-$  emission into stable  $^{32}\text{S}$ , with a lifetime of 14.3 days [73]. This is the main source of temporary radioactivity of NTD silicon, and for a planned resistivity of  $5\ \Omega\text{ cm}$ , the time taken to reach a radioactivity level below  $7.4\text{ Bq g}^{-1}$ , considered as innocuous, is  $\sim 45$  days.

From the crystallographic point of view, a few precautions are, however, essential before using this NTD silicon in electronic industry. The reason being the neutron beam also contains fast neutrons which produce lattice defects in the silicon crystal. These defects are traps for free electrons, and must be first removed by thermal annealing of the irradiated crystals (typically near  $1000^\circ\text{C}$  for a few hours) before a significant measurement of the resistivity change due to NTD can be made. The ratio of the flux of thermal neutrons over the fast neutrons, known as the cadmium ratio, can be roughly controlled by wrapping the small samples in Cd foils, which have a high stopping power for fast neutrons. Large ingots to be irradiated in light water-moderated reactors are usually located far from the core of the reactor so that the output of fast neutrons is attenuated by an adequate amount of water, with Cd ratios  $\sim 500$  or larger. An overview of NTD of silicon and of the advantage of this technique over conventional doping can be found in the review by von Hammon [82]. It must be noted that when NTD is used with germanium, the diversity of the Ge isotopes results in the production of donors (As) and acceptors (Ga) in a well-defined concentration ratio. This was used to obtain crystals with a high doping homogeneity and determine the compensation ratio for low-temperature IR bolometer [28]. Similarly, NTD of other semiconductors was also performed for silicon, for specific purposes including pure research. Table 2.1 summarizes the results of this doping method.

Fast neutron irradiation has been used to produce more exotic nuclear reactions like  $^{28}\text{Si}(n, \alpha)^{25}\text{Mg}$  and  $^{29}\text{Si}(n, \alpha)^{26}\text{Mg}$ , but the practical usefulness of this method is still to be demonstrated [21]. Electrically-active impurities can also be introduced in semiconductors by photonuclear transmutation doping. This technique, in some aspects, complementary of NTD, is based on the absorption of h-e  $\gamma$ -rays (typically  $30\text{ MeV}$ ) by semiconductors. The  $\gamma$ -ray absorption is followed by the emission by the nuclei of a neutron plus an electron or a positron, or of a proton [46]. For instance, in the case of silicon, the two useful nuclear reactions are  $^{28}\text{Si}(\gamma, n, \beta^+)^{27}\text{Al}$  and  $^{28}\text{Si}(\gamma, p)^{27}\text{Al}$ .

The doping of epitaxial layers is realized by the thermal dissociation of metal-organic compounds or molecules containing the doping elements and, in general, this can be well controlled. This is shown in Fig. 2.4 by the real-

**Table 2.1.** Transmutation doping in different semiconductors by the initial (n, $\gamma$ ) reaction

| Material          | Starting element  | $\sigma_n$<br>(barn)                                      | Intermediate product                          | Final dopant                              |
|-------------------|-------------------|-----------------------------------------------------------|-----------------------------------------------|-------------------------------------------|
| Si <sup>a</sup>   | <sup>30</sup> Si  | 0.11                                                      | <sup>31</sup> Si, $\beta^-$ decay             | <sup>31</sup> P (donor)                   |
| SiC <sup>b</sup>  | <sup>30</sup> Si  | "                                                         | as in silicon                                 | <sup>31</sup> P "                         |
| Ge <sup>c</sup>   | <sup>70</sup> Ge  | 3.25                                                      | <sup>71</sup> Ge, $e^-$ capture               | <sup>71</sup> Ga (acceptor)               |
|                   | <sup>74</sup> Ge  | 0.52                                                      | <sup>75</sup> Ge, $\beta^-$ decay             | <sup>75</sup> As (donor)                  |
|                   | <sup>76</sup> Ge  | 0.16                                                      | <sup>77</sup> Ge, double $\beta^-$ decay      | <sup>77</sup> Se "                        |
| GaP <sup>d</sup>  | <sup>69</sup> Ga  | 1.68                                                      | <sup>70</sup> Ga, $\beta^-$ decay             | <sup>70</sup> Ge (donor)                  |
|                   | <sup>71</sup> Ga  | 4.9                                                       | <sup>72</sup> Ga, "                           | <sup>72</sup> Ge "                        |
|                   | <sup>31</sup> P   | 0.18                                                      | <sup>32</sup> P, "                            | <sup>32</sup> S "                         |
| GaAs <sup>e</sup> | Ga                |                                                           | as in GaP                                     | Ge (donor)                                |
|                   | <sup>75</sup> As  | 4.3                                                       | <sup>76</sup> As, $\beta^-$ decay             | <sup>76</sup> Se "                        |
|                   |                   |                                                           |                                               |                                           |
| InP <sup>f</sup>  | <sup>115</sup> In | $\left\{ \begin{array}{c} 160 \\ 40 \end{array} \right\}$ | <sup>116</sup> In, $\beta^-$ decay            | <sup>116</sup> Sn (donor)                 |
|                   | <sup>113</sup> In | $\left\{ \begin{array}{c} 56 \\ 2 \end{array} \right\}$   | <sup>114</sup> In, "                          | <sup>114</sup> Sn "                       |
|                   | P                 |                                                           | <sup>114</sup> In, $e^-$ capture<br>as in GaP | <sup>114</sup> Cd (acceptor)<br>S (donor) |
| InSb <sup>g</sup> | In                |                                                           | as in InP                                     | Sn (donor)                                |
|                   | <sup>121</sup> Sb | 6.2                                                       | <sup>122</sup> Sb, $\beta^-$ decay            | <sup>122</sup> Te "                       |
|                   | <sup>123</sup> Sb | 4                                                         | <sup>124</sup> Sb, "                          | <sup>124</sup> Te "                       |
| ZnS <sup>h</sup>  | <sup>64</sup> Zn  |                                                           | <sup>65</sup> Zn, $e^-$ capture               | <sup>65</sup> Cu (acceptor)               |

The isotope distributions of the different elements are given in Appendix D

<sup>a</sup> [76], <sup>b</sup> [30], <sup>c</sup> [12], <sup>d</sup> [35], <sup>e</sup> [52], <sup>f</sup> [22], <sup>g</sup> [10], <sup>h</sup> [7]

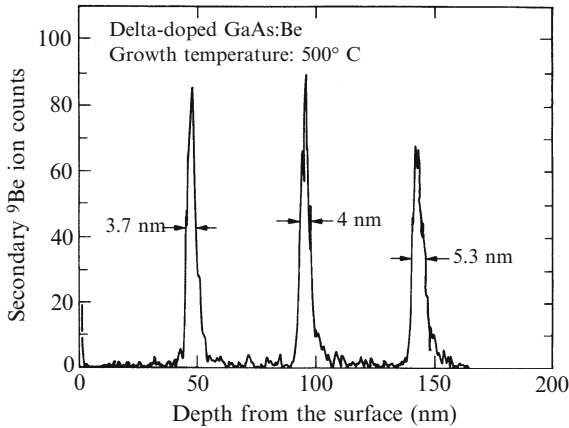


**Fig. 2.4.** SIMS profile of a  $\delta$ -doped GaAs sample with three Be doping spikes. The density of Be atoms in each layer is  $4 \times 10^{12} \text{ cm}^{-2}$  (after [69]). Copyright 1990, American Vacuum Society

ization of the delta-function-like doping profiles of epitaxial layers, obtained by growth-interrupted impurity deposition.

Be-doping profiles with full width at half-maximum of 2 nm have been reported in GaAs by this method. For a review of  $\delta$ -doping and of its interest in III–V semiconductors, see [69].

Another method to locally dope a crystal is the implantation of the dopant. The energy of the dopant ions determines their average penetration depth. This allows the possibility to locate a dopant layer below the crystal surface, and to produce the so-called buried layers of dopants. The incident ions produce lattice defects that must be removed by thermal or laser annealing. Another role of the annealing sequence can be to control the diffusion of the dopant atoms. To summarize, the energies and the doses of the dopant ions as well as further annealing of the implanted zone determine the doping level, the depth and the thickness of the doped layer.

Various techniques have been used for the diffusion of impurities in semiconductors [65]: the diffusion of shallow dopants from the gas phase in closed or open tubes has been a widely-used process in semiconductor technology to form thin doped layers. Fast diffusing transition metals like Cu, Au or Ag can be introduced in the bulk by evaporating or electroplating a thin layer of the metal at the surface of the sample and by annealing. Quenching of the samples after diffusion annealing is then mandatory to limit the formation of complexes. In other cases, a metallic element or different oxides are located in a part of the closed tube where the diffusion takes place. This method is, however, limited to semiconductor compounds where thermal dissociation of the material occurs at moderate temperature. The high melting point of silicon allowed diffusion in the bulk of FAs at high temperature (1380–1400°C). The depth to which the FAs are introduced depends on their diffusion coefficients as well as on the diffusion temperature and duration. This has been used, for instance, to introduce  $^{17}\text{O}$  and  $^{18}\text{O}$  isotopes in silicon with concentrations comparable to that of the most abundant  $^{16}\text{O}$  isotope [50]. More information on the diffusion of FAs in semiconductors is given in Sect. 2.2.2.

Last but not least, the treatment of a semiconductor by a plasma containing a fast diffusing and reactive impurity can lead to its introduction in the material. This has been a widely used method to elucidate the role of hydrogen in semiconductors (see [57]).

What is described above are general methods for doping materials, but the introduction of a FA in a crystal at a given concentration is determined primarily by its solubility. Moreover, it is not possible to dope any crystal with any impurity and some of the reasons for this are discussed later in this chapter.

### 2.1.4 Thermal Treatments and Irradiation

The growth and annealing of crystalline samples at high temperature produce a steady state concentration of elementary defects, because of the thermal

ejection of atoms from their regular sites. A slow cooling-down allows recombination of the interstitial atoms into the empty sites, but a relatively fast cooling-down or a quenching allows the most stable of these defects to survive and/or to agglomerate at RT. This mechanism explains the origin of point defects produced during the growth of some III–V and II–VI compound crystals, as the cooling-down of the solidified fraction is not an equilibrium process. In silicon, extended defects can be produced during the crystal growth like a series of dislocation loops, best known as striations or swirls, which can be decorated by oxygen in CZ silicon. Thermally-produced vacancies can also coalesce to form macroscopic voids which can be present in CZ and FZ silicon crystals at concentrations  $\sim 10^4\text{--}10^7\text{cm}^{-3}$  [42, 72]. The production of shallow acceptors, related to metallic contaminants, by quenching of germanium from temperatures above about 800°C to RT has been discussed in the review by Seeger and Chik [70] and this point is further discussed in Chap. 7. Quenched-in donors were also produced in silicon after annealing at 1000°C [61].

A combination of proton implantation and thermal annealing of CZ or FZ silicon has also been shown to produce shallow donors [85]. Hydrogen can also be introduced in a region near the semiconductor surface by hydrogen plasma treatments as long as the semiconductor surface does not suffer excessive plasma etching.

The main native defects in III–V and II–VI compounds are vacancies and atoms in antisites. For instance, the As antisite ( $\text{As}_{\text{Ga}}$ ) and the As vacancy ( $V_{\text{As}}$ ) are residual defects in LEC-grown GaAs crystals [6]. ZnO is a material whose electrical properties are determined by native lattice defect: the presence of interstitial Zn correlated with O vacancies ( $V_{\text{O}}$ ) seems to be responsible for the n-type electrical conductivity of many crystals, but in high-resistivity crystals obtained by hydrothermal growth, the dominant defect is caused by  $V_{\text{Zn}}$  [8].

Finally, annealing of CZ silicon in the 350–500°C temperature range produces O-related electrically-active centres known as thermal donors (TDs). The atomic structures of these TDs change as a function of the annealing duration. One category, which seems to involve only O and Si atoms in the cores of the centres, can bind two additional electrons [83]. Similar double-donor centres can also be produced in O-doped germanium [11]. These centres are unstable at high temperature, and are destroyed by annealing near 800°C. In CZ silicon containing N or H, short-time annealing in the 300–600°C range also produces donors known as shallow thermal donors (STDs) [2]. The spectra of these H-like donor centres are discussed in Chap. 6.

### 2.1.5 Concentration Measurements

Hall measurements at temperatures where the shallow centres are fully ionized give the free-carrier concentration. This concentration can be assumed to be the net dopant concentration, but it does not determine the compensation or



the presence of other centres of the same kind. Information on the latter category can be obtained from Hall measurements as a function of temperature, from which the average ionization energy can be deduced (see Fig. 1.1). As mentioned in Sect. 1.3.2.1, with some knowledge on the RT carrier mobility, the measurement of the RT resistivity can also be used to obtain a net impurity concentration when the chemical nature of the dopant is known (see for instance [80]). Complementary spectroscopic measurements under band-gap light illumination can cancel the compensation effects (see Sect. 1.3.3).

Secondary-ion mass spectrometry (SIMS) can be used to detect the presence and the depth distribution of a specific impurity by etching out ions (secondary ions) from a material with a  $\text{Cs}^+$  or  $\text{O}_2^+$  ions probe, and measuring the impurity peak by mass spectrometry. This method provides a chemical signature of the impurity, with possible interferences, however, between atomic and molecular ions with the same masses and charges. It cannot discriminate between the isolated impurity and complexes or precipitates in which it is involved. Its sensitivity depends on the background of impurity. SIMS has been used for the detection of boron acceptor in CVD diamond [39]. These absolute methods of concentration measurements have been combined with spectroscopic measurements, which are easier to perform, to produce spectroscopic calibration factors.

## 2.2 Structural Properties

### 2.2.1 Global Atomic Configurations

In crystals, impurities can take simple configurations. But depending on their concentration, diffusion coefficient, or chemical properties and also on the presence of different kind of impurities or of lattice defects, more complex situations can be found. Apart from indirect information like electrical measurements or X-ray diffraction, methods such as optical spectroscopy under uniaxial stress, electron spin resonance, channelling, positron annihilation or Extended X-ray Absorption Fine Structure (EXAFS) can provide more detailed results on the location and atomic structure of impurities and defects in crystals. Here, we describe the simplest atomic structures; more complicated structures are discussed in other chapters. To explain the locations of the impurities and defects whose optical properties are discussed in this book, an account of the most common crystal structures mentioned is given in Appendix B.

The classical doping of semiconductors shows that a FA can replace an atom of the crystal at a regular lattice site. In covalent or partially covalent crystals, the main parameters which must be considered for the possible location of a FA on a substitutional site are its ability to form chemical bonds with its neighbours and the strengths of these bonds. When a crystal is made

up of two different elements, with the sphalerite or wurtzite structure, a substitutional FA can possibly occupy two different lattice sites. This kind of amphoteric behaviour occurs in GaAs, where, depending on the growth conditions, a Si atom can occupy either a Ga site ( $\text{Si}_{\text{Ga}}$ ) where it is a donor or an As site ( $\text{Si}_{\text{As}}$ ) where it is an acceptor. This duality is not a general rule, however, and the doping or contamination of GaAs with carbon produces only the  $\text{C}_{\text{As}}$  acceptor. In binary semiconductors, each atom type of the crystal occupies one sublattice: for instance, in the III–V compounds, the group-III and group-V sublattices. For different reasons, some group-V (–III) atoms can get located on group-III (–V) sublattice, and these antisite atoms can be considered as “internal” impurity atoms. Similarly, a foreign group-V atom can occupy a group-III site (Sb in GaAs, for instance) and act as an “external” antisite. The location of FAs at substitutional sites is very common among semiconductors. This does not necessarily mean that the FA takes the exact equilibrium position of the atom it replaces as, depending on the radius and valence of the FA, lattice distortion can occur.

Small FAs tend to occupy interstitial sites. Figure 2.5 shows possible interstitial locations of isolated FAs in a III–V compound with sphalerite structure.

In the  $T_i$  sites, the impurity is located at a tetrahedral interstitial site, where it is weakly bonded to the crystal lattice. In compounds with the sphalerite or wurtzite structure, with two different substitutional sites, there are also two different  $T_i$  sites: one where the interstitial atom is nearer from atoms of one sublattice and another where it is nearer from atoms of the other sublattice ( $T_{\text{III}}$  and  $T_{\text{V}}$  of Fig. 2.5). As the electronic densities are different at these two sites, the foreign interstitial atoms preferably occupy one of these sites. This  $T_i$  location is also found for Li atoms in silicon and germanium crystals, and as there is no chemical bond between the Li and Si or Ge atoms, the  $2s$  valence electron of the Li atom has a low binding energy, making interstitial lithium ( $\text{Li}_i$ ) a shallow donor in these semiconductors ( $\text{Li}_i$  cannot form in diamond because of the very dense packing in this crystal). Another consequence of the weak bonding and small ionic radius of the  $\text{Li}^+$  ion is its large diffusion coefficient in silicon and germanium. A FA at the  $BC$  location is sometimes called interstitial, but the bonding must be rearranged to allow the foreign atom to form bonds with its neighbours. Besides a rather small size of the atom, this location also implies a strong affinity between the foreign and lattice atoms. For instance, isolated H in silicon and germanium is stable in this  $BC$  configuration at low temperature. The paradigm of such a structure is the so-called interstitial oxygen ( $\text{O}_i$ ) atom bonded to two  $nn$  Si atoms in silicon.

An interstitial atom in an antibonding ( $AB$ ) site is bonded to its nearest neighbour lattice atom. This location is often found in H complexes involving a donor atom and results in the relaxation of the local lattice bonding. There also exists a special interstitial structure, the di-interstitial configuration. Incidentally, Fig. 2.5 shows the ternary symmetry of the sphalerite lattice along a  $\langle 111 \rangle$  direction. This is analogous with the wurtzite structure, where

the  $\langle 111 \rangle$  direction is replaced by the  $c$ -axis direction (Appendix B). In the  $\langle 111 \rangle$  direction, the sphalerite lattice is made of alternate layers of atoms of the two sublattices. It can also be seen in Fig. 2.5 that the stacking sequence is a period of three layers of atoms of the same kind (the so-called **ABC** sequence).

Pairing between identical or different impurities is also found in semiconductors and insulators; and is described here. Pairing of two nearest neighbour substitutional chalcogen (S, Se and Te) atoms is found in silicon doped with these elements [26], and this must be related to their propensity to form polyatomic molecules, like  $S_8$ . Pairing is an efficient process; in S-doped silicon, the concentration of S pairs is larger than the concentration of isolated S. In diamond, two N atoms can occupy nearest neighbour substitutional sites and this  $N_2$  pair is the dominant centre in the IaA natural diamonds [16]. In silicon and germanium, because of the relatively small size of the N atom

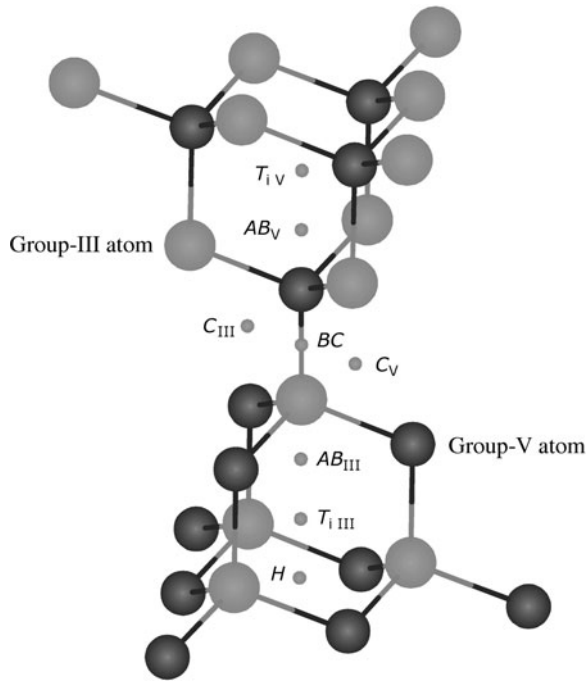


**Fig. 2.5.** High-symmetry sites (small spheres) in a III-V sphalerite lattice oriented along a  $\langle 111 \rangle$  vertical axis (the simple substitutional sites are not indicated).  $BC$  bond-centred,  $AB$  antibonding,  $T_i$  tetrahedral interstitial,  $H$  hexagonal sites are located along the  $\langle 111 \rangle$  axis. The  $T_i$  and  $AB$  sites are noted according to the atoms closest to these sites. The  $C$  site, midway between two next nearest neighbours along a  $\langle 110 \rangle$  axis, is observed according to these atoms. The  $M$  site (not shown) is midway between two adjacent  $C_{III}$  and  $C_V$  sites and also midway between a  $BC$  site and a  $H$  site

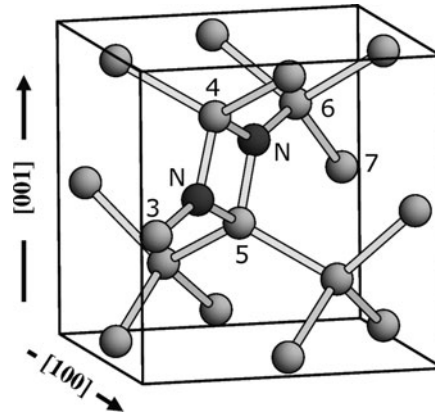


**Fig. 2.6.** Model of the split nitrogen pair in the silicon crystal. In the perfect crystal, the Si atoms 3, 4, 5, 6, and 7 form a zigzag chain along a  $\langle 110 \rangle$  direction in a  $\{110\}$  plane. The introduction of the two N atoms leads to the breaking of the Si-Si bonds between atoms (3,4), (4,5) and (5,6), and to the bonding of one N to atoms 3, 4 and 5 and of the other N to atoms 4, 5 and 6. Courtesy N. Fujita

compared to the lattice atoms and also because of the high strength of the  $N_2$  molecular bond, when introduced in silicon and germanium, most of the nitrogen goes in the form of a nitrogen split pair ( $N_{2i}$ ) depicted schematically in Fig. 2.6. In this configuration, the two N atoms are located at equivalent sites which are distorted interstitial ones. Each of the two Si atoms separating the N atoms (atoms 4 and 5 in Fig. 2.6) is bonded to the two N atoms in order to realize the trivalent bonding of the N atoms, making this pair electrically inactive.

This kind of bonding bears similarities with that for divalent  $O_i$ . The existence of trivalent bonding of oxygen in CZ silicon has been discussed in relation with the possible structures of oxygen TDs produced by annealing in the 350–550°C range [17]. In this configuration, normally divalent oxygen becomes electrically active and acquires a donor character. A limiting case of pairing is observed in the interstitial hydrogen molecule found in different semiconductors after hydrogen-plasma treatment, which is a nearly free rotator ([32], and references therein). In GaP, N is an isoelectronic FA with a relatively high solubility, and at concentrations larger than  $\sim 10^{17} \text{ cm}^{-3}$ , it can first form the so-called  $NN_1$  pair due to  $nnn$   $N_P$  atoms and when increasing  $[N]$  to more distant NN pairs, whose spectroscopic properties were reported in [79]. Pairing can also be attributed to the interaction between atoms of opposite type, for instance the donor-acceptor substitutional pairs found at high dopant concentrations in silicon [54]. Another kind of pairing is a mixed one, between a substitutional acceptor atom (actually a negative ion) and a positively charged interstitial atom. The  $Li_i^+ B_s^-$  pair is an example of such a configuration, but many other pairs involving interstitial transition

metal ions also exist. The mobility of interstitial atoms produced by electron irradiation can also result in pairing: in electron irradiated silicon containing carbon, evidence of the presence of a mixed  $C_iC_s$  pair has been obtained, related to the difference of electronic charge of the two atoms. As mentioned before, the  $H_2$  molecule is a limiting case of homonuclear pairing, but when introduced in semiconductors as a positive or negative ion, hydrogen can pair with many dopants and impurities due to Coulomb interaction, producing hydrogen-related vibrational spectra.

## 2.2.2 Solubilities and Diffusion Coefficients

### 2.2.2.1 Solubility

In many cases, impurities and dopants are introduced in the molten phase, in which they have a definite solubility  $N_{\text{sol-l}}$ . In the solid phase, near the melting point, the solubility  $N_{\text{sol-s}}$  decreases with respect to the liquid phase and the ratio  $N_{\text{sol-s}}/N_{\text{sol-l}}$ , the segregation coefficient, is usually less than unity. The solubility of impurities in crystals can be considered, in most cases, as the maximum concentration of isolated FAs which can be introduced in a crystal before precipitation, formation of cluster of a mixed compound (e.g., SiC in C-doped silicon) or of an alloy. The solubility of an impurity is conditioned by its atomic radius, electronic structure, site(s) in the crystal, eventual binding energies with the atoms of the crystal and tendencies to form a complex or to form pairs. As it generally requires energy to introduce an impurity in a crystal, solubility is a temperature-dependent (thermally activated) process characterized by an activation energy (the heat of solid solution), and for this reason, it is larger near the melting point of the crystal than at RT. When solubility is mentioned, it is mandatory to know the temperature it corresponds to. For solubilities measured near RT, one must distinguish between the equilibrium solubility, corresponding to the cooling down of crystals after the introduction of the FAs under conditions close to thermodynamic equilibrium, and the non-equilibrium solubility. In the second case, the apparent solubility is larger than the equilibrium solubility and the crystal is oversaturated. This situation is encountered naturally for  $O_i$  in CZ silicon. There have been many studies of solubility of  $O_i$  in silicon [58] and the equilibrium solubility  $[O_i]_s$  between the melting point (1414°C) and 850°C can be reasonably represented by [51]:

$$[O_i]_s \text{ (cm}^{-3}\text{)} = 9.0 \times 10^{22} \exp[-1.52 \text{ (eV)} / k_B T] \quad (2.1)$$

Within these limits, the solubility calculated using expression (2.1) varies between  $2.6 \times 10^{18}$  near the melting point and  $1.4 \times 10^{16} \text{ cm}^{-3}$  at 850°C. There is no exact value of the equilibrium solubility of  $O_i$  at RT, but it is expected to be lower than the value at 850°C. The actual value of  $[O_i]$  measured at RT in CZ

silicon is in the  $10^{18} \text{ cm}^{-3}$  range, showing that this material is oversaturated with  $[\text{O}_i]$ . Comparable values have been reported in O-doped germanium [41]. In silicon, nitrogen is not a residual impurity because its solubility is much lower than that of the other group-V elements and of carbon and oxygen. One of the reasons for this can be the fact that its most stable configuration in silicon is the nitrogen split pair presented above. As nitrogen doping improves the mechanical properties of silicon, its doping has been extensively investigated. Non-equilibrium solubilities of dopants can also be deliberately reached after implantation by solid-phase-epitaxial regrowth, flash or laser anneals of the implanted zone. These fast annealing procedures produce a local non-equilibrium situation which is frozen at RT because of the very short cooling down duration. The metastable solubilities obtained by such annealings can be one order of magnitude larger than the equilibrium solubilities [19]. For group-III and group-V dopants in silicon, the smaller the dopant atom, the higher is the solubility. This also holds true for other materials, and the solubility of B in synthetic CVD diamond can reach  $\sim 10^{22} \text{ cm}^{-3}$  ( $\sim 6\%$  at.), leading to metallic conductivity of these heavily-doped diamonds [5]. An order of magnitude of the equilibrium solubility of isolated P in silicon at RT is  $1 \times 10^{20} \text{ cm}^{-3}$  (0.2 atomic %); it is larger than that of Sb ( $\sim 1 \times 10^{19} \text{ cm}^{-3}$ ) and Bi ( $\sim 1 \times 10^{17} \text{ cm}^{-3}$ ). The radius of the impurity is not the only relevant factor: the P and S atoms have comparable covalent radii and in silicon, they are single and double donors, respectively, inducing comparable distortions in the silicon lattice. However, the admitted RT solubility of S is only  $3 \times 10^{16} \text{ cm}^{-3}$ . This is partially related to the chemical bonding arrangement of S, for which tetrahedral bonding produces distortion of the electron density. Another contribution is the propensity of sulphur to form a variety of complexes in silicon (see Sect. 6.3.1.1). The problem of FA solubility in a crystal can be complicated by the fact that the same atom can sometimes occupy either interstitial or substitutional sites, like some TMs in silicon. In such a case, the apparent solubility is higher for the interstitial location. Globally, the TMs are characterized by a solubility in the  $10^{16}$ – $10^{17} \text{ cm}^{-3}$  range, and by diffusion coefficients significantly larger than those of the substitutional shallow donors and acceptors [68]. The interstitial solubility of TMs and of group-IB elements in silicon also depends on the concentration of substitutional acceptors in the material because, as mentioned before, they can form interstitial–substitutional pairs with these acceptors. This is also true for  $\text{Li}_i$ , which form pairs with substitutional acceptors, but there seems to be no consensus on the room temperature solubility of  $\text{Li}_i$  in FZ silicon. A value  $\sim 10^{16} \text{ cm}^{-3}$  can be inferred from the conclusions of [87]. As a rule, the solubility of elements of groups II and VI in silicon decreases compared to that of elements of groups III and V, with the notable exception of O and H. The solubility of C in III–V compounds has been thoroughly investigated as in these crystals, C is in some cases a pollutant and usually a p-type substitutional dopant with a rather large solubility limit (in the  $10^{20} \text{ cm}^{-3}$  range for GaAs). In silicon, the solubility of substitutional C at the melting point is

$\sim 4 \times 10^{17} \text{ cm}^{-3}$  [56] and it is found to be higher in CZ silicon than in FZ silicon because the lattice contraction induced by  $C_s$  is compensated by the lattice dilatation induced by  $O_i$ . In crystals supersaturated with C, annealing can produce precipitation of SiC nanoparticles [4].

Besides the substitutional/interstitial location of the same FA, other centres can exist where more than one FA are involved, like the *nn* substitutional pairs for chalcogens in silicon or nitrogen in diamond so that in these cases, one must consider a universal value of solubility of the FAs.

In most crystals, supersaturated with substitutional or *BC* impurities, these atoms are usually immobile at room temperature because their diffusion coefficients are small at this temperature. However, when annealing is performed at relatively high temperatures where materials are saturated with impurities, precipitation or formation of complexes involving impurities can take place because of their migration. This is the state in CZ silicon where silica precipitates are produced during annealing at 800°C. A limiting case is achieved when the host crystal and the impurity are partially or fully miscible. This is the case with Ge in silicon, giving at high Ge concentrations  $\text{Ge}_x\text{Si}_{1-x}$  alloys, and also with most of the group-III FAs in III–V compounds, like Al in GaAs giving  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  alloys.

### 2.2.2.2 Diffusion Coefficients

The diffusion of dopants in semiconductors has been briefly discussed in Sect. 2.1.3. At an atomic scale, the diffusion of a FA in a crystal lattice can take place by different mechanisms, the most common being the vacancy and interstitial mechanisms in silicon and germanium (see for instance [25]). The interstitial/substitutional or kick-out mechanism, which is an interstitial mechanism combined with the ejection of a lattice atom (self-interstitial) and its replacement by the dopant atom is also encountered for some atoms like Pt in silicon.

When the constant surface concentration of an impurity with diffusion coefficient  $D$  is  $N_{is}$ , its concentration  $N_i(x, t)$  at depth  $x$  from the surface of a plane sample of thickness  $d \gg x$  after a diffusion time  $t$  is given in an ideal case by:

$$N_{ix} = N_{is} \text{erfc} \frac{x}{2\sqrt{Dt}} \quad (2.2)$$

where the complementary error function  $\text{erfc } u = (1 - \text{erf } u) = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-t^2} dt$ . A table of the error function  $\text{erf } u$  can be found p. 142 of [65].

The temperature dependence of the diffusion coefficient or diffusion constant is generally expressed as:

$$D(T) = D_0 \exp[-E_D/k_B T] \quad (2.3)$$

**Table 2.2.** Values of diffusion parameters of some representative foreign atoms in silicon

|                 | Ref. | $D_0$ ( $\text{cm}^2 \text{s}^{-1}$ ) | $E_D$ (eV) | D                             |
|-----------------|------|---------------------------------------|------------|-------------------------------|
| Al              | a    | 1.8                                   | 3.2        | $2 \times 10^{-11}$ (1200°C)  |
| P               | b    | 5.3                                   | 3.69       | $1.2 \times 10^{-12}$ "       |
| S               | c    | 0.047                                 | 1.8        | $3.3 \times 10^{-8}$ "        |
| Li <sub>i</sub> | d    | $2.5 \times 10^{-3}$                  | 0.655      | $4.4 \times 10^{-9}$ (300°C)  |
| Cu <sub>i</sub> | e    | $4.5 \times 10^{-3}$                  | 0.39       | $1.7 \times 10^{-6}$ "        |
| Fe <sub>i</sub> | f    | $9.5 \times 10^{-4}$                  | 0.65       | $1.5 \times 10^{-6}$ (900°C)  |
| Ti <sub>i</sub> | g    | 0.0145                                | 1.79       | $1.1 \times 10^{-8}$ (1200°C) |
| Pt              | h    | 5.9                                   | 3.97       | $1.5 \times 10^{-13}$ "       |
| O <sub>i</sub>  | i    | 0.13                                  | 2.53       | $2.9 \times 10^{-10}$ "       |
| C               | j    | 1.9                                   | 3.1        | $4.7 \times 10^{-10}$ "       |

D is calculated at the temperature indicated in parentheses using expression (2.3)

<sup>a</sup> [63], <sup>b</sup> [48], <sup>c</sup> [62], <sup>d</sup> [60], <sup>e</sup> [49], <sup>f</sup> [38], <sup>g</sup> [33], <sup>h</sup> [68], <sup>i</sup> [51], <sup>j</sup> [55]

where  $E_D$  is an activation energy related to the diffusion mechanism. In Table 2.2, the values of  $D_0$  and  $E_D$  are listed for a few representative dopants and impurities in silicon. Values of D for other FAs in silicon can be found in [20].

The value of the diffusion coefficients of impurities and dopants in semiconductors can be modified by the presence of compensating impurities or of crystal dislocations so that the interpretation of diffusion measurements requires some judgment. It must also be mentioned that as the diffusing species can be ions, the diffusion coefficient can be modified by an electric field.

### 2.2.3 Lattice Distortion and Metastability

FAs in a crystal can induce a local deformation of the lattice. When they are substitutional, this is caused by the difference between their atomic radii and those of the atoms they replace and also by their chemical affinity with the surrounding atoms. According to Vegard's law,<sup>1</sup> substitutional atoms having a smaller (larger) atomic radius than the atom they replace should produce a uniform lattice contraction (expansion) of the crystal proportional to their concentration. With reference to the unperturbed lattice parameter  $a_0$  of cubic crystal, the change  $\Delta a$  of the lattice parameter produced by a concentration  $N_f$  of FAs can be expressed as:

$$\frac{\Delta a}{a_0} = \beta_f N_f, \quad (2.4)$$

<sup>1</sup> Vegard's law is an empirical rule which holds that an approximate linear relation exists between the crystal lattice parameter of an alloy and the concentration of its constituent elements (L. Vegard, Z. Kristallogr. **67**, 239 (1928). See also A.R. Denton, N.W. Ashcroft, Phys. Rev. A **43**, 3161 (1991)).



where  $\beta_f$  is a lattice distortion coefficient. For substitutional impurities in covalent or partially covalent cubic crystals, the sign and order of magnitude of  $\beta_f$  can be obtained by replacing  $\Delta a$  by the difference between the covalent radii of the impurity and of the host crystal,  $a_0$  by the intrinsic atomic separation in the host crystal and  $N_f$  by the number of available sites for impurity sites per unit volume. The value of this coefficient for substitutional boron in silicon, calculated from the atomic radii, is  $\beta_{B(\text{calc})} \sim -5 \times 10^{-24} \text{ cm}^3 \text{ atom}^{-1}$ . For dopants with a covalent radius showing a large difference from that of the atom it replaces, like Tl or Bi in silicon, or P in diamond, this distortion limits their solubility. Another kind of local distortion encountered for substitutional impurities is the lowering of symmetry, like the one for isolated N in silicon or diamond, where the atom is displaced along a N–X bond (X is an atom of the crystal) along a  $\langle 111 \rangle$  direction. A local distortion can also reduce the symmetry of a centre through the Jahn-Teller effect, as for the atomic vacancy in silicon: this defect should normally display tetrahedral symmetry, but it is lowered to  $D_{2d}$ , and can be detected in the paramagnetic states by the dependence of the ESR spectra on the magnetic field orientation (see Sect. 1.3.5). Lattice distortion related to the bond lengths can also occur for an interstitial atom strongly bonded to atoms of the crystal in the  $BC$  configuration of Fig. 2.6. In this particular case, if the structure remains linear, the two  $nn$  atoms of the crystal can be pushed out of their equilibrium positions when the lengths of the new bonds exceed the equilibrium  $nn$  separation.

When the local effect of distortion and the impurity concentration are large, a difference in the average lattice parameter as a function of the impurity concentration can be measured with appropriate X-ray diffraction techniques. In silicon, values of  $\beta_B = -5.2 \times 10^{-24} \text{ cm}^3 \text{ atom}^{-1}$  and  $\beta_O = 4.4 \times 10^{-24} \text{ cm}^3 \text{ atom}^{-1}$  were measured for B and  $O_i$ , respectively [34, 75, 86]. Incidentally, a good agreement is found between the measured value of  $\beta_B$  and the value predicted from Vegard's law. With  $[O_i] \sim 10^{18} \text{ cm}^{-3}$  found mostly in the CZ silicon crystals, the value of  $\beta_O$  corresponds to a relative increase of the lattice parameter of  $4.4 \times 10^{-6}$  compared to high-purity FZ silicon. The distortion induced by substitutional carbon and silicon in GaAs has also been investigated by X-ray diffraction [3, 18].

The lattice distortions induced by substitutional impurities can also be measured locally from the distance between an impurity atom and its nearest neighbours using EXAFS [64]. The results of the EXAFS experiments require sensible interpretations as they do not necessarily follow simple rules like the addition of the covalent radii of the elements involved [43, 84]. Local volume changes of group-V and group-VI donor atoms in silicon have been obtained indirectly from a comparison between the measured spacings of the absorption lines of these donors with the calculated values [59] and the procedure is discussed in Sect. 6.2.1. Interesting conclusions regarding the colour change of ruby as a function of the chromium concentrations have also been drawn from EXAFS measurements [23]. Global lattice expansion or contraction can also

be measured, for instance by X-ray diffraction, in doped layers epitaxied on an undoped substrate of the same material from the positive or negative interface stresses, depending on the atomic radius of the doping atom with respect to that of the atom it replaces. In some cases, first-principle calculations have given a good insight of the local distortion induced by a foreign atom [27, 66].

In crystals with a high concentration of shallow donors or acceptors, another contribution to the volume change at room temperature is the presence of free carriers in the continuum. This effect is related to the minimization of the total energy of the crystal compared to that of the undoped crystal ([24] and references therein). This purely electronic effect has been considered, together with the eventual presence of a high concentration of native defects, in the variation of the lattice parameter of Si-doped GaAs conducting substrates used in the electronic industry [3].

For centres with different charge states, the distortion can be modified by changing the electronic density in the vicinity of the centre. Thus, a change of the charge state of a centre can produce a local lattice relaxation. It is usual to describe the electronic energy states of these centres as a function of configuration coordinates. When a change of the charge state induces lattice relaxation, the equilibrium configuration coordinates can differ in the two states. This situation is represented in Fig. 2.7 in a lattice configuration coordinate diagram, where the energies are represented approximately in 1D by parabolas as a function of a general lattice (configuration) coordinate representing the lattice relaxation.

The optical transition (optical ionization energy  $E_{\text{io}}$ ) takes place without lattice relaxation while the thermal ionization energy  $E_{\text{ith}}$  corresponds to an equilibrium configuration. Figure 2.7 shows that in this particular situation,  $E_{\text{ith}}$  is smaller than  $E_{\text{io}}$ . The difference is the Franck–Condon shift  $E_{\text{FC}}$ . This diagram will be used later with some additions in the discussion of the coupling of the electronic transitions of impurities with the phonon modes of crystal.

It should be noted that, within the same global charge state of a centre, due to differences in electronic densities, lattice relaxation can also occur between the ground state and excited states, with the same consequences of equilibrium configuration coordinates.

A limiting case of distortion is the occurrence of a second atomic configuration of a centre in the same charge state. The idea of this possibility was not obvious at first sight, but experimental results including optical spectroscopy results have led to admit this situation. When two such non-degenerate atomic configurations of a centre coexist, the one with the lowest energy is the stable one while the other is said to be metastable. There is an energy barrier between the two configurations, and its value determines the temperature domain of the metastability. The corresponding centre is often said to be bistable. A relatively well-characterized bistable centre involves a  $\text{B}_\text{s}\text{--Si}_\text{i}$  pair, produced in B-doped silicon by electron irradiation at low temperature. Based on experimental results, it has been known for some time as the interstitial B ( $\text{B}_\text{i}$ ) centre [29]. However, calculations have shown

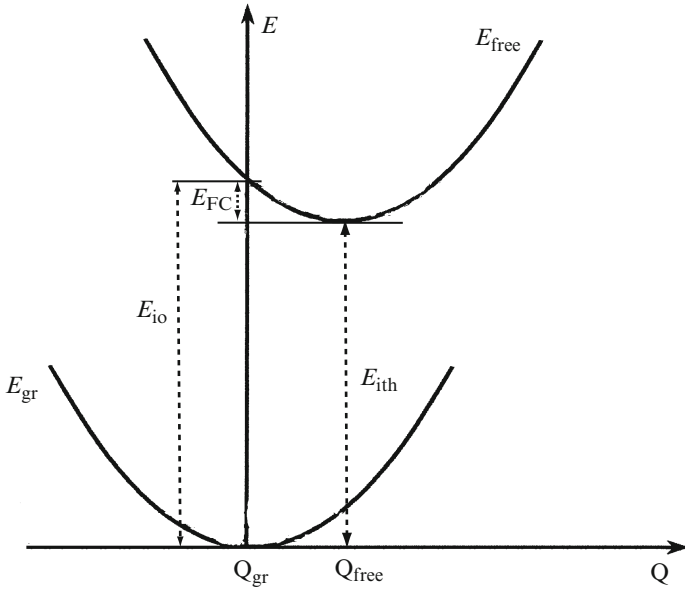


**Fig. 2.7.** Configuration coordinate diagram of the electronic energies of an impurity centre whose lattice equilibrium configurations in the ground and ionized states are represented by configuration coordinates  $Q_{gr}$  and  $Q_{free}$  with different values. The thermal ionization energy  $E_{ith}$  of such a centre is smaller than the optical ionization energy  $E_{io}$  by the Franck–Condon energy  $E_{FC}$

conclusively that the centre results from the trapping of a  $Si_i$  atom produced by electron irradiation of a substitutional B atom, without the usual replacement of the substitutional acceptor atom by the Si self-interstitial [1,77]. In the positive charge state, the stable configuration is a  $B_sSi_i$  pair with  $C_{3v}$  symmetry and the metastable configuration is a  $BSi_i$  pair with an off-centre B atom and a resulting  $C_{1h}$  symmetry. On the contrary, in the negative charge state, the stable configuration is the one with symmetry  $C_{1h}$ . The first members of the O-related TDs series produced in O-containing silicon and germanium by thermal annealing in the 300–500°C range display metastable properties, with consequences on the observation of the electronic and vibrational spectra of these centres.

The change of configuration of a centre induced by its transition into a metastable state produces a lattice distortion which can result in a macroscopic volume change. Transient effects due to the photocreation of electron–hole pairs in n-type GaP and SI GaAs have been attributed to this effect [74].

## References

1. J. Adey, J.P. Goss, R. Jones, P. Briddon, *Phys. Rev. B* **67**, 245325/1–5 (2003)
2. C.A.J. Ammerlaan, in *Properties of Crystalline Silicon, EMIS Datareviews Series No 20*, ed. by R. Hull (INSPEC Publication, London, 1999), pp. 659–662
3. I.C. Bassignana, D.A. Macquistan, G.C. Hillier, R. Streater, D. Beckett, A. Majeed, C. Miner, *J. Cryst. Growth* **178**, 445 (1997)
4. A.R. Bean, R.C. Newman, *J. Phys. Chem. Solids* **32**, 1211 (1971)
5. M. Bernard, A. Deneuve, P. Muret, *Diam. Relat. Mater.* **13**, 282 (2004)
6. J.C. Bourgoin, H.J. von Bardeleben, D. Stiévenard, *J. Appl. Phys.* **64**, R65 (1988)
7. I. Broser, R.H. Franke, *J. Phys. Chem. Solids* **26**, 1013 (1965)
8. Z.Q. Chen, S. Yamamoto, M. Maekawa, A. Kawasuso, *J. Appl. Phys.* **94**, 4807 (2003)
9. R.M. Chrenko, *Phys. Rev B* **7**, 4560 (1973)
10. W.G. Clark, R.A. Isaacson, *J. Appl. Phys.* **38**, 2284 (1967)
11. P. Clauws, *Mater. Sci. Eng. B* **36**, 213 (1996)
12. J.W. Cleland, K. Lark-Horovitz, J.C. Pigg, *Phys. Rev.* **78**, 814 (1950)
13. B. Clerjaud, *Physica B* **170**, 383 (1991)
14. J.F.H. Custers, *Physica* **20**, 183 (1954)
15. J. Czochralski, *Z. Phys. Chem.* **92**, 219 (1918)
16. G. Davies, *J. Phys. C* **9**, L537 (1976)
17. P. Deak, in *Early Stages of Oxygen Precipitation in Silicon*, ed. by R. Jones (Kluwer, Dordrecht, 1996), pp. 163–177
18. T.J. De Lyon, J.M. Woodhall, M.S. Goorsky, P.D. Kirchner, *Appl. Phys. Lett.* **56**, 1040 (1990)
19. R. Duffy, T. Dao, Y. Tamminga, K. van der Tak, F. Roozeboom, E. Augendre, *Appl. Phys. Lett.* **89**, 071915/1–3 (2006)
20. EMIS Datareviews Series No 20, in *Properties of Crystalline Silicon*, ed. by R. Hull (INSPEC Publication, London, 1999)
21. V.V. Emtsev, D.S. Poloskin, E.I. Shek, N.A. Sobolev, in *Defects in Semiconductors 18*, ed. by M. Suezawa, H. Katayama-Yoshida, *Trans. Tech. Mater. Sci. Forum* **196–201**, 163 (1995)
22. S. Fung, R.J. Nicholas, *J. Phys. D* **18**, 259 (1985)
23. E. Gaudry, A. Kiratisin, P. Saintavit, C. Brouder, F. Mauri, A. Ramos, A. Rogale, J. Goulon, *Phys. Rev.* **B67**, 094108/1–10 (2003)
24. W.B. Gauster, *Phys. Rev.* **187**, 1035 (1969)
25. U. Gösele, in *Advances in Solid State Physics*, ed. by P. Grosse vol. 26, (Springer, Heidelberg, 1986), pp. 89–112
26. H.G. Grimmeiss, E. Janzén, in *Handbook of Semiconductors, Completely Revised Edition: Materials Properties and Preparation*, vol. **3b**, ed. by S. Mahajan (Elsevier, Amsterdam, 1984), pp. 1857–1983
27. M. Hakala, M.J. Puska, R.M. Nieminen, *Phys. Rev. B* **61**, 8155 (2000)
28. E.E. Haller, *Infrared Phys.* **25**, 257 (1985)
29. R.D. Harris, J.L. Newton, G.D. Watkins, *Phys. Rev. B* **36**, 1094 (1987)
30. H. Heissenstein, C. Peppermüller, R. Helbig, *Diam. Relat. Mater.* **6**, 1440 (1997)
31. H. Herzer, in *Neutron-Transmutation-Doped Silicon*, ed. by J. Guldberg (Plenum, New York, 1981), pp. 1–17
32. M. Hiller, E.V. Lavrov, J. Weber, *Phys. Rev. B* **74**, 235214/1–9 (2006)

33. S. Hocine, D. Mathiot, Appl. Phys. Lett. **53**, 1269 (1988)
34. H. Holloway, S.L. McCarthy, J. Appl. Phys. **73**, 103 (1993)
35. A. Huber, F. Kuchar, J. Casta, J. Appl. Phys. **55**, 353 (1984)
36. K. Iakoubovskii, G.J. Adriaenssens, Diam. Relat. Mater. **11**, 125 (2002)
37. K. Iakoubovskii, A. Stetsmans, K. Suzuki, J. Kuwabara, A. Sawabe, Diam. Relat. Mater. **12**, 511 (2003)
38. T. Isobe, H. Nakashima, K. Hashimoto, Jpn. J. Appl. Phys. **28**, 1282 (1989)
39. C. Johnston, A. Crossley, M. Werner, P.R. Chalker, in Properties, Growth and Applications of Diamond. EMIS Datareviews Series No 26, ed. by M.H. Nazaré, A.J. Neves (IET, London, 2000), pp. 337–344
40. R. Jones, S. Öberg, F. Berg, B. Rasmussen, B. Nielsen, Phys. Rev. Lett. **72**, 1882 (1994)
41. W. Kaiser, C.D. Thurmond, J. Appl. Phys. **32**, 115 (1961)
42. M. Kato, T. Yoshida, Y. Ikeda, Y. Kitagawara, Jpn. J. Appl. Phys. **35**, 5597 (1996)
43. K.L. Kavanagh, G.S. Gargill III, Phys. Rev. B **45**, 3323 (1992)
44. W. Keller, A. Mühlbauer, in *Floating-Zone Silicon. Preparation and Properties of Solid State Materials*, vol. 5. (Dekker, New York, 1981)
45. B.O. Kolbesen, A. Mühlbauer, Solid State Electron **25**, 759 (1982)
46. V.V. Kozlovskii, L.F. Zakharenkov, Rad. Effects Defects Solids **138**, 75 (1996)
47. W. Lin, in *Oxygen in Silicon, vol. 42 of the Series Semiconductors and Semimetals*, ed. by F. Shimura (Academic, San Diego, 1994), pp. 9–52
48. J.S. Makris, B.J. Masters, J. Electrochem. Soc. **120**, 1252 (1973)
49. A. Mesli, T. Heiser, Defects Diff. Forum **131–132**, 89 (1996)
50. J. Michel, J.R. Niklas, J.M. Spaeth, Phys. Rev. B **40**, 1732 (1989)
51. J.C. Mikkelsen Jr, Mater. Res. Soc. Symp. Proc. (USA) **59**, 19 (1986)
52. M. Sh. Mirianashvili, D.I. Nanobashvili, Sov. Phys. Semicond. **4**, 1612 (1971)
53. K. Nassau, *The Physics and Chemistry of Color: The Fifteen Causes of Color*, 2nd edn. (Wiley-VCH, New York, 2001)
54. R.C. Newman, R.S. Smith, in *Localized Excitations in Solids*, ed. By R.F. Wallis (Plenum Press, New York, 1968), pp. 177–184
55. R.C. Newman, J. Wakefield, J. Phys. Chem. Solids **19**, 230 (1961)
56. T. Nozaki, T. Yatsurugi, N. Akiyama, Y. Endo, Y. Makide, J. Radioanal Chem. **19**, 109 (1974)
57. B. Pajot, in *Hydrogen in Compound Semiconductors*, ed. by S.J. Pearton, Trans Tech, Mater. Sci. Forum **148–149**, 321 (1994)
58. B. Pajot, in *Properties of Crystalline Silicon, EMIS Datareviews Series No 20*, ed. by R. Hull (INSPEC Publication, London, 1999), pp. 488–491
59. B. Pajot, A.M. Stoneham, J. Phys. C **20**, 5241 (1987)
60. S.J. Pearton, (1999) in *Properties of Crystalline Silicon, EMIS Datareviews Series No 20*, ed. by R. Hull (INSPEC Publication, London, 1999), pp. 593–595
61. H.J. Rijks, J. Bloem, L.J. Gilling, J. Appl. Phys. **50**, 1370 (1979)
62. F. Rollert, N.A. Stolwijk, H. Mehrer, Appl. Phys. Lett. **63**, 506 (1993)
63. W. Rosnowski, J. Electrochem. Soc. **125**, 957 (1978)
64. J.E. Rowe, F. Sette, S.J. Pearton, J.M. Poate, Solid State Phenomena **10**, 283 (1990)
65. W.R. Runyan, *Silicon Semiconductor Technology. Texas Instruments Electronic Series* (McGraw Hill, New York, 1965)
66. D. Sasireka, E. Palanyandi, K. Yakutti, Int. J. Quantum Chem. **99**, 142 (2004)

67. B. Schaub, J. Gallet, A. Brunet-Jailly, B. Pellicciari, *Rev. Phys. Appl.* **12**, 147 (1977)
68. W. Schröter, M. Seibt, in *Properties of Crystalline Silicon. EMIS Datareviews Series No 20*, ed. by R. Hull (INSPEC Publication, London, 1999) pp. 543–560
69. E.F. Schubert, *J. Vac. Sci. Tech. A* **8**, 2980 (1990)
70. A. Seeger, K.P. Chik, *Phys. Stat. Sol.* **29**, 455 (1968)
71. F. Shimura, in *Oxygen in Silicon, vol. 42 of the series Semiconductors and Semimetals*, ed. by F. Shimura (Academic, San Diego, 1994), pp. 577–617
72. F. Spaepen, A. Eliat, *IEEE Trans. Instrum. Measure* **48**, 230 (1999)
73. B.D. Stone, D.B. Hines, S.L. Gunn, D. McKown, in *Neutron Transmutation Doping in Semiconductors*, ed. by J.M. Geese (Plenum Press, New York, 1979), pp. 11–26
74. T. Sugiyama, K. Tanimura, N. Itoh, *Appl. Phys. Lett.* **58**, 146 (1990)
75. Y. Takano, M. Maki, in *Semiconductor Silicon 1973*, ed. by H.R. Huff, R.R. Burgess (The Electrochemical Society, Pennington, 1973), pp. 469–481
76. M. Tanenbaum, A.D. Mills, *J. Electrochem. Soc.* **108**, 171 (1961)
77. E. Tarnow, *Europhys. Lett.* **16**, 449 (1991)
78. G.K. Teal, J.B. Little, *Phys. Rev.* **78**, 647 (1950) (abstract only)
79. D.G. Thomas, J.J. Hopfield, *Phys. Rev.* **150**, 680 (1966)
80. W.R. Thurber, R.L. Mattis, Y.M. Liu, J.J. Filliben, *J. Electrochem. Soc.* **127**, 1807 (1980)
81. W. Ulrici, F.M. Kiessling, P. Rudolph, *Phys. Stat. Sol. B* **241**, 1281 (2004)
82. W. von Hammon, *Nucl. Instrum. Meth. Phys. Res. B* **B63**, 95 (1992)
83. P. Wagner, J. Hage, *Appl. Phys. A* **49**, 123 (1989)
84. S. Wei, H. Oyonagi, H. Kawanami, T. Sakamoto, K. Tamura, N.L. Saini, K. Uosaki, *J. Appl. Phys.* **82**, 4810 (1997)
85. S.R. Wilson, W.M. Paulson, W.F. Krolikowski, D. Fathy, J.D. Gressett, A.H. Hamdi, F.D. McDaniel, in *Proceedings of Symposium on Ion Implantation and Ion Beam Processing of Materials*, ed. by G.K. Hubler, O.W. Holland, C.R. Clayton, C.W. White (North Holland, New York, 1984), pp. 287–292
86. D. Windisch, P. Becker, *Phys. Stat. Sol. A* **118**, 379 (1990)
87. R.C. Young, J.W. Westhead, J.C. Corelli, *J. Appl. Phys.* **40**, 271 (1969)

## Bulk Optical Absorption

---

The absorption of impurity centres is observed in the transparency domains of semiconductors and insulators, which are limited by their intrinsic electronic and vibrational absorptions. Further, a brief account of the relevant physical processes and an overview of the intrinsic optical properties of these materials and of their dependence on temperature, pressure and magnetic field is given in this chapter. Some semiconductors have been or are now synthesized in quasi-monoisotopic (qmi) forms because of improvements in their physical properties like thermal conductivity. A comparison of their intrinsic optical properties with those of the crystals of natural isotopic composition is also given. The absorption related to free carriers, due mostly to doping is also discussed at the end of this chapter. A detailed account of the optical properties of semiconductors can be found in the books by Yu and Cardona [107] and by Balkanski and Wallis [4].

### 3.1 Refractive Index and Dielectric Constant

One important macroscopic quantity related to the optical properties of non-metallic solids is their refractive index, which is closely related to their dielectric constant. Maxwell's equations for electromagnetic waves propagating in absorbing materials (see for instance [43]) lead to wave equations for the electric and magnetic fields in the material, and a solution for the amplitude of one component of these fields is:

$$U_j = U_0 \exp[i\omega(t - z/v)] \quad (3.1)$$

for an electromagnetic wave of pulsation  $\omega$  propagating in the  $z$  direction. As the electromagnetic plane waves are transverse,  $U_j$  corresponds to the  $U_x$  or  $U_y$  components of the field. In (3.1), the complex phase velocity  $v$  of the wave is:

$$v = [\mu\varepsilon\mu_0\varepsilon_0 - i\sigma\mu_0\mu/\omega]^{-\frac{1}{2}} \quad (3.2)$$

where  $\varepsilon_0$  and  $\mu_0$  are the permittivity and permeability of vacuum, and  $\varepsilon$  and  $\mu$  the relative dielectric constant and permeability of the material with an electrical conductivity  $\sigma$  at pulsation  $\omega$ . Velocity  $v$  in the material is  $c/\tilde{n}$  where  $c$  is the velocity of the electromagnetic waves in vacuum and  $\tilde{n}$  the complex refractive index at pulsation  $\omega$ . The quantity  $\tilde{n}^2$  is identified with the complex dielectric constant  $\tilde{\varepsilon}$ , with real part  $\varepsilon_R$  or  $\varepsilon_1$  and imaginary part  $\varepsilon_I$  or  $\varepsilon_2$ . For vacuum,  $\tilde{n}$ ,  $\varepsilon$  and  $\mu$  are unity and  $\sigma$  is zero so that  $c = (\varepsilon_0 \mu_0)^{-1/2}$ . In most cases, at optical frequencies, the permeability of the material can be taken as unity and

$$\tilde{n}^2 = \varepsilon_R - i\sigma(\omega)/\omega\varepsilon_0 \quad (3.3)$$

Generally, it can be shown that:

$$\varepsilon_R(\omega) = 1 + P \frac{2}{\pi} \int_0^\infty \frac{\omega' \varepsilon_I(\omega') d\omega'}{\omega'^2 - \omega^2} \quad (3.4)$$

with a similar expression for  $\varepsilon_I$ . Here,  $P$  denotes the principal part of the integral, i.e. the singular point  $\omega' = \omega$  is omitted from the integration. These expressions are known as the Kramers–Kronig relations. The complex refractive index  $\tilde{n}$  is written as  $n + ik$  where  $n$  is the real refractive index and  $k$  the extinction coefficient or absorption index. From the above definitions,  $\varepsilon_R = n^2 - k^2$  and  $\varepsilon_I = 2nk = \sigma(\omega)/\omega\varepsilon_0$ .

The component  $U_j$  of expression (3.1) can then be written as:

$$U_j = U_0 \exp[i\omega(t + nz/c)] \exp[-\omega kz/c] \quad (3.5)$$

In this expression,  $\exp[-\omega kz/c]$  represents the attenuation (or absorption) of the electromagnetic wave component. As the energy flow is proportional to the product of amplitudes of the components of the electric and magnetic vectors, and since both contain the term  $\exp[-\omega kz/c]$ , the energy absorption is proportional to  $\exp[-2\omega kz/c]$ . In absorption spectroscopy, one generally uses the absorption coefficient  $K$  defined by:

$$K = 2\omega k/c \quad (3.6)$$

With this definition, the energy absorption is proportional to  $\exp[-Kz]$ . The reflectivity  $R$  of an electromagnetic wave or radiation propagating in vacuum and normally incident on the plane boundary of a material with complex refractive index  $\tilde{n}$  is  $(\tilde{n} - 1)^2 / (\tilde{n} + 1)^2$ . Its real part is the standard reflectivity:

$$R = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2} \quad (3.7)$$

and whenever  $k$  is small, as it is generally the case for impurity absorption,  $R$  is  $(n - 1)^2 / (n + 1)^2$ . For diamond, silicon, and germanium, the low-frequency reflectivity is 0.17, 0.30, and 0.36, respectively.



In the transparency regions, the transmission through a plane parallel sample as a function of the wavelength  $\lambda$  of the radiation produces a channelled spectrum when the measurement is performed with a spectral bandpass smaller than the fringe spacing. Theoretically,  $T_{\max}/T_{\min}$  of the transmission fringes is  $(1 + R)^2 / (1 - R)^2$ . The transmission maximums and minimums correspond to constructive and destructive interferences, respectively, between beams transmitted with increasing path differences. Under normal incidence, the path difference between two adjacent extrema is  $2nd$  where  $d$  is the sample thickness. For adjacent transmission maximums at wavelengths  $\lambda_1$  and  $\lambda_2$  ( $\lambda_1 > \lambda_2$ ),  $2nd = N\lambda_1 = (N + 1)\lambda_2$ , where  $N$  is the order of interference. Subsequently, one derives  $2nd = \lambda_1\lambda_2 / (\lambda_1 - \lambda_2)$  and thus a value of  $n$  can be obtained; but it must be realized that a linear contribution of  $\lambda$  to the refractive index cannot be detected by this method. When the spectral bandwidth used in spectroscopic measurements is larger than the spacing of the interference fringes, they are averaged out. However, the existence of multiple surface reflections must still be taken into account and, from the summation of a geometric series, the average transmittance  $T$  of a moderately absorbing sample under normal incidence can be calculated as:

$$T = \frac{(1 - R)^2 u}{1 - R^2 u^2} \quad (3.8)$$

where  $u = \exp[-Kd]$ . Similarly, the normal reflectance  $R$  and the absorbance  $A$  are:

$$R = \frac{R [1 + (1 - 2R) u^2]}{1 - R^2 u^2} \quad \text{and} \quad A = \frac{(1 - R) [1 - Ru^2 - (1 - R) u]}{1 - R^2 u^2}$$

For pure elemental semiconductors like silicon, the strong electronic absorption at energies above  $E_g$  produces a small non-linear dispersion of the refractive index below  $E_g$ : in silicon,  $n = 3.57$  near  $E_g$  at room temperature (RT) and it steadily decreases to  $\sim 3.42$  for wavelengths near  $12 \mu\text{m}$  and stays close to this value down to radio frequency energies (see also [20]). For these elemental crystals, the dielectric constant  $\epsilon$  at energies below  $E_g$  is real and equal to  $n^2$ . The refractive index is isotropic for cubic crystals, but for crystals with one anisotropic axis, like those of the wurtzite type, the refractive index for the electric field component of the radiation parallel to this axis ( $n_{//}$ ) is slightly different from that for the component perpendicular to this axis ( $n_{\perp}$ ).

To introduce changes in the dielectric constant related to phonon modes in compound crystals, it is relevant to consider the classical interaction between an atomic system with resonant frequency  $\omega_0$  and an electromagnetic field  $E = E_0 \exp[i\omega t]$ . The 1-D equation of motion for such a system, also known as a Lorentz oscillator, is:

$$m\ddot{x} + \bar{m}\gamma\dot{x} + \bar{m}\omega_0^2 x = qE \quad (3.9)$$

where  $\bar{m}$  is an average mass,  $\gamma$  a damping constant, and  $q$  an effective charge. This equation allows derivation of an expression for the macroscopic resonant polarization  $P_{\text{res}} = Nqx$  of such a system, which is the number  $N$  of dipoles  $qx$  per unit volume induced by the field  $E$ :

$$P_{\text{res}} = \frac{Nq^2E}{\bar{m}(\omega_0^2 - \omega^2 - i\gamma\omega)} \quad (3.10)$$

This is a general expression and it can be used as a model for the classical treatment of electronic as well as atomic oscillators (from here and unless otherwise specified, we omit the tilde indicating complex quantities). When several kinds of oscillators coexist in the crystal, the total polarization is obtained by summing the polarizations of the different entities.

Having derived the microscopic expression for polarization, the focus is now on the macroscopic formulation of the dielectric constant for a cubic crystal. The relative dielectric constant  $\epsilon_r$  (the ratio of absolute dielectric constant  $\epsilon_{\text{abs}}$  with  $\epsilon_0$ ) can be introduced through the average electric field  $E$  acting on a crystal unit cell as:

$$P = (\epsilon_{\text{abs}} - \epsilon_0) E = \epsilon_0 (\epsilon_r - 1) E \quad (3.11)$$

This expression can also be written as  $P = \epsilon_0 \chi^{(1)} E$ , where  $\chi^{(1)}$  is the linear susceptibility of the crystal. Field  $E$  takes into account the polarization  $P$  of the crystal induced by an external field  $E_0$  and, for a crystal with a spherical shape,  $E$  is simply  $E_0 - P/3\epsilon_0$  [49].

Alternatively, the relative dielectric constant is then defined as:

$$\epsilon_r = \frac{\epsilon_0 E + P}{\epsilon_0 E} \quad (3.12)$$

The polarization induces a depolarization field  $E_1 = -P/3\epsilon_0$  which is the average electric field on the volume of a crystal unit cell. The local field is then:

$$E_{\text{loc}} = \frac{(\epsilon_r + 2) E}{3} \quad (3.13)$$

The proportionality coefficient between the polarization and the local field is the polarizability of the crystal  $\alpha = P/E_{\text{loc}}$ , given by:

$$\alpha = \frac{3\epsilon_0 (\epsilon_r - 1)}{\epsilon_r + 2} \quad (3.14)$$

This expression is known as the Clausius Mossotti relation. To simplify, the polarizability of the crystal can be taken as the sum of the electronic and atomic contributions. The electronic polarizability,  $\alpha_{\text{elec}}$ , corresponds to the coupling of the electronic cloud of the otherwise immobile atoms with the electromagnetic wave, and it is a high-frequency process, whose contribution can be considered more or less frequency-independent below  $E_g$ . The atomic

polarizability  $\alpha_{\text{at}}$  corresponds to the coupling of the vibrational motion of the ions with the electric field. Assuming properly averaged ionic or atomic mass  $\overline{M}$  and resonant frequency  $\omega_0$ ,  $\alpha_{\text{at}}$  takes the general form:

$$\alpha_{\text{at}} = \frac{Nq^2}{\overline{M}(\omega_0^2 - \omega^2 - i\gamma\omega)} \quad (3.15)$$

For frequencies below  $E_g$ , the contribution of the two effects leads to a frequency-dependent dielectric constant  $\varepsilon(\omega)$  given by:

$$\frac{\varepsilon(\omega) - 1}{\varepsilon(\omega) + 2} = \frac{\alpha_{\text{elec}} + \alpha_{\text{at}}}{3\varepsilon_0} \quad (3.16)$$

In compound crystals, the  $\omega_0$  values considered are  $\omega_{\text{LO}}$ , the frequency of the longitudinal optical phonons on the high-energy (h-e) side, and  $\omega_{\text{TO}}$ , the frequency of the transverse optical phonons, on the low-energy side. The dielectric constant at frequencies above  $\omega_{\text{LO}}$  is denoted as  $\varepsilon_\infty$  while that below  $\omega_{\text{TO}}$  is denoted as  $\varepsilon_s$  (the index s represents static, despite the fact that  $\varepsilon_s$  shows a small dispersion between the value just below  $\omega_{\text{TO}}$  and the one at radiofrequencies<sup>1</sup>). It can be seen from expressions (3.14) and (3.15) that above  $\omega_0$ , the ionic contribution decreases such that  $\varepsilon_\infty$  is smaller than  $\varepsilon_s$ . Typical values are given in Table 3.1.

A consequence of the Kramers–Kronig relation is that, for a semiconductor or an insulator, the static dielectric constant  $\varepsilon_s$  is:

$$\varepsilon_s = 1 + \frac{2}{\pi} \int_0^\infty 2\text{nk} \frac{d\omega}{\omega} \quad (3.17)$$

This expression shows that a high value of  $\varepsilon_s$  or the refractive index necessitates a large amount of absorption throughout the electromagnetic spectrum. This is the reason why crystals with a low  $E_g$ , for which the fundamental electronic absorption extends far in the infra-red, display high values of the dielectric constant, as shown in Table 3.1. There can be discrepancies in the values reported in different references for the dielectric constants  $\varepsilon_s$  and  $\varepsilon_\infty$  because they present a small variation with energy.

For compound crystals, the lattice contribution, which must also be taken into consideration in the total absorption, decreases with the covalent character, which is larger for the III-V compounds than for the II-VI compounds.

The specified values of  $\varepsilon_s$  are considered as the low-frequency value of  $n^2$ . Usually, the low-temperature dielectric constant (or refractive index) is slightly lower than that at RT [88]. LHeT values of  $\varepsilon_s$  for group-IV crystals have also been obtained indirectly from a comparison between experimental and calculated line spacings of shallow donor impurities (see Table 5.3).

<sup>1</sup> The notation  $\varepsilon_s$  is preferred compared to  $\varepsilon_0$  to avoid confusion with the permittivity of free space.

**Table 3.1.** Correlation between the RT band gap  $E_g$  (eV) and dielectric constants of some semiconducting and insulating crystals for energies below  $E_g$ 

| Crystal               | $E_g$ | $\varepsilon_\infty$ | $\varepsilon_s$ | Crystal    | $E_g$      | $\varepsilon_\infty$ | $\varepsilon_s$ |
|-----------------------|-------|----------------------|-----------------|------------|------------|----------------------|-----------------|
| MgO (NaCl)            | 7.6   | 2.9                  | 9.8             | 3C-SiC (s) | $\sim 2.3$ | 6.90                 | 9.72            |
| c-BN (s)              | 6.4   | 4.5                  | 7.1             | ZnTe (s)   | 2.28       | 7.28                 | 9.67            |
| AlN (w)               | 6.2   | 4.84                 | 8.5             | GaP (s)    | 2.27       | 9.11                 | 11.11           |
| C <sub>diam</sub> (d) | 5.48  | 5.86                 | 5.70            | AlAs (s)   | 2.15       | 8.16                 | 10              |
| w-ZnS                 | 3.8   | 5.13                 | 9.6             | CdSe (w)   | 1.71       | 6.2, 6.3             | 10.16, 9.29     |
| c-ZnS                 | 3.68  | 5.1                  | 8.0             | AlSb (s)   | 1.62       | 9.88                 | 11.22           |
| w-GaN                 | 3.44  | 5.8, 5.35            | 9.5             | CdTe (s)   | 1.53       | 6.9                  | 11.00           |
| c-GaN                 | 3.30  | 5.3                  | 9.7             | GaAs (s)   | 1.42       | 10.89                | 13.08           |
| ZnO (w)               | 3.4   | 3.75, 3.7            | 8.75, 7.8       | InP (s)    | 1.34       | 9.52                 | 12.56           |
| 2H-SiC (w)            | 3.3   | 7.23, 6.85           |                 | Si (d)     | 1.12       | 12.43                | 11.68           |
| 6H-SiC                | 2.86  | 6.52, 6.70           | 9.66, 10.03     | GaSb (s)   | 0.73       | 14.4                 | 15.7            |
| ZnSe (s)              | 2.67  | 5.4                  | 7.6             | Ge (d)     | 0.67       | 16.8                 | 15.98           |
| CdS (w)               | 2.49  | 5.32                 | 9.12, 8.45      | InAs (s)   | 0.35       | 12.25                | 15.12           |
| AlP (s)               | 2.45  | 7.54                 | 9.8             | InSb (s)   | 0.18       | 15.7                 | 17.9            |

In the parentheses, d, s and w stand for diamond, sphalerite, and wurtzite, respectively. For elemental crystals,  $\varepsilon$  decreases continuously from  $\varepsilon_\infty$  to  $\varepsilon_s$ . For compound semiconductors,  $\varepsilon_\infty$  is for energies above  $E_{LO}$  and  $\varepsilon_s$  for energies below  $E_{TO}$ . In wurtzite-type crystals, the first and second values of the dielectric constants are for  $\mathbf{E} // c$  and  $\mathbf{E} \perp c$ , respectively

The dispersion of the refractive index of alkali halides and of other materials at energies above  $\omega_0$  has been used to produce reasonable monochromatic radiation. In prism monochromators, a parallel beam of polychromatic radiation incident on a prism made from these materials is dispersed, with angular deviations depending on the dispersion  $\omega^2 dn/d\omega$  of the refractive index with the photon energies. Before the advent of grating monochromators and Fourier transform spectrometers, the prism monochromators were widely used in optical spectroscopy and they are still used for specific experiments.

What has been presented above is based on the interaction of electrons or atoms with the electric field through a quadratic harmonic potential. When potentials including higher-order terms are used, the polarization, electric dipole moment, and optical susceptibility include, in turn, higher order terms whose contributions are the basis of non-linear optics and anharmonic effects.

## 3.2 Intrinsic Lattice Absorption

### 3.2.1 One-Phonon Effect

Like molecules, crystals can also vibrate as a whole. Their vibrations can be excited thermally, and they can display a residual vibrational motion at zero

Kelvin (the zero point motion). This latter effect is explained by quantum mechanics, and it can in turn explain absorption features of impurities in crystalline matrices. The presentation of the fundamental vibrational modes of crystals is based on the harmonic approximation, where one only considers the interactions between an atom or an ion and its nearest neighbours. Within this approximation, an harmonic crystal made of  $N$  ions can be considered as a set of  $3N$  independent oscillators, and their contribution to the total energy of a particular normal mode with pulsation  $\omega_s(q)$  is:

$$(n_{ks} + 1/2) \hbar \omega_s(q) \quad (3.18)$$

where  $n_{ks}$  is any positive integer value or 0. The analogy with the normal modes of the radiation field in a cavity, where one does not speak of quantum number of excitation modes, but rather of photons, has led to call phonons as the corresponding excitations of harmonic crystal. This has also been extended to situations involving anharmonicity.

The periodic pattern of displacement of the atoms about their equilibrium positions can be characterized by a wavelength  $\lambda$ , which can take any value between infinity (the average size of the crystal) and the lattice constant  $a$  (for simplicity, we consider a cubic crystal). In a given direction of propagation of the deformation, it is convenient to use the propagation or wave vector  $\mathbf{q}$ , with an amplitude  $q = 2\pi/\lambda$ . This vector has the periodicity of the reciprocal lattice, and the study of the  $q$ -dependent physical quantities can be restricted to the first Brillouin zone (BZ). The fundamental energy spectrum of the crystal is determined by the pulsations  $\omega$  of the individual atoms or ions of crystals as a function of the propagation vector  $\mathbf{q}$ . These pulsations, or vibrational modes, are multi-valued functions of  $\mathbf{q}$  that can be characterized by two kinds of dispersion curves. Those with pulsation (or energy) 0 at  $\mathbf{q} = 0$  (long wavelengths) show a nearly linear behaviour near the origin, and their proportionality coefficients are the sound velocities in the crystals. Hence, they are called acoustic modes, and they correspond to neighbouring atoms vibrating in phase near  $\mathbf{q} = 0$ . The energy spectrum of crystals with more than one atom per unit cell also displays dispersion curves with a maximum energy at  $\mathbf{q} = 0$ , corresponding to vibrational modes where neighbouring atoms have opposite displacements. When these atoms are different, the resulting first-order dipole moment gives rise to optical absorption, and the corresponding dispersion curves are therefore called optic modes. Along the main symmetry directions of the crystals, one differentiates between the longitudinal acoustic and optic modes (LA and LO), where the atomic displacements are parallel to  $\mathbf{q}$  and transverse acoustic and optic modes (TA and TO) where they are perpendicular to  $\mathbf{q}$ . For random orientations, the distinction between pure longitudinal or transverse modes is generally no longer valid. There are two transverse modes corresponding to the propagation of the atom along mutually perpendicular axes, and they can be either degenerate or not, depending on the symmetry of the branches in the crystal considered.

As already mentioned, because of the lattice periodicity of the crystals, the dispersion curves are studied for propagation vectors lying only in the first BZ of the crystal.

In elemental (homonuclear) crystals with cubic symmetry, the LO and TO branches are degenerate at  $\mathbf{q} = 0$  (the  $\Gamma$  point of the BZ), and the phonons at that point are denoted as O ( $\Gamma$ ). The situation is different in compound crystals, where the energy of the LO branch is larger than that of the TO branch. This difference in compound crystals is attributed to the contribution of an electric field effect to the restoring forces, and it can be shown that at  $\mathbf{q} = 0$ :

$$\omega^2(\text{LO}) = \frac{\varepsilon_s}{\varepsilon_\infty} \omega^2(\text{TO}) \quad (3.19)$$

This expression is known as the Lyddane–Sachs–Teller relation [61].

The creation of an optical phonon by photon absorption requires the coupling of electromagnetic radiation with a dipole moment. For elemental crystals, the two neighbouring atoms are the same and there is no first-order dipole moment, hence no one-phonon absorption is observed, but the opposite displacement of the atoms results in a change of the polarizability of the crystals. This change can be detected by Raman scattering with a frequency shift corresponding to the O ( $\Gamma$ ) frequency, also known as the Raman frequency of the crystal. This is also true for compound crystals, and the Raman scattering of both LO and TO modes is detected in these crystals [66]. The one-phonon absorption is only observed in compound crystals. The radiation that is incident normal to the crystal surface can only couple with the TO modes, and to comply with momentum conservation, the wave vector  $\mathbf{q}$  of the phonon so created is zero. This absorption is very strong and the refractive index of the crystal near TO frequencies becomes complex, with an imaginary part corresponding to absorption. The high value of the absorption index  $k$  results in a nearly metallic reflectivity.

The study of the one-phonon density of states of crystals has shown the existence of singularities corresponding to critical points (*CPs*) located within or at the surface of the BZs along particular directions (the BZs for diamond and sphalerite structures are the same as the one shown in Fig. B2 of Appendix B). They arise from the topology of the  $\omega_t(\mathbf{q})$  dispersion curves, where the index  $t$  refers to a given phonon branch. It can be shown that the density of vibrational state  $g(\omega)$  can be written as:

$$g(\omega) \propto \sum_t \int_{S_t - (\omega)} \frac{dS_t}{|\nabla_{\mathbf{q}} \omega_t(\mathbf{q})|} \quad (3.20)$$

where  $S_t$  is the surface in the BZ for which  $\omega_t(\mathbf{q}) = \omega$ . These *CPs* are those for which  $\nabla_{\mathbf{q}} \omega(\mathbf{q}) = 0$ , and for the diamond-like crystals, they correspond to points X, L, K and W of Fig. B2. They are defined by:

$$\begin{aligned}\mathbf{q}_X &= (2\pi/a) (1, 0, 0) \\ \mathbf{q}_L &= (2\pi/a) (1/2, 1/2, 1/2) \\ \mathbf{q}_K &= (2\pi/a) (3/4, 3/4, 0) \\ \mathbf{q}_W &= (2\pi/a) (1, 1/2, 0)\end{aligned}$$

This analysis is based on topological considerations, but other *CPs* can emerge depending on the actual shape of the dispersion curves in the BZ [50]. Sometimes, the  $\Gamma$  point is included in the *CPs*, but when this is done, this can be only for the optical branches. The degeneracy of the TO and LO branches at the  $\Gamma$  point for the diamond structure. A similar topological degeneracy of the LA and LO branches at the X point (noted L(X)) also exists for this structure. Dispersion curves of phonons in diamond are shown in Fig. 3.1. The curves for silicon and germanium are qualitatively similar.

In binary crystal with large differences between the masses of the two atoms (e.g. in GaP or InP), the frequencies of the LA phonons at the BZ boundaries is significantly smaller than that of the TO phonons, and this difference is usually referred to as the phonon gap.

Because the reflectivity at energies near the TO mode is strongly frequency-dependent, this effect has been used with alkali halides in infrared spectroscopy

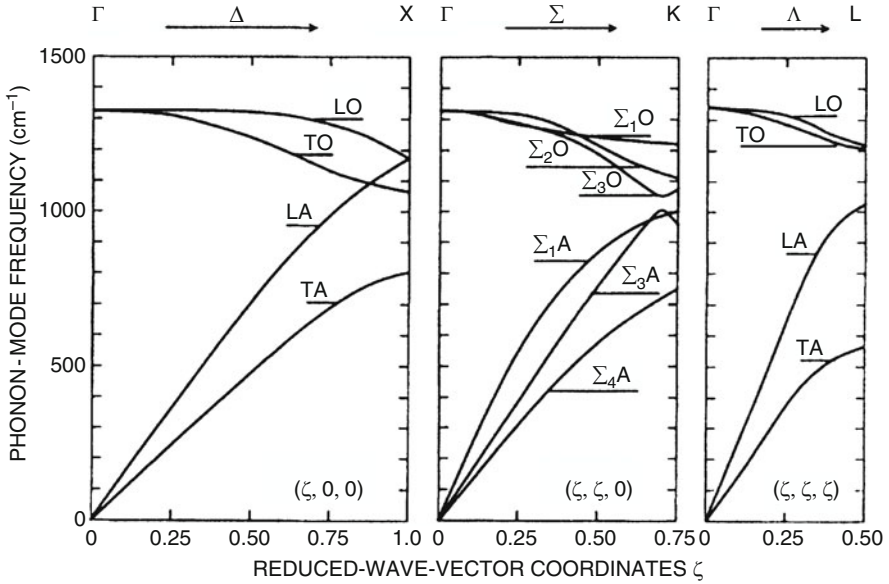


**Fig. 3.1.** Phonon dispersion curves of diamond along the main symmetry directions calculated from a Born-von Karman model fitted to neutron scattering experimental data (after [50]). The frequencies are expressed in wavenumber  $\tilde{\nu} = \omega/2\pi c$ . Along the  $[110]$  directions ( $\Sigma$ ), the modes are neither purely longitudinal nor transverse, and three branches exist for each category. Copyright 1992 by the American Physical Society

**Table 3.2.** RT energies ( $\text{cm}^{-1}$ ) of phonons in some semiconducting and insulating crystals with the cubic and hexagonal structures compiled from literature

|                   | Cubic TO ( $\Gamma$ ) | LO ( $\Gamma$ ) | Cubic            | TO ( $\Gamma$ ) | LO ( $\Gamma$ ) | Hexagonal        | TO ( $E_2$ ) | TO ( $E_1$ ) | LO ( $A_1$ ) |
|-------------------|-----------------------|-----------------|------------------|-----------------|-----------------|------------------|--------------|--------------|--------------|
| C <sub>diam</sub> | 1132.4                |                 | GaSb             | 223.6           | 232.6           | 2H-SiC           | 764          | 799          | 968          |
| SiC               | 796.2                 | 972.2           | InP              | 303.7           | 345.0           | AlN              | 656          | 670          | 890          |
| Si                | 520.2                 |                 | InAs             | 217.3           | 238.6           | w-GaN            | 570          | ~560         | 735          |
| Ge                | 301                   |                 | InSb             | 179.1           | 190.4           | InN              | 488          | 476          | 586          |
| c-BN              | 1056                  | 1306            | MgO              | 402             | 718             | ZnO              | 439          | 379          | 577          |
| AlAs              | 361.7                 | 403.7           | c-ZnS            | 271             | 352             | w-ZnS            | 274          | 274          | 352          |
| AlSb              | 318.7                 | 340.0           | ZnSe             | 213             | 253             | CdS <sup>a</sup> | 256          | 243          | 305          |
| GaN               | 552                   | 739             | ZnTe             | 177             | 207             | w-CdSe           | 172          | 172          | 210          |
| GaP               | 367.3                 | 403.0           | CdTe             | 140             | 169             |                  |              |              |              |
| GaAs              | 268.5                 | 291.9           | CaF <sub>2</sub> | 261             | 482             |                  |              |              |              |

<sup>a</sup>At 25 K

to select IR energies by successive reflections on these materials (the German term *Reststrahlen* (residual ray) method has been coined for this technique). Table 3.2 gives values of the frequencies of optical phonons in some semiconducting and insulating materials with cubic and hexagonal structures. For those with the cubic structure, these values correspond to the zone-centre phonons. For the crystals with the wurtzite structure, the different phonons are usually denoted by the *IRs* of the  $C_{6v}$  point group and the strongest Raman lines in the usual scattering geometry are produced by the  $A_1$  LO phonon at the zone centre along the  $c$  axis and by the  $E_2$  TO folded phonon. When two structures of the same compound exist, the frequency of the  $E_1$  zone-centre TO phonon of the wurtzite-type crystals is relatively close to the one of the TO ( $\Gamma$ ) phonon.

A decrease in temperature produces a decrease of the lattice spacing and a corresponding increase of the phonon mode frequencies.<sup>2</sup> A hydrostatic pressure also reduces the lattice spacings of the crystals and one of the consequences is an increase of the phonon modes with pressure [74, 95]. The variation of the phonon frequencies with the isotopic composition has been measured in many semiconductors, and the shifts observed can generally be accounted for by considering a virtual crystal with an average mass corresponding to the isotopic composition (the virtual crystal approximation (VCA)). For instance, extensive results for C<sub>diam</sub> were given by Hass et al. [37] and they show a variation of O ( $\Gamma$ ) Raman frequency from  $\sim 1282$  to  $1333 \text{ cm}^{-1}$  between qmi<sup>13</sup>C<sub>diam</sub> and <sup>12</sup>C<sub>diam</sub> at RT. However, these results also show a departure from the VCA. A general account of the subject can be found in the review by Cardona and Thewalt [18]. The energies of some optical

<sup>2</sup> In a temperature domain below  $\sim 100 \text{ K}$ , a temperature decrease can result in an increase of the lattice spacing, as in silicon or in some sphalerite-type crystals.



and acoustical lattice phonons can also be obtained from the observation of phonon replicas on the low-energy side of photoluminescence (PL) electronic recombination no-phonon lines.

The primitive cells of the  $nH$  and  $3nR$  SiC polytypes contain  $n$  formula (Si-C) units, and the unit cell of the polytypes along the  $c$ -axis is  $n$  times larger than that of the basic  $3C$  SiC polytype. The BZ of the corresponding polytype is thus reduced in the  $\Gamma - L$  direction by a factor  $1/n$  [70]. One then speaks of folded BZ and some of the folded acoustical phonons with non-zero frequencies at the zone centre are IR- and Raman-active. Their absorptions, with lines as sharp as  $0.03 \text{ cm}^{-1}$  at LHeT have been reported for the  $6H$  and  $15R$  SiC polytypes ([77], and references therein).

### 3.2.2 Multi-Phonon Absorption and Anharmonicity

Higher-order lattice absorption or Raman scattering has been observed in elemental [36,98] as well as in compound semiconducting and insulating crystals. Higher-order effects can arise from two mechanisms: (a) anharmonic coupling between phonons, arising from third and higher order terms in the potential energy, and (b) second and higher order terms in the electric moment. Fundamentally, these effects are similar to those leading to overtones, summation or difference bands in molecular spectroscopy. In process (a), the anharmonic mechanism has been described [14] by the coupling of a photon with a TO phonon, which subsequently couples with two other phonons. The net result can be either the creation of two phonons (summation process) or the creation of one phonon and the annihilation of the other (difference process). The condition for process (a) to occur is the existence of a first-order dipole moment, and it is therefore ruled out in elemental crystals. In process (b), where the first-order dipole moment can be zero, the photon couples directly with two phonons, the first one producing an asymmetry in the electronic charge distribution, which is then displaced by the second phonon. The phonons involved in both processes are the short-wavelength phonons for which the nearest-neighbour atomic motion is more asymmetric than the one of the zone-centre phonons. As a result, a second-order electric moment is produced that couples with the photon. The net result is the same as for anharmonicity. The above description implies that both the anharmonicity and the effect of higher-order moment can be present in compound crystal while multi-phonon absorption of elemental crystals can only be explained by second-order dipole moment. The absorption due to the summation process is observed at energies above that of the zone-centre phonons while that due to the difference process is observed below, in the far infra-red.

The absorption coefficient for a multi-phonon combination can be expressed as the product of three terms. The first one is the matrix element of the coupling term between the phonons involved in the process. It is non-zero only for specific phonon combinations determined by selection rules derived from symmetry considerations. The second one describes the temperature

dependence of the phonon population, and the third one is related to the phonon density of states. The IR and Raman selection rules for two- and three-phonon summation processes in the diamond and sphalerite structures have been derived by Birman [6]. It is found that in the diamond-like crystals, the two-phonon combinations are usually IR active when they originate from different branches (e.g. TO (X) + LO (X) or LO (L) + LA (L)), but the overtones are forbidden. In sphalerite-like crystals, some overtones, like 2TO ( $\Gamma$ ) are allowed, and they are IR active. Tables of the symmetry-allowed three-phonon combinations in the diamond and sphalerite structures can also be found in [6].

The temperature-dependent term represents the difference in the occupation numbers of the phonon states involved in the process. As phonons are bosons, the occupation number for a phonon of pulsation  $\omega$  at temperature  $T$  is given by the Bose–Einstein statistics as

$$n(\omega, T) = [\exp(\hbar\omega/k_B T) - 1]^{-1} \quad (3.21)$$

For two-phonon processes involving branches  $t$  and  $t'$  and phonons with wave vectors  $\mathbf{q}$  and  $-\mathbf{q}$ , the temperature-dependent term is:

$$[(n_{\mathbf{q}t} + 1)(n_{-\mathbf{q}t'} + 1) - n_{\mathbf{q}t}n_{-\mathbf{q}t'}] \text{ (summation process)} \quad (3.22a)$$

or

$$[n_{\mathbf{q}t}(n_{-\mathbf{q}t'} + 1) - (n_{\mathbf{q}t} + 1)n_{-\mathbf{q}t'}] \text{ (difference process)} \quad (3.22b)$$

Similar relationships can be obtained for three-phonon processes. At low temperature,  $n(\omega, T)$  is much smaller than unity and the above expression tends to unity for summation processes, and to zero for the difference processes, which are, therefore, not observed at low temperature. At higher temperature, the absorption intensity increases for both processes [45], at a difference with the one-phonon process, which is temperature-independent.

We have mentioned the existence of *CPs* in the one-phonon density of states, but this can be measured only for compound crystals. The situation is different in multi-phonon absorption because the high-frequency phonons of the BZ boundary are mostly involved (note that in three-phonon processes, the  $\mathbf{q} = 0$  zone-centre phonons can also be involved without problem for momentum conservation). For the two-phonon absorption, the density of states is proportional to an integral similar to the one in expression 3.20, with  $\omega_t$  replaced by the sum of the two pulsations  $\omega_t$  and  $\omega_{t'}$  of the phonons of the combination. Besides the trivial case where  $\omega_t = \omega_{t'} = 0$ , the condition  $\nabla_{\mathbf{q}}(\omega_t(\mathbf{q}) + \omega_{t'}(\mathbf{q})) = 0$  is fulfilled when  $\nabla_{\mathbf{q}}(\omega_t) = \nabla_{\mathbf{q}}(\omega_{t'}) = 0$  or when  $\nabla_{\mathbf{q}}(\omega_t) = -\nabla_{\mathbf{q}}(\omega_{t'})$ . The observed two-phonon absorption is the sum of the contributions of the possible two-phonon processes. Figure 3.2 shows the RT absorption of silicon in the two- and three-phonon absorption region. In the two-phonon region, it is fitted with the two-phonon dispersion curves

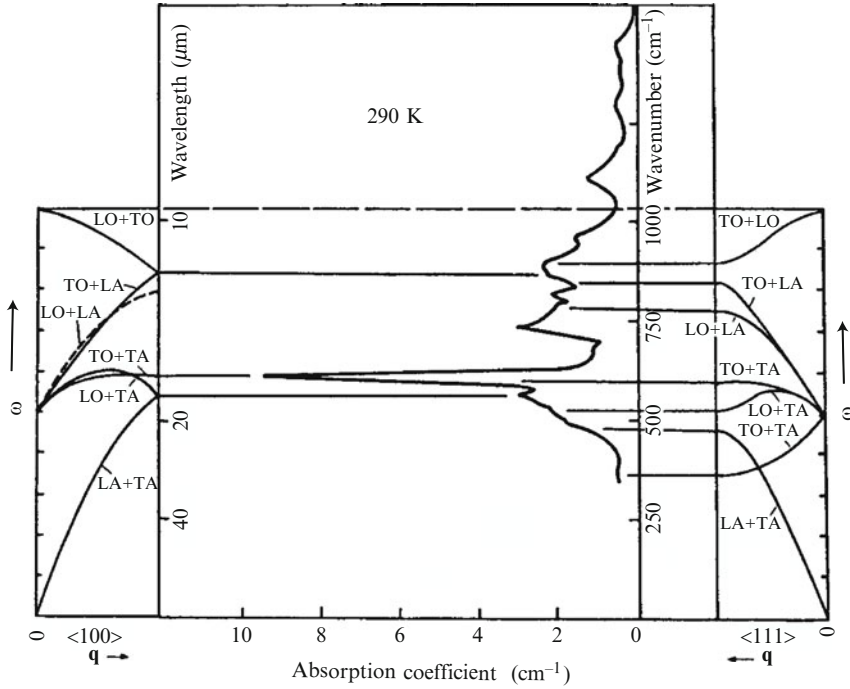


**Fig. 3.2.** RT two-phonon absorption in silicon fitted to the two-phonon dispersion curves along the  $\Delta$  ( $\langle 100 \rangle$ ) and  $\Lambda$  ( $\langle 111 \rangle$ )  $\mathbf{q}$  vectors of the first BZ. The fit shows the importance of the two-phonon combinations near the edges of the zone boundary [43], after [46]. With permissions from Oxford University Press and from the Institute of Physics

for silicon along the  $\Delta$  and  $\Lambda$  directions of the BZ. As already mentioned, the multi-phonon absorption in compound crystals can arise both from anharmonicity and from induced dipole moments and, as shown in Fig. 3.3, it is stronger than in elemental crystals.

For TO and LA phonons with wave vectors at the boundary of the first BZ, the value of the phonon gap for compound crystals is  $\omega(\text{TO}) - \omega(\text{LA})$ , with small variations considered depending on the BZ point considered. In the multi-phonon spectrum of InP shown in Fig. 3.3, this gap is close to the difference of the order of  $100 \text{ cm}^{-1}$  between  $\omega(2\text{TO}(X))$  and  $\omega(\text{TO}(X) + \text{LA}(X))$ .

### 3.3 Electronic Absorption

#### 3.3.1 Energy Gap and Fundamental Absorption

Electromagnetic radiation can be absorbed by an intrinsic semiconductor or insulator crystal to promote an electron from the valence band (VB)

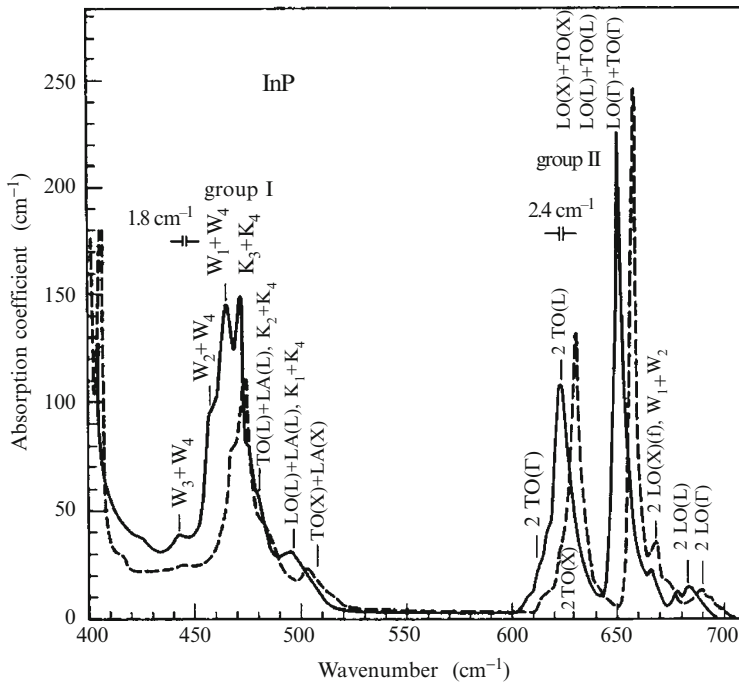


**Fig. 3.3.** Absorption of InP in the two-phonon absorption region at 300 K (*full line*) and 20 K (*dashed line*). The practically absorption-free domain between groups I and II correspond to the phonon gap between the optic and acoustic modes. The very strong one-phonon TO absorption is at  $\sim 304 \text{ cm}^{-1}$  [97]. Copyright Wiley-VCH Verlag GmbH & Co. KGa. Reproduced with permission

to the conduction band (*CB*). In a molecular orbital representation of the bond between two nearest neighbours in a valence crystal, the first step is the transition of the electron from a bonding state to an antibonding state, separated by an energy of the order of the energy gap. The energy of the electron in this antibonding state is small, so that it can be thermally ionized in the continuum. In the semiconductor representation, the electron in the antibonding state can be considered as a free exciton that is an electron-hole pair bonded by Coulomb interaction. It is usual to represent the electron energies in crystalline solids as a function of the wave vector  $\mathbf{k}$  of the electron along directions of the reciprocal lattice in the first BZ. These energies are labelled  $E_b(\mathbf{k})$  where index  $b$  refers to a particular band, and it can be shown that the velocity of an electron in the *CB* is  $\mathbf{v}_c(\mathbf{k}) = \hbar^{-1} \nabla_{\mathbf{k}} E_c(\mathbf{k})$ . An effective-mass tensor  $[M^{-1}(\mathbf{k})]_{ij} = \mp \hbar^{-2} \partial^2 E_b(\mathbf{k}) / \partial k_i \partial k_j$  can be similarly derived, where the  $-$  and  $+$  signs refer to a band maximum (for holes) and to a band minimum (for electrons). The mass tensor plays an important role in the spectroscopy of impurities in semiconductors, especially when a mag-

netic field is involved. The optical interband transitions take place between the extrema of the valence and conduction bands. Near extrema  $E_c$  or  $E_v$  of the conduction or valence bands, it is possible to express the energy as:

$$E_b(\mathbf{k}) = E_b \pm \hbar^2 (k_1^2/2m_1 + k_2^2/2m_2 + k_3^2/2m_3) \quad (3.23)$$

where  $E_b$  equals  $E_c$  or  $E_v$ . The  $+$  and  $-$  signs refer to the conduction and valence bands, respectively. The effective mass parameters  $m_i$  are different for the two bands. For the *CB*, the absolute energy minimum can occur at  $\mathbf{k} = 0$ , but can also occur at  $\mathbf{k} \neq 0$  while the *VB* maximum occurs mostly at  $\mathbf{k} = 0$ . The maximum *VB* states are related to the atomic bonding between the atoms of the crystal. This results in a threefold electronic degeneracy when electron spin is neglected for diamond, silicon and germanium covalent crystals with *p*-like bonds. When spin-orbit (*s-o*) interaction is considered, the valence band edge splits into fourfold degenerate  $p_{3/2}$ -like states separated from twofold degenerate  $p_{1/2}$ -like states by the *s-o* splitting energy, usually denoted by  $\Delta_{so}$ . The constant energy surfaces about the extrema are ellipsoids or warped spheres specified by their principal axes  $\mathbf{k}_i$ , the three effective masses  $m_i$  and the location in *k*-space of the ellipsoids, which determine the symmetry of the ellipsoids and the orientational degeneracy of the extrema in *k*-space. In the case of revolution symmetry, as for the *CB*s in group IV non-metallic crystals, there are only two electron effective-mass parameters, a longitudinal mass  $m_{nl}$  along the main axis of the ellipsoid and a transverse mass  $m_{nt}$  along the two perpendicular axes. For the onset of the optical absorption, one is generally concerned with the absolute maximum of the *VB* and the absolute minimum of the *CB*. It is this energy difference that determines the values of the band gaps  $E_g$  given in Appendix C. In all the non-metallic group-IV crystals, the absolute minimum of the *CB* is for  $\mathbf{k} \neq 0$  and it is material-dependent. In such a case, the optical transitions between these two extrema imply a change in the electron momentum and they are forbidden to zeroth order. Indirect absorption can, however, take place, with the difference in electron momentum being compensated by annihilation or creation of lattice phonons of opposite momentum, but this so-called indirect absorption has some influence on the lifetime of the intrinsic electrons in the *CB*. Thus, whenever the band gap of semiconductors is a relevant parameter, such materials are labelled as indirect-band-gap semiconductors. As an example of the electronic structure of semiconductor crystals, Fig. 3.4 shows the one for crystalline Ge, calculated by the pseudopotential method and represented in the first BZ of the fcc lattice. This calculation includes the effect of the *s-o* coupling of the *VB* electrons; when *s-o* coupling is neglected, the  $\Gamma_8^+$  and  $\Gamma_7^+VB$ s are replaced by the  $\Gamma_5^+$  band (see Table 3.3). The electronic bands at critical points of the BZ are noted following irreducible representations (*IRs*) of the representations of the symmetry point groups associated with these points (see Appendix B and Chap. 2 of [107] for more details). The *CB* minimum ( $L_6^+$ ) is at point L of the BZ of germanium and the constant-energy surfaces correspond to eight half-ellipsoids at this point with their main axis

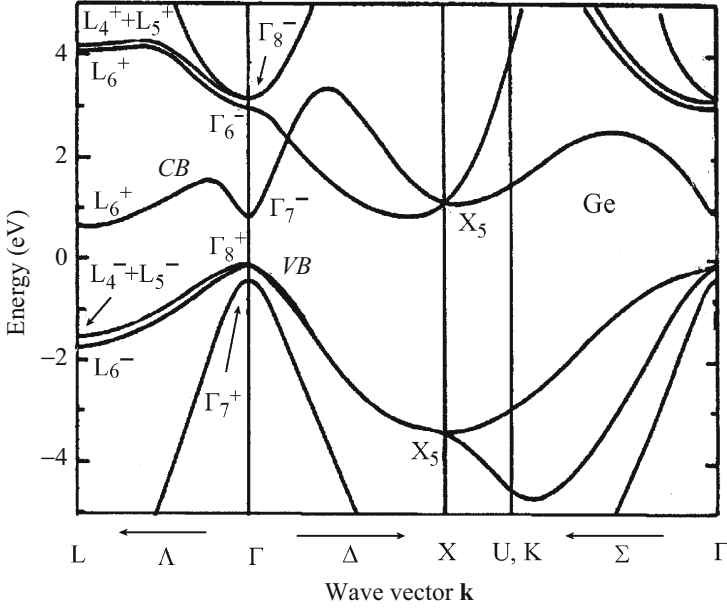


**Fig. 3.4.** Band structure of germanium calculated from empirical pseudopotentials including s-o coupling as a function of the electron wave vector along selected directions of the reciprocal lattice. The s-o splitting  $\Delta_{so}$  is the energy difference between  $\Gamma_8^+$  and  $\Gamma_7^+$ . The light- and heavy-hole VBs are the  $\Gamma_8^+$  to  $L_6^-$  and  $\Gamma_8^+$  to  $L_4^- + L_5^-$  bands, respectively. The energy reference is the VB maximum at the  $\Gamma$  point after [21]

along  $\langle 111 \rangle$  direction. By a suitable choice of primitive cells in  $k$ -space, they can be represented by four ellipsoids, the half-ellipsoids on opposite faces being joined together by translations through suitable lattice vectors, yielding the fourfold degeneracy of the CB minimum of germanium. The band gap  $E_g$  of germanium is the energy difference between the  $\Gamma_8^+$  and  $L_6^+$  points and the direct band gap the one between the  $\Gamma_8^+$  and  $\Gamma_7^+$  points. Away from the  $\Gamma$  point, the degeneracy of the upper VB is lifted so that at the  $\Gamma$  point, the curvatures of the two sub-bands are different. The VB with the lowest curvature is usually called the heavy hole valence band, with effective mass  $m_{hh}$  and the one with the highest curvature the light hole valence band, with effective mass  $m_{lh}$ . The effective mass of the holes in the s-o split  $\Gamma_7^+$  band is denoted by  $m_{so}$ .

This representation takes into account the s-o coupling, and is necessary for the study of the optical properties related to the VB. This is usually not the case for those related to the CB and Table 3.3 gives the correspondence between the IRs of the double group used above and those of the standard group used for instance by Cohen and Bergstresser [25] to label the electronic

**Table 3.3.** Correspondence between the IRs of some particular points of the electronic band structure of cubic crystals with and without s-o coupling [80]

|      | Diamond structure ( $O_h^T$ )                                         |                                                                                   | Sphalerite structure ( $T_d^2$ )                                         |                                                                          |
|------|-----------------------------------------------------------------------|-----------------------------------------------------------------------------------|--------------------------------------------------------------------------|--------------------------------------------------------------------------|
|      | Double group<br>(s-o coupling)                                        | Standard group<br>(no spin)                                                       | Double group<br>(s-o coupling)                                           | Standard group<br>(no spin)                                              |
| $VB$ | $\Gamma_8^+ (4)$<br>$\Gamma_7^+ (2)$                                  | $\Gamma_5^+ (\Gamma_{25'}) (3)$                                                   | $\Gamma_8 (4)$<br>$\Gamma_7 (2)$                                         | $\Gamma_5 (\Gamma_{15}) (3)$                                             |
| $CB$ | $\Gamma_7^- (2)$<br>$\Gamma_6^- (2)$<br>$\Gamma_8^- (4)$<br>$X_5 (4)$ | $\Gamma_2^- (\Gamma_{2'}) (1)$<br>$\Gamma_5^- (\Gamma_{15}) (3)$<br><br>$X_1 (2)$ | $\Gamma_6 (2)$<br>$\Gamma_7 (2)$<br>$\Gamma_8 (4)$<br>$X_6 (2), X_7 (2)$ | $\Gamma_1 (1)$<br>$\Gamma_5 (\Gamma_{15}) (3)$<br><br>$X_1 (1), X_3 (1)$ |

The notation used in [7] and the dimensions of the IRs are given in parentheses

band structure with different symmetry points of the BZ that we are concerned with here.

The group-IV materials are not the only indirect-gap cubic semiconductors. For instance, GaP and the III-V compounds with sphalerite structure involving Al are also indirect-gap semiconductors. There is a difference between the two structures, however: while the energy dispersion curves of diamond-type crystals are degenerate at the X point of the BZ (see Fig. 3.4), this degeneracy is lifted for the sphalerite structure into a lower band,  $X_1$  and a higher band,  $X_3$  ( $X_6$  and  $X_7$ , respectively when s-o interaction is considered) separated typically by an energy of  $\sim 0.4$  eV. It turns out that the relative ordering of these two bands depends on the origin of the coordinate system, which can be chosen at a group-III or group-V site (the same reasoning holds also for the II-VI compounds) through a potential that differs for the two sites [67]. When this potential attracts electron on one site, the electron states on that site are the lowest and they belong to the  $CB$  minimum. For GaP, it has been found that this potential is positive and it attracts electrons on a P site and repels electrons on a Ga site. As a consequence, an electron on the  $X_1$  band is concentrated on a P site and on the  $X_3$  band on a Ga site. This has important consequences for donors at P or Ga sites in GaP and this is discussed in Chap. 6.

Logically, when the both extrema of  $CB$  and  $VB$  of a semiconductor lie at the same value of  $\mathbf{k}$ , the gap is said to be direct. III-V compounds like InP, GaAs and InSb belong to this category, with extrema for  $\mathbf{k} = 0$ . As already mentioned, in the crystals with the diamond or sphalerite structure, the electron wave functions at the top of the  $VB$  at  $\mathbf{k} = 0$  are triply degenerate. They form a basis for a three-dimensional IR of the diamond ( $O_h$ ) or sphalerite ( $T_d$ ) symmetry point group. This IR is  $\Gamma_5^+$  for diamond and  $\Gamma_5$  for sphalerite (see Table 3.3). Under s-o interaction, the  $\Gamma_5^+ VB$  splits into the  $\Gamma_8^+$  and  $\Gamma_7^+$  bands separated by  $\Delta_{so}$ . In an isolated atom,  $\Delta_{so}$  increases as  $Z^{\sim 4}$  and a similar trend is observed in crystals. In most crystals, the band with the highest energy is  $\Gamma_8^+ (O_h)$  or  $\Gamma_8 (T_d)$ . One exception is CuCl, where  $\Gamma_7$  is about 60 meV above  $\Gamma_8$  (the energies are taken as negative below the  $VB$

maximum) and this is due to the hybridization of the Cu 3d levels with the Cl 3p levels, because their energies are similar [32].

In germanium and in other indirect-gap semiconductors, the direct  $\Gamma_8^+ \rightarrow \Gamma_7^-$  transitions from the *VB* to *CB* can be detected in the fundamental absorption region by an increase of the absorption cross-section, as shown in Fig. 3.5.

The fundamental absorption of semiconductors and insulators is very strong and the value of  $E_g$  determines the visual aspect of intrinsic polished crystals (the visible spectrum extends from about 400 to 750 nm, that is for photons between 3.10 and 1.65 eV). The crystals with  $E_g < 1.65$  eV display a quasi-metallic aspect due to their intrinsic absorption in the visible region, correlated with a high reflectivity; those with  $E_g$  between 1.65 and 3.10 eV are transparent, with a colour depending on the value of  $E_g$  while those with  $E_g > 3.10$  eV are colourless when pure.

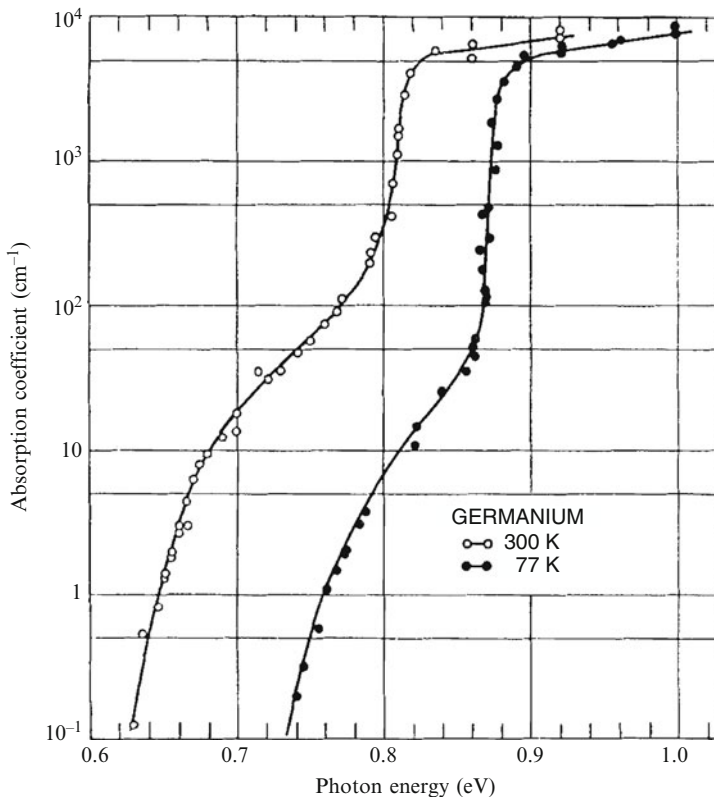


**Fig. 3.5.** Semi-logarithmic plot of the intrinsic absorption in germanium at 77 and 300 K. The lower values of the absorption coefficient correspond to indirect transitions. The inflections of the absorption coefficients near  $10^2 \text{ cm}^{-1}$  correspond to the onset of the direct transitions [72]. Copyright 1959, with permission from Elsevier



**Table 3.4.** Selected band-structure parameters of indirect-band-gap cubic crystals

|                     | C <sup>a</sup> <sub>diam</sub> | 3C-SiC           | Si <sup>a</sup>      | Ge <sup>a</sup>  | GaP <sup>a</sup>  | AlSb <sup>a</sup> |
|---------------------|--------------------------------|------------------|----------------------|------------------|-------------------|-------------------|
| $\mathbf{k}_{\min}$ | $\sim 0.75\mathbf{k}$ (X)      | $\mathbf{k}$ (X) | $0.84\mathbf{k}$ (X) | $\mathbf{k}$ (L) | $\mathbf{k}$ (X)* | $\mathbf{k}$ (X)* |
| $m_{nl}$            | $1.7^b$                        | $0.667^d$        | $0.9163^\ddagger$    | 1.57             | $0.90^l$          | 1.8               |
| $m_{nt}$            | $0.31^b$ ( $0.36^c$ )          | $0.247^d$        | $0.1905^\ddagger$    | 0.0807           | $0.25^l$          | 0.259             |
| $m_{hh}$            | 1.08                           |                  | 0.54                 | $0.35^\dagger$   | $0.67^\dagger$    | $0.872^\dagger$   |
| $m_{lh}$            | 0.36                           | 0.45             | 0.15                 | $0.043^\dagger$  | $0.17^\dagger$    | $0.091^\dagger$   |
| $m_{so}$            | 0.15                           |                  | 0.24                 | 0.095            | 0.465             |                   |
| $\Delta_{so}$ (meV) | $6^e - 13^f$                   | $14.4^g$         | $42.65^h$            | $296^i$          | 80                | 673               |
| Direct gap (eV)     | 7.3                            | 7.0              | 3.48                 | 0.81             | 2.90              | 2.38              |
| $\gamma_1$          | $3.61^j$                       | 2.8              | 4.28                 | $13.3^k$         | 4.05              | 4.15              |
| $\gamma_2$          | $0.09^j$                       | 0.16             | 0.375                | $4.24^k$         | 0.49              | 1.01              |
| $\gamma_3$          | $1.06^j$                       | 0.65             | 1.45                 | $5.69^k$         | 1.25              | 1.75              |

$\mathbf{k}_{\min}$  denotes the wave-vector symmetry and modulus for the absolute *CB* minimum with respect to the critical points of the BZ. The electron and hole effective masses are in units of  $m_e$ .  $\Delta_{so}$  is the s-o splitting of the *VB*. The direct gap corresponds to  $\Gamma_8(VB) - \Gamma_6(CB)$  for sphalerite and  $\Gamma_8^+ - \Gamma_7^-$  for diamond. The *VB* parameters  $\gamma_i$  are in units of  $2m_e/\hbar^2$

\* See text <sup>†</sup> Values near from  $k = 0$  along the [111] direction <sup>‡</sup> [39], <sup>a</sup> [64], <sup>b</sup> [19], <sup>c</sup> [71], <sup>d</sup> [47], <sup>e</sup> [84], <sup>f</sup> [102], <sup>g</sup> [103], <sup>h</sup> See Sect. 7.2.1.2, <sup>i</sup> [1], <sup>j</sup> [85], <sup>k</sup> [40], <sup>l</sup> [76]

There are a few cubic crystals for which an optical transition between the maximum of the *VB* and the absolute minimum of the *CB* is symmetry-forbidden. This is notably the case for  $\text{Cu}_2\text{O}$ , where the absolute minimum of the *CB* is about  $\sim 0.8$  eV above the *VB* (direct thermal gap) while the direct optical gap is 2.2 eV [23].

Choosing the  $z$  axis along  $\mathbf{k}_{\min}$  and taking the electron energy origin at  $\mathbf{k}_{\min}$ , the energy  $E$  of a conduction electron near  $\mathbf{k}_{\min}$  for the indirect-gap semiconductors of Table 3.4 is:

$$E = \frac{\hbar^2}{2} \left[ (\mathbf{k}_z - \mathbf{k}_{\min})^2 / m_{nl} + (\mathbf{k}_x^2 + \mathbf{k}_y^2) / m_{nt} \right] \quad (3.24)$$

and the constant energy surfaces in the  $\mathbf{k}$ -space are prolate revolution ellipsoids with their main axis along  $z$ . The band structure of the sphalerite-type crystals is similar to that of the diamond-type crystals, with a few differences, however, but for most of them, the *CB* minimum is at  $\mathbf{k} = 0$ .

In the vicinity of the *VB* maximum at  $\mathbf{k} = 0$ , the expressions for the constant-energy surfaces of the *VB* electrons in the highest-energy band of the diamond- or sphalerite-type crystals are usually given as functions of three parameters  $A$ ,  $B$  and  $C$ . These maxima are warped spheres in the  $\mathbf{k}$ -space given by:

$$E_{(3/2)\pm} = -Ak^2 \mp [B^2k^4 + C^2 (\mathbf{k}_x^2 \mathbf{k}_y^2 + \mathbf{k}_y^2 \mathbf{k}_z^2 + \mathbf{k}_z^2 \mathbf{k}_x^2)]^{1/2} \quad (3.25)$$

which can be seen as the sum of a spherical and a cubic contribution.  $E_{(3/2)+}$ , with a smaller energy dispersion (a corresponding larger mass) than  $E_{(3/2)-}$

is the heavy-hole  $VB$  ( $E_{\text{hh}}$ ) and  $E_-$  the light-hole  $VB$  ( $E_{\text{lh}}$ ) (Fig. 3.4). The dispersion curves of the constant-energy surface for the holes of the  $VB$  split by s-o coupling is:

$$E_{(1/2)} = -\Delta_{\text{so}} + Ak^2$$

and they are spheres in the  $\mathbf{k}$ -space.

New  $VB$  parameters  $\gamma_1$ ,  $\gamma_2$ , and  $\gamma_3$  were introduced by Luttinger [60] in his description of holes in the silicon  $VB$ . These so-called Luttinger  $VB$  parameters, which have been adopted for other semiconductors, are different from the ones in (3.25) as holes were considered instead of electrons:

$$\frac{\hbar^2}{2m_e}\gamma_1 = -A \quad \frac{\hbar^2}{m_e}\gamma_2 = -B \quad \frac{\hbar^2}{m_e}\gamma_3 = \sqrt{B^2 + C^2/3}$$

In the practical case, these parameters are given in units of  $\hbar^2/2m_e$  so that  $\gamma_1 = -A$ ,  $\gamma_2 = -B/2$  and  $\gamma_3 = \frac{1}{2}\sqrt{B^2 + C^2/3}$ . The Hamiltonian for holes in the upper  $VB$  of silicon using these parameters, known as the Luttinger Hamiltonian  $H_L$  is:

$$H_L \frac{1}{m_e} \left[ \left( \gamma_1 + \frac{5}{2}\gamma_2 \right) \frac{p^2}{2} - \gamma_2 (p_x^2 J_x^2 + p_y^2 J_y^2 + p_z^2 J_z^2) - 2\gamma_3 (\{p_x p_y\} \{J_x J_y\} + \text{cp}) \right] \quad (3.26)$$

where  $p_i$  are the components of the hole linear momentum and  $J_i$  the components of the angular momentum operator corresponding to spin 3/2. The cyclic permutation is denoted by cp and  $\{ab\} = (ab + ba)/2$ . This Hamiltonian is found to be suitable for diagonalization, specially in the presence of additional perturbations and it has also been used for a description of the upper  $VB$  of other cubic semiconductors. For sphalerite-type crystals with symmetry point group  $T_d$ , the Hamiltonian must include a term taking into account the asymmetry of these crystals with respect to inversion. This additional term is written as:

$$H_A = \frac{2C}{\sqrt{3}\hbar} (p_x \{J_x, V_x\} + p_y \{J_y, V_y\} + p_z \{J_z, V_z\}) \quad (3.27)$$

where  $V_x = J_y^2 - J_z^2$ ,  $V_y = J_z^2 - J_x^2$  and  $V_z = J_x^2 - J_y^2$ . Parameter  $C$  in expression (3.27) is different from the one in expression (3.25). Estimations of the values of parameter  $C$  of expression (3.27) for different semiconducting compounds have been calculated by Cardona and Christensen [16]. For InSb,  $C$  is  $\sim 8.7 \times 10^{-8}$  meV cm and this value is in reasonable agreement with the one ( $9.3 \times 10^{-8}$  meV cm) obtained by Pidgeon and Groves [83] from magneto-optical reflection measurements at 1.5 K. In many practical cases, the contribution of  $H_A$  is neglected.

Hamiltonian (3.26) will be used to explain the principles of the calculation of the shallow acceptor levels in these crystals. For a magnetic field  $\mathbf{B}$ , derived

from a vector potential  $\mathbf{A}$  through  $\mathbf{B} = \nabla \times \mathbf{A}$ , satisfying the condition  $\nabla \times \mathbf{A} = 0$ , the hole momentum  $\boldsymbol{\pi}$  can be written in SI units as:

$$\boldsymbol{\pi} = -i\hbar\nabla + e\mathbf{A}$$

and an expression similar to (3.26) can be obtained for the EM Hamiltonian with the addition of field-dependent *VB* parameters  $\kappa$  and  $q$  introduced in [60]. The term  $H_B$ , linear in  $\mathbf{B}$ , added to Hamiltonian (3.26) can be written as:

$$H_B = \mu_B (g_1 \mathbf{B} J) + g_2 (B_x J_x^3 + B_y J_y^3 + B_z J_z^3) \quad (3.28)$$

where parameters  $g_1$  and  $g_2$  are called the *g*-factors of the *VB* [5]. These *g*-factors are related to Luttinger *VB* parameters by  $g_1 = 2\kappa$  and  $g_2 = 2q$ .

From the experimental side, the band-structure parameters are mainly determined from the cyclotron resonance (CR) spectra of electron and holes (see for instance [4]). Some of these parameters can also be obtained from the Zeeman splitting of electronic transitions of shallow impurities involving levels for which the electronic masses can be taken as those of free electrons or holes, or from the magnetorefectivity of free carriers. Average effective masses can also be deduced from the Hall-effect measurements or from other transport measurements. Calculation methods that have been used to obtain band-structure parameters free from experimental input are the *ab-initio* pseudopotential method, the k-p method and a combination of both. These theoretical methods are presented in Chap. 2 of [107]. *VB* parameters at  $\mathbf{k} = 0$  including  $\kappa$  and  $q$  have been calculated for several semiconductors with diamond and zinc-blended structures by Lawaetz [55].

Table 3.4 gives a few relevant band-structure parameters of group-IV and group-III–V crystals. The structure of the *CB* near from its minimum is generally simpler to model than that of the *VB*. The *CB* parameters are known, therefore, with a reasonable accuracy from the experimental data. For diamond,  $m_{nt} = 0.31 m_e$  is deduced from the Zeeman splitting of  $2p_{\pm 1}$  (P) in  $C_{\text{diam}}$  [19] and  $m_{nl} = 1.7 m_e$  from the ratio  $\gamma = m_{nt}/m_{nl}$  whose determination is explained in the text accompanying Table 5.3.

This is not the case for the *VB* and there is still a significant uncertainty on the exact values of the *VB* parameters of diamond (see for instance [102]). For silicon and germanium, there is only a moderate dispersion of the values of these parameters. Gray tin ( $\alpha$ -Sn) is a semi-metal stable below 13°C, where the energy separation (0.14 eV) between  $\Gamma_8$  (v, c) and the conduction band minimum at  $L_6^+$  is sometimes called the optical energy gap because it corresponds to the onset of a higher absorption [58], but the absorption coefficient of  $\alpha$ -Sn at energies below this onset is already in the  $10^4 \text{ cm}^{-1}$  range. The *VB* s-o splitting of  $\alpha$ -Sn is 0.8 eV.

The X point is on the  $\Delta$  axis of the BZ with  $\langle 100 \rangle$  orientation and the absolute energy minimum of the *CB* of the corresponding cubic crystals of Table 3.4 is sixfold degenerate in k-space. For germanium, it is only fourfold

degenerate. For GaP and AlSb, the *CB* minima are also along the  $\langle 100 \rangle$  directions at  $0.925 \mathbf{k}$  ( $X_1$ ) and  $0.90 \mathbf{k}$  ( $X_1$ ), respectively. The energy dispersion curve of these crystals shows a small maximum  $\Delta E$  (see Table 3.5) at the  $X_1$  point with respect to the two nearby minima and this configuration has been coined the camel's back structure. This situation is depicted in Fig. 3.6.

The existence of the camel's back structure and of the already mentioned relative minimum of the *CB* at the  $X_3$  point, introduces complexity in the determination of the values of the electron effective masses for the interpretation of experimental data [51]. The energy dispersion at the camel's back for GaP and AlSb are described by the expression:

$$E(k) = \frac{\hbar^2}{2} \left( k_{//}^2/m_l + k_{\perp}^2/m_t \right) - \left( (\Delta/2)^2 + \Delta_0 \hbar^2 k^2 / 2m_l \right)^{1/2} \quad (3.29)$$

where  $k_{//}$  and  $k_{\perp}$  are the components of  $\mathbf{k}$  parallel and perpendicular to the  $\langle 100 \rangle$  direction and  $m_l$  and  $m_t$  the effective masses parallel and perpendicular to the  $\langle 100 \rangle$  direction. Parameter  $\Delta_0$  describes the non-parabolicity of

**Table 3.5.** CB parameters of three cubic crystals with camel's back structure near the CB minimum  $X_1$  at the X point of the BZ. The values for GaAs apply under hydrostatic pressure above  $\sim 4$  GPa. The effective masses are in  $m_e$  units

|                  | $\Delta E$ (meV) | $\Delta$ (meV) | $\Delta_0$ (meV) | $m_l$ | $m_t$ |
|------------------|------------------|----------------|------------------|-------|-------|
| GaP <sup>a</sup> | 2.7              | 355            | 422.6            | 0.90  | 0.251 |
| AlSb             | 7.4              | 261            |                  | 1.8   | 0.259 |
| GaAs             | 9.3              | 304            |                  | 1.8   | 0.257 |

<sup>a</sup> [76]

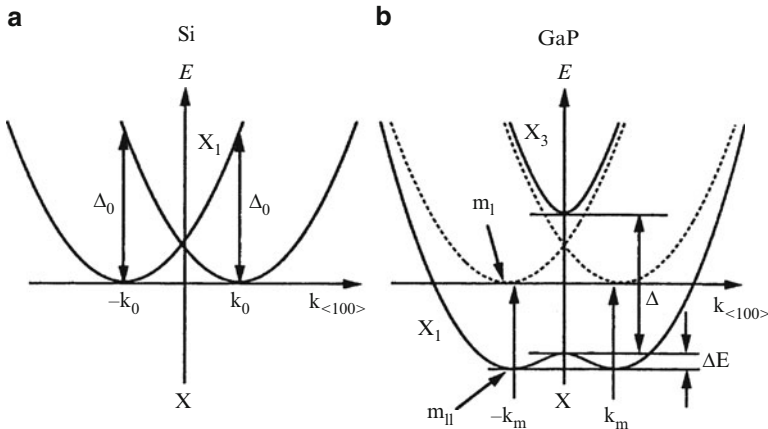


**Fig. 3.6.** Comparison between the CB minima at the X point in silicon and in GaP. In silicon, the CB minima are on the  $\mathbf{k}_{\langle 100 \rangle}$  axis at  $\sim \pm 0.84 \mathbf{k}$  (X). In GaP, there is a splitting of the two dashed curves of silicon at the crossing point giving the upper  $X_3$  band and the lower  $X_1$  band showing the camel's back [76]. Reproduced with permission from the Physical Society of Japan

the  $CB$  and  $\Delta$  is the separation between the  $X_1$  and  $X_3$  minima. The apparent effective mass  $m_{//}$  at the minima of the  $X_1$  camel back is given by:

$$m_{//} = m_l \left(1 - (\Delta/\Delta_0)^2\right)^{-1} \quad (3.30)$$

The relevant numerical values are given in Table 3.5 and the value for  $m_{//}$  deduced from these values is  $3.06m_e$ . The direct-gap crystal GaAs has been added to this table as it is possible to convert it under hydrostatic pressure into an indirect-gap structure with a minimum at the  $X_1$  point [44].

Calculation of  $CB$  parameters in the vicinity of the  $X_1$  point in III–V semiconductors have been performed by Kopylov [51]. It must be pointed out that at the  $X_1$  point, because of the local curvature of the  $CB$ , the effective mass is negative.

The electron effective masses  $m_n$  at the  $CB$  minimum at  $\mathbf{k} = 0$  are generally smaller than the ones for  $\mathbf{k} \neq 0$   $CB$  minima, as can be judged from Table 3.6. The Luttinger  $VB$  parameters have been determined by many authors, though biased in some cases by the values used in the most recent calculations of the shallow-acceptor levels. The situation is complicated by the fact that for semiconductors like InSb, where there is an interaction between the valence and the conduction bands, effective Luttinger  $VB$  parameters  $\tilde{\gamma}_i$  have been defined by [82] as:

$$\tilde{\gamma}_1 = \gamma_1 - \frac{E_P}{3E_g} \text{ and } \tilde{\gamma}_i = \gamma_i - \frac{E_P}{6E_g} \text{ for } i = 2, 3$$

where  $E_P$  is known as Kane energy and is related to the  $VB$ – $CB$  interaction. It is of the order of 20 eV. For InSb, the parameters  $\tilde{\gamma}_i$  are sometimes given as the Luttinger parameters and this can create some confusion.

**Table 3.6.** Experimentally-determined effective masses (in units of  $m_e$ ) at  $k = 0$  extrema and VB Luttinger parameters for some direct-band-gap cubic semiconductors

|                    | GaAs                | GaSb               | InP                 | InAs               | InSb                         | ZnSe              | ZnTe               | CdTe              |
|--------------------|---------------------|--------------------|---------------------|--------------------|------------------------------|-------------------|--------------------|-------------------|
| $m_n$              | 0.0662 <sup>a</sup> | 0.041              | 0.0793 <sup>b</sup> | 0.022 <sup>c</sup> | 0.0139 <sup>c</sup>          | 0.13              | 0.122 <sup>d</sup> | 0.093             |
| $m_{hh}$           | 0.53                | 0.8                | 0.58                | 0.4                | 0.42                         |                   |                    | 0.84              |
| $m_{lh}$           | 0.08                | 0.05               | 0.12                | 0.026              | 0.016                        |                   |                    | 0.12              |
| $m_{so}$           | 0.15                |                    | 0.12                | 0.14               |                              |                   |                    |                   |
| $\Delta_{so}$ (eV) | 0.341               | 0.76               | 0.108               | 0.39               | 0.850 <sup>c</sup>           | 0.40 <sup>c</sup> | 0.91               | 0.80              |
| $\gamma_1$         | 6.98 <sup>e</sup>   | 11.80 <sup>f</sup> | 6.28 <sup>f</sup>   | 19.67 <sup>f</sup> | 35.65 <sup>i</sup><br>(3.25) | 3.77 <sup>f</sup> | 3.90 <sup>g</sup>  | 5.30 <sup>h</sup> |
| $\gamma_2$         | 2.25                | 4.03               | 2.08                | 8.37               | 15.70(1.3)                   | 1.24              | 0.80               | 1.70              |
| $\gamma_3$         | 2.9                 | 5.26               | 2.76                | 9.29               | 16.97<br>(0.0)               | 1.67              | 1.70               | 2.00              |

At this  $CB$  minimum,  $m_n$  can be considered as nearly isotropic. For germanium,  $m_n$  at  $\mathbf{k} = 0$  is 0.038 [1]. For InSb, values of the effective Luttinger parameters are given in parentheses. The Luttinger parameters of Lawaetz are calculated values

<sup>a</sup> [52], <sup>b</sup> [42], <sup>c</sup> [64, 65], <sup>d</sup> [24], <sup>e</sup> [92], <sup>f</sup> [55], <sup>g</sup> [30], <sup>h</sup> [56], <sup>i</sup> [105]

The structure of the  $VB$  maximum of the wurtzite-type crystals differs from that of the sphalerite-type crystals. This difference, which determines the intrinsic optical features of these crystals, is due to the combination of the crystal field mentioned in Appendix B with the s-o coupling. Ignoring the s-o coupling and the crystal field, the  $VB$  maximum of wurtzite at  $\mathbf{k} = 0$  is made of two degenerate bands associated with the one-dimensional  $\Gamma_1$  and two-dimensional  $\Gamma_5$   $IR$ s of the  $C_{6v}$  symmetry point group. The combined effect of the crystal field and of the s-o coupling is to lift 1) the degeneracy between the  $\Gamma_1$  and  $\Gamma_5$  bands and 2) the intrinsic degeneracy of the  $\Gamma_5$  band. In the double group representation of  $C_{6v}$  due to the introduction of spin, the  $VB$  maximum then corresponds to the  $\Gamma_9$   $IR$ , separated from two bands both corresponding to the  $IR$   $\Gamma_7$ . These three  $VB$ s are usually denoted by  $A$ ,  $B$  and  $C$  in order of decreasing energy. The separations  $E_{AB}$  and  $E_{AC}$  between the  $\Gamma_9$  ( $A$ ),  $\Gamma_7$  ( $B$ ) and  $\Gamma_7$  ( $C$ ) bands as a function of the crystal field and s-o energy parameters  $\Delta_{cf}$  and  $\Delta_{so}$  have been calculated as [41]:

$$E_{AB} = \frac{1}{2}(\Delta_{so} + \Delta_{cf}) - \left[ \frac{1}{4}(\Delta_{so} + \Delta_{cf})^2 - \frac{2}{3}\Delta_{so}\Delta_{cf} \right]^{\frac{1}{2}} \quad (3.31a)$$

$$E_{AC} = \frac{1}{2}(\Delta_{so} + \Delta_{cf}) + \left[ \frac{1}{4}(\Delta_{so} + \Delta_{cf})^2 - \frac{2}{3}\Delta_{so}\Delta_{cf} \right]^{\frac{1}{2}} \quad (3.31b)$$

Most wurtzite-type crystals are direct band-gap materials (2H-SiC is an exception) and interband transitions can take place between these three  $VB$ s and the  $\Gamma_7$   $CB$  minimum. These materials are anisotropic and this anisotropy reflects on the selection rules for the optical transitions and on the effective masses. The  $\Gamma_9(A) \rightarrow \Gamma_7(CB)$  transitions are only allowed for  $\mathbf{E} \perp c$  while the two  $\Gamma_7(B, C) \rightarrow \Gamma_7(CB)$  transitions are allowed for both polarizations. However, the relative values of the transition matrix elements for the  $\Gamma_7(B, C) \rightarrow \Gamma_7(CB)$  transitions can vary with the material. For instance, in w-GaN, the  $\Gamma_7(B) \rightarrow \Gamma_7(CB)$  transition is predominantly allowed for  $\mathbf{E} \perp c$  while the  $\Gamma_7(C) \rightarrow \Gamma_7(CB)$  transition is predominantly allowed for  $\mathbf{E} // c$  [22]. Table 3.7 gives band structure parameters of representative materials with the wurtzite structure.

A few semiconductors have  $VB$  extrema at other points of the BZ, like the direct-gap lead chalcogenides (PbS, PbSe, PbTe), with rocksalt structure, where the valence and conduction bands extrema are both located at the L point of the BZ.

When two semiconducting materials are fully miscible, a semiconducting alloy is obtained. Binary semiconducting alloys are scarce (SiC is a definite compound) and the best known (and used) is  $\text{Ge}_{1-x}\text{Si}_x$ . The addition to germanium of a small percentage of silicon opens the band gap relatively rapidly up to  $x \sim 0.15$ , while above this value, the increase is smaller [8]. The value  $x \sim 0.15$  corresponds to the cross-over from Ge-like alloys with  $CB$  minimums at the L points of the BZ, along  $\langle 111 \rangle$  directions, to Si-like alloys with  $CB$  minimums along  $\langle 100 \rangle$  directions (see Table 3.4). Many ternary alloys are known, like those of the  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  family, used as intrinsic photodetectors

**Table 3.7.** Selected band structure parameters of four compounds with the wurtzite structure. The energies for ZnO and GaN are given at LHeT and at 80 K for CdSe and CdS (the effective masses are expressed in units of  $m_e$ )

|                                   | <i>w</i> -CdSe | ZnO                 | <i>w</i> -GaN | <i>w</i> -ZnS |
|-----------------------------------|----------------|---------------------|---------------|---------------|
| $\Gamma_9(A) - \Gamma_7(CB)$ (eV) | 1.829          | 3.4370 <sup>a</sup> | 3.504         | 3.864         |
| $\Gamma_9(A) - \Gamma_7(B)$ (meV) | -26            | -9.5 <sup>a</sup>   | -6            | -29           |
| $\Gamma_9(A) - \Gamma_7(C)$ (meV) | -1, 429        | -49.8 <sup>a</sup>  | -43           | -117          |
| $\Delta_{so}$ (meV)               |                | 16 <sup>a</sup>     | 12            | 86            |
| $\Delta_{cf}$ (meV)               | 39             | 43 <sup>a</sup>     | 37.5          | 58            |
| $m_{n\perp}, m_{n//}$             | 0.12           |                     | 0.19          | 0.28          |
| $m_{h\perp}(A), m_{h//}(A)$       | 0.45 > 1       | 0.59, 0.59          | 0.33, 2.03    | 0.48, 1.4     |
| $m_{h\perp}(B), m_{h//}(B)$       |                | "                   | 0.34, 1.25    |               |
| $m_{h\perp}(C), m_{h//}(C)$       |                | 0.35, 0.31          | 2.22, 0.15    |               |

<sup>a</sup> [86]

in the  $\sim 50$ – $200$  meV region of the electromagnetic spectrum [101]. Their band gap values vary from nominally zero at RT for HgTe to 1.53 eV for CdTe. Between 77 K and RT, the most widely used expression [35] of the variation of the direct band gap of these alloys with  $x$  and  $T$  is:

$$E_g [\text{Hg}_{1-x}\text{Cd}_x\text{Te}] \text{ (eV)} = -0.302 + 1.93x + 5.35 \times 10^{-4}T(1 - 2x) - 0.81x^2 + 0.832x^3$$

There exists many III–V ternary and quaternary alloys, and we just mention here the  $\text{In}_{1-x}\text{Ga}_x\text{As}$  family, that has many applications in microelectronics. The variation of the direct band gap of these alloys at RT is given by:

$$E_g [\text{In}_{1-x}\text{Ga}_x\text{As}] \text{ (eV)} = 0.324 + 0.7x + 0.4x^2$$

A list of the band gaps of ternary and quaternary III–V compound alloys can be found in [64]. There are, however, more complicated situations found for instance in the  $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$  alloys, which are of interest because tunable laser diodes are made from them. While both compounds are semiconducting, there are strong indications that the  $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$  alloy with  $x = 0.38$  has a zero band gap at RT [27].

To try to make things more quantitative, for direct-gap semiconductors, assuming spherical effective masses  $m_n$  and  $m_h$  for electrons and holes, the interband absorption coefficient  $K(\omega)$  can be shown (see for instance [43]) to be proportional to

$$|\mathbf{p}_{cv}|^2 (2\bar{m})^{3/2} \frac{(\hbar\omega - E_g)^{1/2}}{\hbar\omega} \quad (3.32)$$

where  $\mathbf{p}_{cv}$  is the momentum matrix element governing the transition probability between the valence and conduction bands and  $\bar{m}$  the reduced effective mass  $(m_n m_h) / (m_n + m_h)$ . This energy dependence is closely followed in the vicinity of  $E_g$  by semiconductors like InSb.

The indirect transitions involve the creation (emission) or annihilation (absorption) of a phonon for momentum conservation. It has been proposed

that in the vicinity of the indirect-band-gap energy, the absorption coefficient with phonon annihilation was:

$$K_a \propto n(\omega_{\text{ph}})(\hbar\omega - (E_g - \hbar\omega_{\text{ph}}))^2 \quad (3.33)$$

where  $n(\omega_{\text{ph}})$  in (3.33) is the occupation number for the annihilated phonon. Similarly, the absorption coefficient with phonon creation is

$$K_c \propto (1 + n(\omega_{\text{ph}}))(\hbar\omega - E_g - \hbar\omega_{\text{ph}})^2 \quad (3.34)$$

where  $n(\omega_{\text{ph}})$  in (3.34) is the occupation number for the created phonon. It follows that the indirect absorption should be proportional to the sum of expressions (3.33) and (3.34). The phonons  $\omega_{\text{ph}}$  involved in the momentum-conserving process for the indirect-band-gap absorption of semiconductors must have wave vectors  $\mathbf{q}$  opposite to the electron wave vectors  $\mathbf{k}_{\text{min}}$  given in Table 3.4.

In indirect-gap semiconductors, this phonon-assisted electronic absorption is revealed by kinks in the vicinity of the electronic absorption edge. They are due to the different energies of the momentum-conserving phonons involved as well as to the above-discussed different phonon processes. The evolution of this near band gap absorption with temperature can be seen in Fig. 3.7

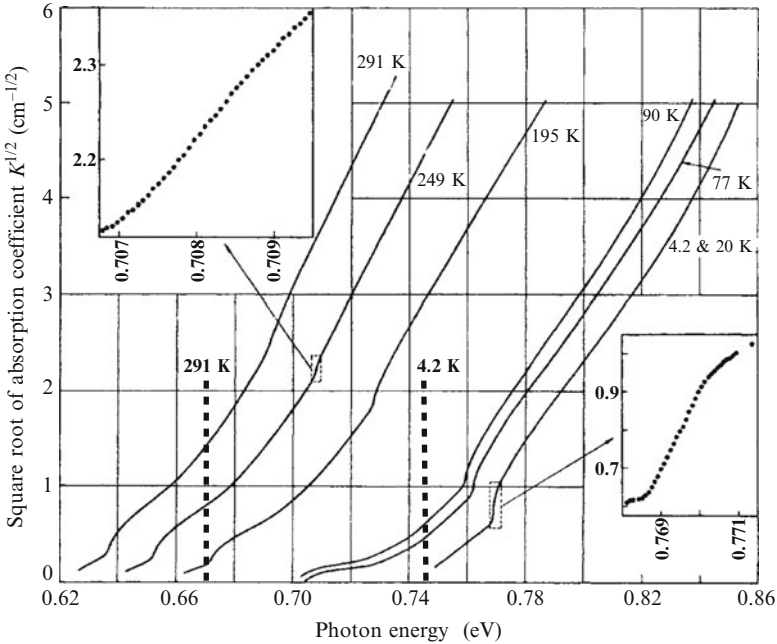


**Fig. 3.7.** Absorption of  $^{\text{nat}}\text{Ge}$  near the band gap energy for different temperatures. It is plotted as a function of the square root of the absorption coefficient for a better appreciation of the structures. The insets provide a better appreciation of the details of the measurements. The positions of  $E_g$  at 291 K and 4.2 K that can be derived, indicated by the dotted bars, are 0.670 and 0.745 eV, respectively (after [62])



for germanium, combined with the temperature dependence of  $E_g$ . At low temperature, only phonon creation can occur and  $K_a$  is zero at  $E_g$ . A detailed interpretation of these spectra can be found in the original reference [62] and in [43]. In indirect-band-gap semiconductors, accurate determination of the band gap at low temperature relies mainly on the interpretation of the free exciton spectra.

The interband absorption of semiconductors produces free electrons and holes in the conduction and valence bands. These free carriers produce intrinsic photoconductivity above the band gap in adequate structures, and several types of infrared photoconductors have been built on this principle [43].

When a semiconductor is illuminated with the band-gap radiation, excess electrons and holes are photo-created. They can form free excitons or be trapped by ionized impurities, but their ultimate fate is their annihilation by thermal or radiative recombination. The formation of free excitons will be discussed in Sect. 3.3.2, but in direct band-gap semiconductors, electron-hole radiative recombination can also occur at an energy close to  $E_g$  if the pumping beam is kept at a low level. This can provide an accurate determination of  $E_g$  [87].

Band gap energies at RT and LHeT of different semiconductors and insulators are given in Appendix C.

In the presence of a magnetic field  $\mathbf{B}$ , the calculations of Landau [54] have shown that the energy of electrons in metals becomes quantized in a plane perpendicular to the field, but remains continuous in the direction of the field. The result is an helical motion of the electrons in the plane perpendicular to  $\mathbf{B}$  with the Landau energy  $E_N = \hbar\omega_c(N + 1/2)$ , ignoring the electron spin. In this expression, which can also be written as  $2\mu_B\mathbf{B}(N + 1/2)$ ,  $\omega_c = eB/m_e$  is the cyclotron pulsation and  $N$  can be 0 or a positive integer. In semiconductors, the band structure in the presence of a magnetic field becomes complicated in the direction perpendicular to the field as the continuum of the valence and conduction bands split into different Landau level ladders characterized by different total angular momenta  $J$  and spacings. In addition, the spin degeneracy of these Landau levels is removed (for s-type bands,  $J = 1/2$  level is split into sublevels with  $M_J = +1/2$  and  $-1/2$ ). When a degeneracy of the VB occurs for  $\mathbf{k} = 0$ , this degeneracy is also lifted by the magnetic field. Subsequently, the absorption coefficient for interband transitions in the presence of a magnetic field takes the form:

$$K(\mathbf{B}, \omega) \propto \hbar\omega_c \sum_l (\hbar\omega - E_N)^{-1/2} \quad (3.35)$$

where

$$E_N = E_g + (N + 1/2) \hbar\omega_c + \mu_B (g_c M_{Jc} - g_v M_{Jv}) B \quad (3.36)$$

The effective mass involved for the cyclotron pulsation is a reduced mass  $\overline{m}$  comparable to the one used for the interband transitions in expression (3.32) and for each band,  $(N + 1/2) \hbar\omega_c$  is  $1.1577 \times 10^{-1} (N + 1/2) B m_e / m^*$  (meV T<sup>-1</sup>). The effective electron  $g$ -factors in the valence and conduction

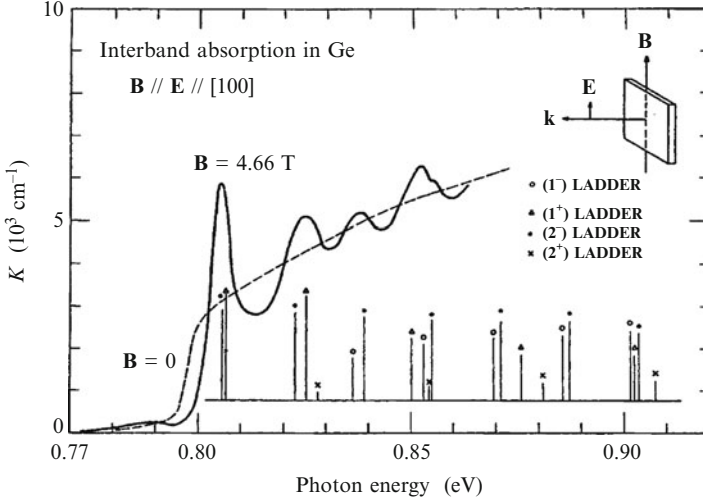


**Fig. 3.8.** Direct magnetoabsorption in germanium at RT. The polarization condition is usually referred as  $\pi$  polarization. The calculated peaks  $1^-$  and  $2^-$  correspond to transitions from spin-split levels of the Landau ladder of the heavy hole valence band and the  $1^+$  and  $2^+$  ones to corresponding transitions for light hole VB. With the ordinate scale used, the indirect absorption is barely visible (after [13])

bands are  $g_c$  and  $g_v$ . The selection rules require that  $\Delta N = 0$ , whatever the polarization, with  $\Delta M_J = 0$  for  $\mathbf{B} \parallel \mathbf{E}$  and  $\Delta M_J = \pm 1$  for  $\mathbf{B} \perp \mathbf{E}$ . The net result is that the onset of absorption is shifted to higher energies by  $\hbar\omega_c/2$ , and the absorption displays an oscillatory behaviour. Figure 3.8 illustrates this effect for the direct magnetoabsorption of a  $3\text{ }\mu\text{m}$ -thick Ge sample at RT.

The electronic band gaps are correlated with the cohesive energies of the materials and, for covalent crystals, with the atomic binding energies. Hence, for group IV elements, the band gap decreases as the atomic number of the element increases. This rule is also followed by binary compounds with one element fixed, and it allows for a very few exceptions like PbSe and PbTe with band gaps of 0.26 and 0.29 eV, respectively, at RT.

When temperature is lowered, the band gaps usually increase [15]. There again, a few materials like lead sulphides or some copper halides are exceptions with a band gap *increasing* with temperature [96]. A quantitative analysis of the temperature dependence of the energy gaps must consider the electron–phonon interaction, which is the predominant contribution, and the thermal expansion effect. The effect of thermal expansion can be understood intuitively on the basis of the decrease of the interatomic distances when the temperature is decreased. A quantitative analysis of the electron–phonon contributions is more difficult, and most calculations have been performed for direct band-gap structures [75]. Multi-parameter calculations of the temperature dependence of band gaps in semiconductors can be found in [81].

From a practical viewpoint, an increase of the absorption of CdTe near the RT band gap ( $\sim 1.5$  eV) has been correlated with  $10.06\text{ }\mu\text{m}$  laser illumination [73]. It has been attributed to the temperature-induced shift of the band gap to lower energies generated by residual absorption of the crystal at  $10.06\text{ }\mu\text{m}$ . The band-gap increase of silicon between RT and LHeT is  $\sim 50$  meV, and recent measurements at ultra-high resolution of the shift with temperature of the strongest B acceptor bound exciton line of qmi  $^{28}\text{Si}$  between 4.8 and 1.3 K show a band-gap increase of  $\sim 1$  GHz or  $4\text{ }\mu\text{eV}$  in this temperature domain [17].

The positions of the energy bands are also pressure-dependent and this results in a change of the value of the band gap under a hydrostatic pressure. As a rule, the direct band gaps increase with pressure and the order of magnitude of the linear part of the increase for II–V and III–V compounds is  $100\text{ meV GPa}^{-1}$  [29]. Figure 3.9 shows the increase of  $E_g$  with hydrostatic pressure for InP at RT.

The indirect band gap of InP ( $\sim 2.03$  eV at zero pressure), decreases with increasing pressure and produces the low-energy tail observed at the highest pressures in Fig. 3.9. The same trend exists in indirect-band-gap semiconductors, and for silicon, this decrease amounts to  $\sim 14\text{ meV GPa}^{-1}$  at RT [100]. At very high hydrostatic pressures, the diamond lattice can become unstable: for instance, the opacity of indirectgap semiconductors silicon and germanium in the IR for pressures above about 10 GPa ( $\sim 100$  kbar) is attributed to a change from cubic to the tetragonal  $\beta$ -Sn metallic phase.

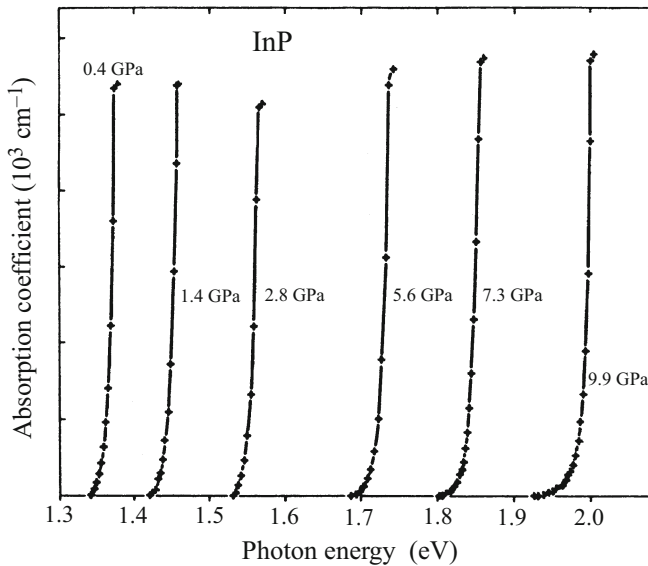


**Fig. 3.9.** Variation with hydrostatic pressure of the direct band-gap absorption threshold of InP at RT (1 GPa is taken for 10 kbar) (after [69])

The decrease of the indirect band gaps of silicon and germanium at RT under uniaxial stress along different axes has been measured indirectly by Bulthuis [11] and the values found to lie between  $-50$  and  $-100$  meV GPa $^{-1}$ .

Finally, a band-gap change can also occur when the isotopic composition of the crystal changes. Natural diamond is  $^{12}\text{C}_{0.989}^{13}\text{C}_{0.011}$ , but qmi  $^{13}\text{C}_{\text{diam}}$  crystals have been grown and their physical properties investigated. In a 99%  $^{13}\text{C}_{\text{diam}}$  sample, an *increase* of 13.6 meV of the indirect band gap – a relative increase of 0.25% – has been measured in comparison with  $^{\text{nat}}\text{C}_{\text{diam}}$  [26]. The major contribution to this upward shift has been attributed to the effect of the isotope change on the mean-square displacement of the crystal atoms in relation with the electron–phonon coupling. The other contribution is the effect of the negative volume change due to the decrease of the zero-point vibration frequency [26]. Values of the isotope shift (IS) of  $E_g$  in silicon have been deduced from the ISs of excitons bound to shallow impurities (BEs) measured by PL at LHeT [38, 48] and a value of the IS of +0.98 meV/amu (+0.084%) can be deduced from these results. For germanium, a value of the IS of  $E_g$  of +0.36 meV/amu (+0.049%) is reported by Parks et al. [79]. In compound crystals, the sign of the IS can depend on the nature of the atom replaced: in CuCl, it has been observed that the direct band gap (3.206 eV at LHeT) increased by 364  $\mu\text{eV}/\text{amu}$  when increasing the mass of the Cl atom, but *decreased* by 76  $\mu\text{eV}/\text{amu}$  when increasing the mass of the Cu atom [32]. A simple explanation can be related to the usual band structure of many compound crystals, for which the upper valence band corresponds to the valence electrons of the most electronegative element, and the conduction band to the valence electrons of the most positive element. However, for CuCl, the role of phonon modes in the gap renormalization is determinant and it explains the above isotope effects as well as the increase of the band gap with temperature [32].

In nanocrystals with average radii typically below 10 nm, the band gap increases due to confinement. This is shown in Fig. 3.10 for the excitonic gap (the energy required to create an exciton) of CdS [94].

The review by Yoffe [106] provides a good account of the optical properties of nanocrystals in compound semiconductors (see also [89]).

### 3.3.2 Excitons

At the beginning of the chapter, an analogy between the band gap excitation and that of an electron in an anti-bonding state in a quasi-molecular description was mentioned. In the electron band scheme, this situation is described as an exciton, resulting only from Coulomb attraction between the electron and the positive hole. A steady-state concentration of excitons is produced in semiconductors by continuous or pulsed illumination at energies higher than  $E_g$ . Excitons, which can be seen as pseudo-hydrogenic atoms where the role of the positive ion is taken by the positive hole, are free to propagate as a whole in the crystal during their lifetimes, hence the name free excitons (FEs). Their

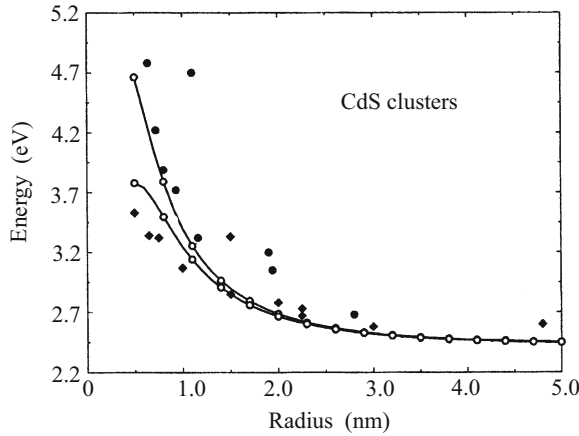


**Fig. 3.10.** Calculated direct excitonic gap of wurtzite-type (upper line) and sphalerite-type (lower line) CdS spherical clusters as a function of the cluster radii, compared with the experimental results. Full diamonds and circles are for sphalerite- and wurtzite-type clusters, respectively. The exciton binding energy in bulk CdS is  $\sim 0.03$  eV (after [94]). Copyright 1996, American Institute of Physics

binding energy  $E_{\text{ex}}$  depends obviously on the effective masses of the particles, on the static dielectric constant of the crystal and on its ionicity. The dissociation of these so-called Mott–Wannier excitons results in a free electron and a free hole. The energy  $E_{\text{gx}} = E_{\text{g}} - E_{\text{ex}}$  required to create such a pair is often referred to as the excitonic gap. For a direct-gap semiconductor with spherical energy bands, the exciton levels can be fitted to a hydrogen-like series whose energies are given by:

$$E_{\text{ex}}(n) = R_{\infty \text{eff}}/n^2 \quad (3.37)$$

where  $R_{\infty \text{eff}}$  is an effective Rydberg  $R_{\infty} \bar{m}/\varepsilon_s^2$ , where  $R_{\infty}$  is weighted by the reduced effective mass  $\bar{m}$  of the exciton and by the static dielectric constant  $\varepsilon_s$ . Figure 3.11 shows a well-resolved spectrum of the exciton absorption in GaAs [28]. From the difference between the energies of  $n = 1$  and 2 transitions at 1.5149 and 1.5180 eV, respectively, the exciton ground state energy  $E_{\text{ex}}$  in GaAs is found to be 4.13 meV. This value compares well with 4.2 meV obtained from  $\bar{m} = 0.05m_e$  and  $\varepsilon_s = 12.7$ .

The FE binding energy increases with ionicity: it is nearly 2% of the band gap for ZnO and about 6% for CuCl. This rather high value is due to the change from the  $sp^3$  hybridization of the orbitals for most of the semiconductors to  $p-d$  hybridization for CuCl. The FE binding energies for covalent and mainly covalent crystals are smaller, and for Ge, Si, and C<sub>diam</sub>, the indirect FE binding energies correspond to 0.56, 1.32, and 1.46% of the band gap, respectively. Excitons can recombine or decay thermally (with a small probability because of the energies involved) or radiatively, with the emission

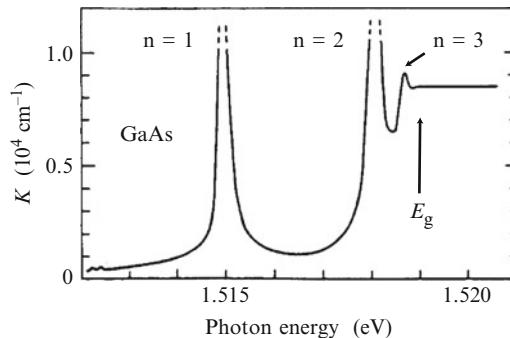


**Fig. 3.11.** 1s, 2s and 3s FE absorption lines in GaAs at 1.2 K (note the ordinate scale). The saturation of the 1s and 2s lines is indicated by the dashed part. The exciton binding energy is 4.1 meV. The energy gap  $E_g$  of GaAs is indicated (after [28]). Copyright 1985, with permission from Elsevier

of a photon, which can be detected by standard PL methods. In indirect-gap semiconductors, a direct absorption of FEs like the one shown in Fig. 3.11 is forbidden because momentum is not conserved in such a transition, and its intensity is very small, and this is also true from FE recombination involving only the emission of one photon at energy  $E_{gx}$ . What is observed in these materials are PL lines at energies smaller than  $E_{gx}$  assisted by the emission of one or two momentum-conserving phonons ([99] and reference therein). The measurement of the absorption leading to the creation of free indirect excitons in germanium has shown the existence of a splitting of the exciton ground state, which can be explained by the departure of the cubic symmetry by the introduction of the *CB* ellipsoids [108]. This property is predicted for the indirect excitons in indirect-band-gap semiconductors and numerical values of the splitting of these FEs have been calculated by Lipari and Altarelli [59]. In the 1970s, there have been many studies on the internal absorption of the indirect FE corresponding to transitions between ground and excited states. These transitions have been measured in germanium in the very far IR ( $\sim 1$ – $4$  meV) under band-gap excitation (see for instance [10, 33, 53, 91]). The energies of the lines observed are in good agreement with the energies of the transitions predicted from the calculations taking into account the FE ground-state splitting [59]. For germanium, the experimental values of  $E_{ex}$  for the indirect FE are 3.14 and 4.15 meV and the splitting is expected to be smaller for silicon.

The IS of the excitonic gap  $E_{gx}$  of the indirect FE has been measured in qmi Ge samples and it is  $+0.36$  meV/amu [79]. In  $^{nat}\text{Ge}$ , ( $^{72.59}\text{Ge}$ ), values of  $E_{gx}$  between 740.6 and 741.0 meV at LHeT have been given. Assuming a value of 740.8 meV and adding the binding energy of FE, taken as 4.2 meV results in a value of  $\sim 745$  meV for the indirect band gap of  $^{nat}\text{Ge}$  at LHeT.

The absorption due to the formation of direct excitons associated with the  $\Gamma_7^- CB$  (see Fig. 3.4) have also been observed at energies above  $E_g$  in very thin silicon and germanium samples [63], and for germanium,  $E_{ex}(\Gamma_7^-)$  of the direct FE is  $\sim 1.5$  meV [57].

The FEs produced at low temperature by illumination with photons in the vicinity or above  $E_g$  have finite lifetimes that depend on temperature (see [34] for silicon), their binding energies, and on the band structure of the semiconductor (the lifetime is larger in semiconductors with indirect gap than direct gap). During their lifetime, they can diffuse in the crystal and be trapped by impurities and defect to become bound excitons (BEs) with energies slightly different from that of the FE.

In ionic crystals, the exciton can be considered as an ion in an excited state. This excitation, called a Frenkel exciton, can also propagate in the crystal through similar ions. The excitation energies of the Frenkel excitons are significantly larger than the binding energies of the Mott–Wannier excitons. A thorough treatment of the optical properties of excitons in semiconductors and insulators can be found in [107].

### 3.3.3 Free-Carrier Effects

In semiconductors with small band gaps and small electron effective masses, a high concentration of n-type dopants produces a large accumulation of electrons in the  $CB$ . This can prevent the interband transitions with the lowest energies, and an efficient interband absorption takes places only at energies larger than  $E_g$ . The above explanation was provided independently by Burstein [12] and Moss [68] to explain the h-e shift of the band gap observed in InSb with increasing free electron concentrations (from a value of 0.18 eV up to an apparent band-gap value of  $\sim 0.6$  eV for an electron concentration of  $\sim 10^{19} \text{ cm}^{-3}$ ). This energy shift, coined the Burstein–Moss effect, has been observed in PbS [78] and in GaSb [31]. This effect has also been put forward to explain most of the substantial low-energy shift (from about 2 eV to near 0.7 eV) of the band gap of InN in samples with moderate decrease of the carrier concentrations [104]. The low value of the band gap of InN has been attributed to Mie scattering by In metallic clusters or droplets in the samples [9, 90] and a value of the band gap near 1.3 eV was proposed. However, the last results published confirm a band-gap value of  $\sim 0.8$  eV with a moderate Burstein–Moss effect [2].

We have assumed up to now that besides lattice absorption, intrinsic semiconductors were essentially transparent to photon energies less than the band gap at RT and below. Now, like electrons in metals, the free carriers in semiconductors can absorb electromagnetic radiation to increase their energies. In the calculation of the intrinsic free-carrier concentrations in the  $VB$  and  $CB$  of a semiconductor, one has to consider the effective densities of states

(DoS)  $N_c$  and  $N_v$  in the conduction and valence bands and the fact that electrons obey the Fermi–Dirac distribution. These effective DoS can be expressed generically as a function of the DoS effective mass  $m_{\text{dos}}^*$  ( $m_{\text{cdos}}$  or  $m_{\text{vdos}}$ ) as  $2 (m_{\text{dos}}^* k_B T / 2\pi\hbar^2)^{3/2}$ . This DoS effective mass depends on the dispersion of the energy bands of the semiconductors. For non-degenerate parabolic bands, it is simply  $m_n$  or  $m_h$ . For electronic bands that have ellipsoidal symmetry near their extremum,  $m_{\text{dos}}^* = (m_{xx}m_{yy}m_{zz})^{1/3}$ . When there are  $M_c$  equivalent  $CB$  minimums, as for group-IV semiconductors, this must be taken into account in the DoS effective mass: for  $CB$  electrons in these materials,  $m_{\text{cdos}} = \left[ M_c (m_{n\ell} m_{nt}^2)^{1/2} \right]^{2/3}$ . With the  $CB$  parameters of Table 3.4,  $m_{\text{cdos}}$  is 1.66, 1.062 and 0.547 for  $\text{C}_{\text{diam}}$ , silicon and germanium, respectively, in  $m_e$  units. For energy bands that are degenerate at their extremum, one must consider the individual bands separately and for the  $VB$  of the group IV semiconductors,  $m_{\text{vdos}} = (m_{\text{hh}}^{3/2} + m_{\text{lh}}^{3/2})^{2/3}$ . In the intrinsic regime, there are as many free holes as free electrons and their concentrations  $n_i$  at temperature  $T$  is:

$$n_i = 2 \left( \frac{m_e k_B T}{2\pi\hbar^2} \right)^{3/2} (m_{\text{cdos}} m_{\text{vdos}})^{3/4} e^{-\frac{E_g}{2k_B T}} \quad (3.38)$$

with  $m_{\text{cdos}}$  and  $m_{\text{vdos}}$  in units of  $m_e$ , (3.38) written as:

$$n_i (\text{cm}^{-3}) = 4.84 \times 10^{15} T^{3/2} (m_{\text{cdos}} m_{\text{vdos}})^{3/4} e^{-\frac{E_g}{2k_B T}}$$

This expression is derived from the more general case where the electron and hole concentrations in the conduction and valence bands are  $n$  and  $p$  with  $np = n_i^2$ . At RT, taken as 300 K, the intrinsic carrier concentration  $n_i$  is  $\sim 1.1 \times 10^{10} \text{ cm}^{-3}$  in silicon, but it increases to about  $4 \times 10^{13} \text{ cm}^{-3}$  in germanium to reach  $2 \times 10^{16} \text{ cm}^{-3}$  in intrinsic InSb.

In the classical electron transport model in metals or semiconductors, for a material with a free electron concentration  $n$  and an average electron scattering time (also called relaxation time)  $\tau$ , the DC conductivity is  $\sigma_0 = ne^2\tau/m^*$ . In this classical expression,  $m^*$  ( $m_c^*$  or  $m_v^*$ ) is the conductivity effective mass, which is an average mass different from the DoS effective mass (see for instance [4]). In cubic semiconductors with degenerate  $CB$  extrema, the conductivity effective mass for electrons is:

$$m_c^* = \frac{3m_{nl}m_{nt}}{m_{nt} + 2m_{nl}} \quad (3.39)$$

and for holes, it is given by:

$$\frac{1}{m_v^*} = \frac{m_{\text{hh}}^{1/2} + m_{\text{lh}}^{1/2}}{m_{\text{hh}}^{3/2} + m_{\text{lh}}^{3/2}} \quad (3.40)$$

For non-degenerate  $CB$ s,  $m_c^*$  is equal to  $m_n$ . On the basis of a free-electron model, with an equation of motion analogous to expression (3.9) but without



restoring force and with an appropriate electron effective mass  $m^*$ , the polarization  $P$  for a free-electron concentration  $N$  is:

$$P = -\frac{Ne^2E}{m^*(\omega^2 + i\gamma\omega)} \quad (3.41)$$

where  $\gamma = \tau^{-1}$  is the collision frequency for electrons. Defining  $\omega_p^2$  as  $Ne^2/m^*\epsilon_0$ , where  $\omega_p$  is the plasma frequency, the dielectric function can be written as:

$$\epsilon(\omega) = \tilde{n}^2(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i\gamma)} \quad (3.42)$$

In a semiconductor, when considering expression (3.41), the contribution to the dielectric function of the high-frequency interband transitions at energies  $\geq E_g$  is considered by replacing 1 by the high-frequency dielectric constant  $\epsilon_\infty$ .

From the modified expression, one derives:

$$n^2 - k^2 = \epsilon_\infty - \frac{\omega_p^2}{\omega^2 + \gamma^2} \quad (3.43a)$$

and

$$2nk\omega = \gamma \frac{\omega_p^2}{\omega^2 + \gamma^2} \quad (3.43b)$$

For small absorptions and at IR frequencies high compared to collision frequencies, these expressions reduce to:

$$n^2 = \epsilon_\infty - \frac{\omega_p^2}{\omega^2} \quad (3.44a)$$

and

$$2nk\omega = \gamma \frac{\omega_p^2}{\omega^2}. \quad (3.44b)$$

For an intrinsic semiconductor with refractive index  $n$ , where the mean lifetimes between collisions are  $\tau_n$  and  $\tau_h$  for electrons and holes, respectively, it leads to an energy-dependent free-carrier absorption coefficient  $K_{fc}$  given by the contribution of the free electrons and holes:

$$K_{fc} = \frac{n_i e^2}{m_e \epsilon_0 c \omega^2 n} \left( \frac{1}{m_c^* \tau_n} + \frac{1}{m_v^* \tau_h} \right) \quad (3.45)$$

with  $m_c^*$  and  $m_v^*$  in  $m_e$  units. For an extrinsic semiconductor,  $n_i$  in expression (3.45) is replaced by the actual free-carrier concentration  $n$  or  $p$  and only the appropriate term is left in the parentheses.

Expression (3.45) predicts a free-carrier absorption proportional to the square of the wavelength of the radiation when the scattering time is independent of energy. An energy dependence of  $\tau$  rises at low energy from the

interaction between free electrons and acoustic phonons; in this case, it can be shown that absorption follows a  $\lambda^p$  wavelength dependence with  $p$  between 2 and 3. For free electron absorption (n-type semiconductor), a practical expression relating the absorption coefficient to  $\lambda^2$  is:

$$K_{fc} \text{cm}^{-1} = 5.26 \times 10^{-17} \frac{\lambda^2 (\mu\text{m}^2) n (\text{cm}^{-3})}{nm_c^* \mu_n (\text{cm}^2/\text{Vs})} \quad (3.46)$$

where  $\mu_n = e\tau_n/m_c^*$  is the electron mobility. The RT free-carrier absorption of InSb, a semiconductor of technological interest shows, for intrinsic crystals, a very weak energy dependence between the band gap and the onset of the multi-phonon absorption. The average value of this absorption coefficient near 100 meV is about  $10 \text{ cm}^{-1}$  and the deviation from (3.45) can be attributed to the free-hole absorption. Such a dependence has been observed in n-type InSb and n-type silicon [3, 93].

In p-type semiconductors with moderate band gaps, the *VB* states of lower energy are occupied at RT by the free holes released by the shallow acceptors. Direct absorption from electrons can then take place between the occupied *VB* states and the empty upper states. The direct  $\Gamma_8^+ \rightarrow \Gamma_7^+$  transition (see Fig. 3.4) at  $k = 0$  is parity forbidden, but direct transitions for  $k \neq 0$  are observed. Depending on the location of the Fermi level with respect to the different *VBs*, transitions can take place from the s-o split and/or light-hole *VBs* to the heavy-hole *VB* and from the light-hole to the heavy-hole *VBs*. This kind of inter-valence band absorption has been specially studied in p-type Ge, where it gives rise at RT to three broad absorption bands: the ones at 0.37 and 0.27 eV, with absorption cross-sections  $K/p$  near  $1 \times 10^{-16} \text{ cm}^2$ , are due to transitions from the spin-split *VB* to the heavy- and light-holes *VBs*, respectively, and the one at  $\sim 0.08 \text{ eV}$  to transitions from the light to heavy hole bands ([12], and references therein).

Expression (3.7) for normal reflectivity shows that when  $n = 1$  and  $k$  is small in comparison,  $R$  and the reflectance  $R$  tend to zero. From (3.44a), this occurs at a frequency given by  $\omega_{R=0}^2 = \omega_p^2 / (\varepsilon_\infty - 1)$ . A good illustration of this point is shown in Fig. 3.12 for n-type InSb.

At slightly lower frequencies, for  $\omega^2 = \omega_p^2 / \varepsilon_\infty$ ,  $n$  goes to zero and the reflectance rises to values near unity. The determination of  $\omega_{R=0}$  when the free-carrier concentration and  $\varepsilon_\infty$  are known allows determination of the conductivity effective mass. For non-parabolic *CBs*, the values of  $m^*$  so obtained for different filling factors of the *CB* are different from those measured at the bottom of the *CB*.

The plasma frequency corresponds to an oscillation as a whole of the electronic charge density with respect to the fixed ionic charge. By analogy with the phonon excitation, the corresponding excitation is called plasmon and it can be considered as the quantization of classical plasma oscillation. The plasmon oscillation is longitudinal with respect to its propagation and is comparable to the TO phonon mode. The macroscopic electric field associated

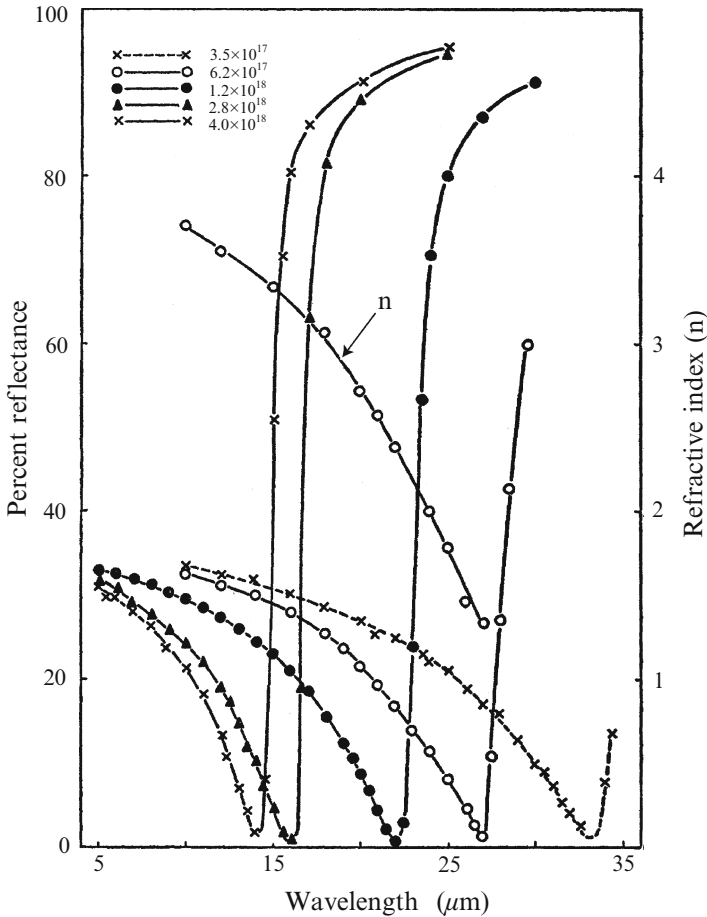


**Fig. 3.12.** RT reflectance minima for n-type InSb samples with different free-carrier concentrations between 248 and  $\sim 35$  meV. The spectral variation of the refractive index  $n$  of the sample with  $n = 6.2 \times 10^{17} \text{ cm}^{-3}$  is also shown (after [93]). Copyright 1957 by the American Physical Society

with plasmons can give rise to Raman scattering. For some carrier concentrations, the plasma frequency can approach the LO phonon frequency and interaction between the two modes occurs.

## References

1. R.L. Aggarwal, Phys. Rev. B **2**, 446 (1970)
2. H. Ahn, C.H. Shen, C.L. Wu, S. Gwo, Thin Solid Films **494**, 69 (2006)
3. M. Balkanski, A. Aziza, E. Amzallag, Phys. Stat. Sol. B **31**, 323 (1969)

4. M. Balkanski, R.F. Wallis, *Semiconductor Physics and Applications*. (Oxford University Press, Oxford, 2000)
5. G.L. Bir, E.I. Butikov, G.E. Pikus, *J. Phys. Chem. Solids* **24**, 1467 (1963)
6. J.L. Birman, *Phys. Rev.* **131**, 1489 (1963)
7. L.B. Bouckaert, R. Smoluchowski, E. Wigner, *Phys. Rev.* **50**, 58 (1936)
8. R. Braunstein, A.R. Moore, F. Herman, *Phys. Rev.* **109**, 695 (1958)
9. O. Briot, B. Maleyre, S. Ruffenach, B. Gil, C. Pinquier, F. Demangeot, J. Frandon, *J. Cryst. Growth* **269**, 22 (2004)
10. M. Buchanan, T. Timusk, in *Proceedings of 13th International Conference on the Physics of Semiconductors*, ed. by F.G. Fumi (Tipografia Marves, Rome, 1976), pp. 821–824
11. K. Bulthuis, *Phys. Lett.* **25A**, 512 (1967)
12. E. Burstein, *Phys. Rev.* **93**, 632 (1954)
13. E. Burstein, G.F. Picas, R.F. Wallis, F. Blatt, *Phys. Rev.* **113**, 15 (1959)
14. E. Burstein, in *Phonons and Phonon Interactions in Solids*, ed. by T.A. Bak (Benjamin, New York, 1964), pp. 276–342
15. J. Camassel, D. Auvergne, *Phys. Rev. B* **12**, 3258 (1975)
16. M. Cardona, N.E. Christensen, G. Fasol, *Phys. Rev. Lett.* **56**, 2831 (1986)
17. M. Cardona, T.A. Meyer, M.L.W. Thewalt, *Phys. Rev. Lett.* **92**:196403/1–4, (2004)
18. M. Cardona, M.L.W. Thewalt, *Rev. Mod. Phys.* **77**, 1173 (2005)
19. N. Casanova, E. Gheeraert, E. Bustarret, S. Koizumi, T. Teraji, H. Kanda, J. Zeman, *Phys. Stat. Sol A* **186**, 291 (2001)
20. D. Chandler-Horovitz, P.M. Armitharaj, *J. Appl. Phys.* **97**, 123526/1–8 (2005)
21. J.R. Chelikowski, M.L. Cohen, *Phys. Rev. B* **14**, 556 (1976)
22. G.D. Chen, M. Smith, J.Y. Lin, H.X. Jiang, S.H. Wei, M. Asif Khan, C.J. Sun, *Appl. Phys. Lett.* **68**, 2784 (1996)
23. W.Y. Ching, Y.N. Xu, K.W. Wong, *Phys. Rev. B* **40**, 7684 (1989)
24. B. Clerjaud, A. Gélinau, D. Galland, K. Saminadayar, *Phys. Rev. B* **19**, 2056 (1979)
25. M.L. Cohen, T.K. Bergstresser, *Phys. Rev.* **141**, 789 (1966)
26. A.T. Collins, S.C. Lawson, G. Davies, H. Kanda, *Phys. Rev. Lett.* **65**, 891 (1990)
27. J.O. Dimmock, I. Melngailis, A.J. Strauss, *Phys. Rev. Lett.* **16**, 1193 (1966)
28. G.W. Fehrenbach, W. Schäfer, R.G. Ulbrich, *J. Lumin.* **30**, 154 (1985)
29. M.D. Frogley, J.L. Sly, D.J. Dunstan, *Phys. Rev. B* **58**, 12579 (1998)
30. D. Fröhlich, A. Nöthe, K. Reimann, *Phys. Stat. Sol. B* **125**, 653 (1984)
31. C. Ghezzi, R. Magnanini, A. Parisini, B. Rotelli, L. Tarricone, A. Bosacchi, S. Franci, *Semicond. Sci. Tech.* **12**, 858 (1997)
32. A. Göbel, T. Ruf, M. Cardona, C.T. Lin, J. Wrzesinski, M. Steube, K. Reimann, J.C. Merle, M. Joucla, *Phys. Rev. B* **57**, 15183 (1998)
33. N.V. Guzeev, V.A. Zayats, V.L. Kononenko, T.S. Mandel'shtam, V.N. Murzin, *Sov. Phys. Semicond.* **8**, 1061 (1974)
34. R.B. Hammond, R.N. Silver, *Appl. Phys. Lett.* **36**, 68 (1980)
35. G.L. Hansen, J.L. Schmit, *J. Appl. Phys.* **54**, 1639 (1983)
36. J.R. Hardy, S.D. Smith, *Phil. Mag.* **6**, 1163 (1961)
37. K.C. Hass, M.A. Tamor, T.R. Anthony, W.F. Banholzer, *Phys. Rev. B* **45**, 7171 (1992)
38. S. Hayama, G. Davies, J. Tan, J. Coutinho, R. Jones, K.M. Itoh, *Phys. Rev. B* **70**, 035202/1–9 (2004)

39. J.C. Hensel, H. Hasegawa, M. Nakayama, Phys. Rev. **138**, A225 (1965)
40. J.C. Hensel, K. Suzuki, Phys. Rev. B **9**, 4219 (1974)
41. J.J. Hopfield, J. Phys. Chem. Solids **15**, 97 (1960)
42. M.A. Hopkins, R.J. Nicholas, P. Pfeffer, W. Zawadzki, D. Gauthier, J.C. Portal, M.A. DiForte-Poisson, Semicond. Sci. Tech. **2**, 568 (1987)
43. J.T. Houghton, S.S. Smith, *Infra-Red Physics* (Oxford University Press, London, 1966)
44. L. Hsu, S. Zehender, E. Bauser, E.E. Haller, Phys. Rev. B **55**, 10515 (1997)
45. M. Ikezawa, M. Ishigame, J. Phys. Soc. Jpn. **50**, 3734 (1981)
46. F.A. Johnson, Proc. Phys. Soc. **73**, 265 (1959)
47. R. Kaplan, R.J. Wagner, H.J. Kim, R.F. Davis, Solid State Commun. **55**, 67 (1985)
48. D. Kararaiskaj, M.L.W. Thewalt, T. Ruf, M. Cardona, M. Konuma, Solid State Commun. **123**, 87 (2002)
49. C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1996)
50. C.A. Klein, T.M. Hartnett, C.J. Robinson, Phys. Rev. B **45**, 12854 (1992)
51. A.A. Kopylov, Solid State Commun. **56**, 1 (1985)
52. M. Koshevnikov, B.M. Ashkinadze, E. Cohen, R. Arza, Phys. Rev. B **52**, 17165–17171 (1995)
53. D. Labrie, T. Timusk, Phys. Rev. B **27**, 3605 (1983)
54. L.D. Landau, Z. Phys. **64**, 629 (1930)
55. P. Lawaetz, Phys. Rev. B **4**, 3460 (1971)
56. Le-Si-Dang, G. Neu, R. Romestain, Solid State Commun. **44**, 1187 (1982)
57. G.H. Li, A.R. Goñi, K. Syassen, M. Cardona, Phys. Rev. B **49**, 8017 (1994)
58. R.E. Lindquist, A.W. Ewald, Phys. Rev. **135**, A191 (1964)
59. N.O. Lipari, M. Altarelli, Phys. Rev. B **15**, 4883 (1977)
60. J.M. Luttinger, Phys. Rev. **102**, 1030 (1956)
61. R.H. Lyddane, R.G. Sachs, E. Teller, Phys. Rev. **59**, 673 (1941)
62. G.G. McFarlane, T.P. McLean, J.E. Quarrington, V. Roberts, Phys. Rev. **108**, 1377 (1957)
63. G.G. McFarlane, T.P. McLean, J.E. Quarrington, V. Roberts, J. Phys. Chem. Solids **8**, 388 (1959)
64. O. Madelung (ed.) *Semiconductors: Group IV Elements and III-V Compounds*. In Data in Science and Technology, ed. R. Poerschke (Springer, Berlin, 1991)
65. O. Madelung (ed.) *Semiconductors: Other than Group IV Elements and III-V Compounds*. In Data in Science and Technology, ed. R. Poerschke (Springer, Berlin, 1992)
66. A. Mooradian, G.B. Wright, Solid State Commun. **4**, 431 (1966)
67. T.N. Morgan, Phys. Rev. Lett. **21**, 819 (1968)
68. T.S. Moss, Proc. Phys. Soc. Lond. B **67**, 775 (1954)
69. H. Müller, R. Trommer, M. Cardona, Phys. Rev. B **21**, 4879 (1980)
70. S. Nakashima, H. Harima, Phys. Stat. Sol. A **162**, 39 (1997)
71. F. Nava, C. Canali, C. Jacoboni, L. Reggiani, F. Kozlov, Solid State Commun. **33**, 475 (1980)
72. R. Newman, W.W. Tyler, in *Photoconductivity in Germanium*, ed. by F. Seitz, D. Turnbull. Solid State Physics Advances in Research and Application, vol **8**. (Academic, New York, 1959), pp. 49–107
73. A.V. Nurmikko, Appl. Phys. Lett. **26**, 175 (1974)

74. F. Occelli, P. Loubeyre, R. Letoullec, *Nature Mater.* **2**, 151 (2003)
75. D. Olgun, M. Cardona, A. Cantarero, *Solid State Commun.* **122**, 575 (2002)
76. M. Oshikiri, K. Takehana, T. Asano, G. Kido, *J. Phys. Soc. Jpn.* **65**, 2936 (1996)
77. B. Pajot, C.J. Fall, J.L. Cantin, H.J. von Bardeleben, R. Jones, P.R. Briddon, F. Gendron, in *Proceedings of 25th International Conference on Physics of Semiconductor*, Osaka, 2000, ed. by N. Miura, T. Ando. (Springer, Berlin, 2001), pp. 1583–1584
78. E.D. Palik, D.L. Mitchell, J.N. Zemel, *Phys. Rev.* **135**, A763 (1964)
79. C. Parks, A.K. Ramdas, S. Rodriguez, K.M. Itoh, E.E. Haller, *Phys. Rev. B* **49**, 14244 (1994)
80. R.H. Parmenter, *Phys. Rev.* **100**, 573 (1955)
81. R. Pässler, *Phys. Rev. B* **66**, 085201/1–18 (2002)
82. C.R. Pidgeon, R.N. Brown, *Phys. Rev.* **146**, 575 (1966)
83. C.R. Pidgeon, S.H. Groves, *Phys. Rev.* **186**, 824 (1969)
84. C.J. Rauch, *Phys. Rev. Lett.* **7**, 83 (1961)
85. L. Reggiani, D. Waetcher, S. Zukotynski, *Phys. Rev. B* **28**, 3550 (1983)
86. D.C. Reynolds, D.C. Look, B. Jogai, C.W. Litton, G. Cantwell, W.C. Harsch, *Phys. Rev. B* **60**, 2340 (1999)
87. N.L. Rowell, *Infrared Phys.* **28**, 37 (1988)
88. G.A. Samara, *Phys. Rev. B* **27**, 3494 (1983)
89. K. Sattler, in *The Energy Gap of Cluster Nanoparticles, and Quantum Dots*, ed. by H.S. Nalwa. *Handbook of Thin Films Materials*, vol. 5 Nanomaterials and Magnetic Thin Films. (Academic, New York, 2002), pp. 61–97
90. T.V. Shubina, S.V. Ivanov, V.N. Jmerik, D.D. Solnyshkov, V.A. Vekshin, P.S. Ko'pev, A. Vasson, J. Leymarie, A. Kavokin, H. Amano, K. Shimono, A. Kasic, B. Monemar, *Phys. Rev. Lett.* **92**, 117407/1–4 (2004)
91. V.I. Sidorov, Ya. E. Pokrovskii, *Sov. Phys. Semicond.* **6**, 2015 (1973)
92. M.S. Skolnick, A.K. Jain, R.A. Stradling, J. Leotin, J.C. Ousset, *J. Phys. C* **9**, 2809 (1976)
93. W.G. Spitzer, H.Y. Fan, *Phys. Rev.* **106**, 882 (1957)
94. A. Tomasulo, M.V. Ramakrishna, *J. Chem. Phys.* **105**, 3612 (1996)
95. R. Trommer, H. Müller, M. Cardona, P. Vogl, *Phys. Rev. B* **21**, 4869 (1980)
96. Y.W. Tsang, M.L. Cohen, *Phys. Rev. B* **3**, 1254 (1971)
97. B. Ulrici, E. Jahne, *Phys. Stat. Sol. B* **74**, 601 (1976)
98. R. Vogelgesang, A.D. Alvarenga, H. Kil, A.K. Ramdas, S. Rodriguez, M. Grimditch, T.R. Anthony, *Phys. Rev. B* **58**, 5408 (1998)
99. M.A. Vouk, E.C. Lightowers, *J. Phys. C* **10**, 3689 (1977)
100. B. Welber, C.K. Kim, M. Cardona, S. Rodriguez, *Solid State Commun.* **17**, 1021 (1975)
101. R.K. Willardson, A.C. Beer (eds.), *Semiconductors and Semimetals*, vol. 18. Mercury Cadmium Telluride. (Academic, New York, 1981)
102. M. Willatzen, M. Cardona, N.E. Christensen, *Phys. Rev. B* **50**, 18054 (1994)
103. M. Willatzen, M. Cardona, N.E. Christensen, *Phys. Rev. B* **51**, 13150 (1995)
104. J. Wu, W. Walukiewicz, K.M. Yu, J.W. Ager III, E.E. Haller, H. Lu, W.J. Schaff, Y. Saito, Y. Nanishi, *Appl. Phys. Lett.* **80**, 3967 (2002)
105. M.V. Yakunin, *Sov. Phys. Semicond.* **21**, 859 (1987)
106. A.D. Yoffe, *Adv. Phys.* **50**, 1 (2001)
107. P.Y. Yu, M. Cardona, *Fundamentals of Semiconductors*, 3rd edn. (Springer, Berlin, 2001)
108. S. Zwerdling, B. Lax, L.M. Roth, K.J. Button, *Phys. Rev.* **114**, 80 (1959)

# Methods and Techniques of Absorption Spectroscopy of Solids

## 4.1 Introduction

As a function of the underlying physical process, the absorption of electromagnetic radiation by impurities in semiconductors and insulators extends from energies near the band gap, lying in the UV region, to the very far IR. The discrete absorption spectra, especially those obtained at low temperature, can include very narrow absorption lines, with full width at half maximum (FWHM) as low as  $0.005 \text{ cm}^{-1}$  ( $\sim 0.6 \mu\text{eV}$ ). This means that the absorption spectroscopy of impurities in semiconductors and insulators can be considered in some aspects as a high-resolution spectroscopy. Low-temperature transmission experiments with semiconductors also require sensitive spectrometric systems because of the reflection losses of crystals with high refractive indices and of the transmission losses of the optical cryostat windows. Typically, the transmission spectrum of the sample recorded is given by expression (3.8). In addition to impurities or defects, the sample can also present intrinsic lattice absorption in the spectral region of interest, and the total absorption coefficient  $K$  at a given energy is the sum of an intrinsic part  $K_i$  and an extrinsic part  $K_e$ . When the intrinsic contribution interferes with the impurity spectra, for instance in the case of multiphonon absorption, the transmission of an intrinsic reference sample of the same thickness  $d$  is measured and the ratio of the two spectra is free from the intrinsic contribution. Quantitatively, it can be verified that the relative transmission  $T_{\text{rel}}$ , ratio of the raw transmission  $T_{i+e}$  of the sample and the raw transmission  $T_i$  of the reference sample is given by:

$$T_{\text{rel}} = \frac{u_e (1 - R^2 u_i^2)}{(1 - R^2 u_i^2 u_e^2)}, \quad (4.1)$$

where  $u_i = \exp[-K_i d]$  and  $u_e = \exp[-K_e d]$ . There is still a small intrinsic contribution, but for  $K_i d$  much smaller or much larger than unity,  $T_{\text{rel}}$  reduces to  $(1 - R^2) u_e / (1 - R^2 u_e^2)$  or to  $\sim u_e$ , respectively, which can be reversed to provide a  $K_e$  value.

For technological purposes, it can be also desirable to obtain a distribution map of a defect centre in a semiconductor wafer. One then chooses an absorption or PL line of this centre and scans its intensity at different points of the wafer.

The measured peak absorption coefficient,  $K_{\max}$ , for a discrete impurity transition depends on the oscillator strength of the transition and on the impurity concentration. The measured profile of a recorded line is the convolution product of its true profile by the instrumental function of the spectroscopic device used. It depends significantly on the ratio of the true FWHM of the line to the spectral resolution (the spectral band width) of the spectroscopic device. When this ratio is of the order of 3 or above, the measured FWHM can be considered as the true FWHM and the observed profile is close to the true profile. For lower values of this ratio, the measured FWHM increases steadily while the measured value of  $K_{\max}$  decreases, and it is assumed that when the ratio becomes  $\sim 1/3$  or smaller, the measured FWHM is the spectral resolution and the measured profile the instrumental function. This effect is known as instrumental broadening. For isolated lines, the absorption coefficient can be integrated over the entire line to give an integrated absorption  $IA$ :

$$IA = \int_{\tilde{\nu}_{\min}}^{\tilde{\nu}_{\max}} K(\tilde{\nu}) d\tilde{\nu}$$

where the integration is over the spectral extent of the line, here the wavenumber, denoted by  $\tilde{\nu}$ . This integrated absorption is independent of the spectral resolution. For continuous absorption,  $K$  is specified at a definite energy. When the concentration  $N$  of impurities producing a given absorption is known, one can define a more general quantity, the absorption cross-section  $\sigma$  ( $\text{cm}^2$ ) =  $K_{\max}/N$ , which is physically significant when instrumental broadening is considered, or an integrated absorption cross-section  $\sigma_{\text{IA}}$  ( $\text{cm}$ ) =  $IA/N$ , which is the same whatever the spectral resolution. For a given impurity and a given line of its spectrum,  $(\sigma_{\text{IA}})^{-1}$  is the impurity concentration for unit  $IA$  of that line and constitutes an integrated calibration factor of that line.

The correction for instrumental broadening is known as deconvolution. Deconvolution procedures that can be used with dispersive spectrometers have been described (see for instance [51]). In this book, unless otherwise specified, the FWHMs indicated are considered to be corrected for instrumental broadening.

For low intensities of probing radiation, the absorption coefficient is independent of intensity, but for large intensities, the absorption decreases because of saturation effects (discussed later in the chapter).

In classical optical absorption measurements, the absorption of a sample under different conditions as a function of the energy of the incident electromagnetic radiation is studied. This can be achieved in two ways: one can either take a broadband source and use a spectrometer to disperse the electromagnetic spectrum, or use a monochromatic tunable source. There is also a



technique known as excitation spectroscopy, which can be used in absorption as well as in PL modes. In this technique, a monochromator is set at the energy of a chosen absorption or PL line of a sample while the sample is illuminated with monochromatic light of varying energy by a second monochromator or a tunable source. The excitation spectrum is a record of the intensity change of the absorption or PL line through the first monochromator as a function of the energy of the additional exciting radiation.

A discrete transition between two levels of a centre in a crystal is characterized by its energy and a FWHM, which is the sum of the widths of the ground and excited states. In an ideal case, for given experimental conditions and for an homogeneously distributed centre, this FWHM is the same throughout the crystal and it can be defined as the homogeneous width of the transition. Eventually, because of local distortions or of inhomogeneities in the local electric field, a small change in the transition energy can occur locally. This can be due for instance to the random distribution of other centres or defects, producing strains in the crystal, or to the random distribution of a centre in a very disproportionate alloy. The observed absorption line is then the superposition of lines with slightly different energies corresponding to sites with different perturbations. The observed line width, corresponding to the energy distribution of the sum of the different lines, is larger than the homogeneous line width and the profile is said to be described by inhomogeneous broadening. When the lifetime of the excited state of the transition is large, giving a small homogeneous line width, it is possible, by illuminating the sample with laser radiation whose energy is within the inhomogeneous line width of an absorption transition, to excite selectively centres with the same homogeneous width. This produces a dip (a spectral hole) in the inhomogeneous absorption line and the technique is known as hole burning. This possibility was first demonstrated by Szabo [45] to study the effect of a ruby laser illumination on the in homogeneously broadened  $R_1$  line of Cr in ruby at 693.4 nm. Hole burning informs on the homogeneous line width of the transition, and also on the resonant excitation transfers [29].

In some experiments, the absorption of a transition is measured at a given energy as a function of the incident power. This is usually performed with a pulsed laser, for which the power dynamics can be adjusted in a broad range and where the repetition rate can be controlled. The transmitted energy can be measured directly with a variable attenuator placed in front of the detector to avoid its saturation for high incident power, or in a pump-probe geometry. What is generally observed as a function of the incident power is first a constant value of the absorption followed, for increasing power, by a decrease of the absorption, which can reach a point where it goes to zero. Such an effect is known as saturated absorption or optical bleaching. The kinetics of the absorption decrease, observed for both electronic and vibrational transitions [3, 46], also allows determination of the lifetimes of the excited states.

For sufficiently high power intensities, non-linear effects can give rise to two-photon absorption (TPA) where simultaneous absorption of two photons

with energy  $\hbar\omega_1$  produces a transition at energy  $2\hbar\omega_1$ , and the possibility of such an effect was predicted by Maria Göppert–Mayer [11]. An experimental verification of TPA was provided by [18], who reported a blue fluorescence at 425.0 nm (2.917 eV) of  $\text{Eu}^{2+}$  salts in  $\text{CaF}_2$  as a consequence of the illumination with the red light of a ruby laser at 694.3 nm (1.796 eV). TPA is theoretically explained by the presence of an intermediate virtual state at mid-point between the initial and final states. The possibility to observe TPA of shallow donors in semiconductors has been discussed by Golka and Mostowski [10] and examples of such absorptions for donors in GaAs are presented in Sect. 6.8.1.1.

An electronic or vibrational excited state has a finite global lifetime and its de-excitation, when it is not metastable, is very fast compared to the standard measurement time conditions. Dedicated lifetime measurements are a part of spectroscopy known as time domain spectroscopy. One of the methods is based on the existence of pulsed lasers that can deliver radiation beams of very short duration and adjustable repetition rates. The frequency of the radiation pulse of these lasers, tuned to the frequency of a discrete transition, as in a free-electron laser (FEL), can be used to determine the lifetime of the excited state of the transition in a pump-probe experiment. In this method, a pump energy pulse produces a transient transmission dip of the sample at the transition frequency due to saturation. The evolution of this dip with time is probed by a low-intensity pulse at the same frequency, as a function of the delay between the pump and probe pulses.<sup>1</sup> When the decay is exponential, the slope of the decay of the transmission dip as a function of the delay, plotted in a log-linear scale, provides a value of the lifetime of the excited state.

Impurity photoconductivity (extrinsic photoconductivity) is a type of absorption measurement where the detector is the sample itself. Classical photoconductivity occurs when the absorption of an electron or of a hole takes place between a discrete state and a continuum, where it can contribute to the electrical conductivity. When the final state of a discrete transition is separated from the continuum by an energy comparable to  $k_B T$  at the measurement temperature, the electron or the hole in this state can be thermally ionized in the continuum and give rise to photoconductivity at the energy of the discrete transition. This two-step process, which is temperature-dependent, is known as photo-thermal ionization spectroscopy (PTIS) and is discussed in more detail later in the section on extrinsic photoconductors.

Under a directional perturbation, a uniaxial stress or a magnetic field, the absorption of impurities in a crystalline sample shows dichroism with respect to the polarization of the radiation used for the absorption measurement. This means that the features of the spectra are different for a polarization parallel or perpendicular to the direction of the perturbation. It includes the polarization rules and there is no mention of dichroism at this point. In the spectroscopy of paramagnetic centres with related absorption lines, magnetic circular dichroism (MCD), the difference between the absorption of left- and right-circularly

---

<sup>1</sup> In the pump-probe geometry, the two beams are crossed.

polarized radiation, can be used to detect the absorption associated with the broad features of paramagnetic centres.

At low energies, in the meV energy range, acoustic phonon spectroscopy with superconducting thin film tunnel junctions evaporated onto opposite surfaces of a sample has been used as a technique complementary to optical spectroscopy [7]. In this technique, used in silicon and germanium, phonons are generated and detected by appropriate biasing of the junctions. Biased at voltages  $2\Delta_G/e$  above the energy gap  $2\Delta_G$  of the superconductor, a phonon line that can be tuned by the voltage is generated. Inversely, biased at voltages below the gap, a junction becomes a phonon detector with energies sufficient to excite extra quasiparticles (i.e to break Cooper pairs) in the thin film of the detector junction. With  $Al-Al_2O_3-Al$  and  $Sn-SnO_x-Sn$  junctions as phonon generators and detectors, respectively, the available phonon spectrum extends from 280 to 3000 GHz ( $\sim 9.3$ – $100\text{ cm}^{-1}$  or  $\sim 1.2$ – $12.4\text{ meV}$ ), and spectral resolutions of 2 GHz ( $\sim 0.07\text{ cm}^{-1}$  or  $\sim 8\text{ }\mu\text{eV}$ ) can be achieved. The typical sample thickness is 1–2 mm. The  $Al$  critical temperature of 1.2 K determines the operating temperature ( $\sim 1\text{ K}$  and below) of this phonon spectrometer (the critical temperature of  $Sn$  is 3.2 K). This type of high-resolution acoustic phonon spectroscopy has been developed and used between 1976 and 2000 at the University of Stuttgart to study low energy electronic and vibrational excitations, mainly in silicon and germanium ([26], and references therein).

## 4.2 Radiation Sources and Spectrometers

### 4.2.1 Tunable Sources

Tunable sources are essentially tunable lasers, and several kinds of devices of this type are known. Among them are the dye laser, the sapphire:Ti laser, the laser diode and the free electron laser (FEL). The dye laser consists of a fixed frequency laser (UV or visible) pumping a dye solution cell in an optical cavity. The dye solution can emit laser radiation at frequencies within the fluorescence curve of the solution. The emitted laser frequency is tuned through the fluorescence curve by inserting an adjustable dispersing element (a grating which is part of the optical cavity, a prism, and/or a Fabry–Perot etalon). The dye lasers operate in the visible and near IR region of the spectrum. The laser diodes are made from direct-gap compound semiconductors, and those whose output extends the farthest in the IR are the  $Pb_{1-x}Sn_xTe$  diodes. Most of these diodes are operated near LHeT, and their peak emission corresponds to the band gap of the alloy. They can be tuned by varying the temperature of the diode in a controlled manner or, for a more restricted range, by varying the injection current intensity. Resolutions  $\sim 0.001\text{ cm}^{-1}$  ( $0.12\text{ }\mu\text{eV}$ ) near  $1000\text{ cm}^{-1}$  ( $124\text{ meV}$ ) have been reported with a temperature-tuned  $Pb_{0.86}Sn_{0.14}Te$  laser diode and used for the study of vibrational modes of  $ReO_4^-$  molecules in KI crystals at LHeT [5]. Another option is to use magnetic field tuning by changing the Landau level separation of the semiconductor (the electron effective

masses of these lead salts are relatively small). FEL radiation is the coherent synchrotron radiation of a relativistic electron beam crossing the gaps of a series of magnets arranged to produce zones of alternating magnetic fields. The magnetic fields of this array of magnets, called an undulator (or a wiggler), accelerate the electrons sinusoidally and the coherent radiation emitted depends on the electron energy. As an example, the CLIO FEL in Orsay, France, can be tuned between 10.3 and 413 meV ( $120 - 3\mu\text{m}$ ) with a minimum relative spectral width between 0.2 and 1%. These tunable sources have mainly been used for very-high resolution molecular spectroscopy and also for experiments with semiconductors, like the FEL at Rijnhuizen, in the Netherlands (FELIX). Impressive results have recently been obtained on bound-exciton absorption in  $^{28}\text{Si}$  using a tunable Yb-doped fibre laser [50]. In the late Soviet Union, submillimetre microwave generators known as backward-wave tubes (BWT), which can deliver monochromatic radiation power of  $\sim 1\text{ mW}$ , have been used as sources in the very far IR and adapted to the absorption spectroscopy of impurities in semiconductors in the 0.25–2 mm (5–0.6 meV) spectral region [9].

#### 4.2.2 Broadband Sources

The alternative to tunable sources is the absorption spectrometer, composed schematically from a broadband incoherent source, a monochromator and a detector. Additional equipment is also needed, as additional sources for band gap excitation. Each part of the equipment is specific to the spectral range investigated.

With increasing energies, the most utilized broadband sources are (1) the continuous spectrum of the high-pressure xenon–mercury arc lamp with a quartz envelope, used in the far IR from  $\sim 1\text{ meV}$  to about  $20\text{ meV}$  ( $1.24\text{ mm} - 60\mu\text{m}$ ), (2) the quasi-black body emission of the Joule-heated SiC element (globar<sup>TM</sup>), operated in air or in vacuum at a temperature near  $1500\text{ K}$ , useful in the  $20 - 600\text{ meV}$  ( $\sim 60 - 2\mu\text{m}$ ) spectral range, and (3) a tungsten filament in a quartz envelope, operated near  $3000\text{ K}$  in an iodine atmosphere to reduce evaporation of the metal (the so-called quartz-halogen lamp), generally used in the  $0.5 - 3.4\text{ eV}$  ( $\sim 2.5\mu\text{m} - 360\text{ nm}$ ) range. The quartz-halogen lamp also produces a small amount of IR radiation below  $0.5\text{ eV}$  due to the heating of the quartz envelope by the tungsten filament. The most common UV source is the deuterium lamp. This latter source provides a continuous spectrum between  $3.35$  and  $7.5\text{ eV}$  ( $\sim 370 - 165\text{ nm}$ ). Above  $7.5\text{ eV}$ , emission lines predominate, but with a  $\text{MgF}_2$  UV-transmitting window, it can still be used up to  $\sim 10.8\text{ eV}$  ( $115\text{ nm}$ ). Continuous far IR coherent and incoherent radiation are produced by synchrotron radiation, covering a broad energy range, from UV to IR, and it is superior to the high-pressure mercury arc at energies below  $20\text{ cm}^{-1}$ . In the 1960s, spectrometers for the  $2 - 15\mu\text{m}$  spectral region were equipped with a Nernst filament as a source. It consisted of a mixture of yttrium and zirconium oxides in a small rod, electrically heated to  $\sim 2000\text{ K}$ .

This filament was highly resistive for Joule heating from room temperature and required an initial proximity heating.

### 4.2.3 Spectrometers

Two main categories of monochromators can be distinguished: one is the dispersive monochromator where an energy spectrum dispersed in space is obtained with a reflection or a transmission diffraction grating (more rarely now with a prism). The other is the Fourier transform spectrometer (FTS). The principles of these two types of spectrometers are described below.

#### 4.2.3.1 Dispersive Monochromators

Dispersive monochromators use either a prism or a diffraction grating as a dispersive element. Before the grating monochromators were introduced at the end of the 1960s, prisms were used in a spectral range where the refractive index of the prism material presented energy dispersion with wavelength. The dispersion used was the one on the h-e side of the lattice absorption bands, which could be converted into spatial dispersion of a polychromatic source due to the prism geometry. Quartz was used as a prism material in the visible-near IR region and different alkali halide materials were used in the infrared, with a lower energy limit of about 25 meV or  $200\text{ cm}^{-1}$  ( $50\text{ }\mu\text{m}$ ) for caesium iodide. A dispersive grating monochromator comprises schematically an entrance slit on which the output of the broadband source is focused, a collimating mirror, usually spherical, a plane reflection diffraction grating (in the visible region, transmission diffraction gratings are also used), and an exit slit. The divergent beam from the entrance slit is made parallel by a spherical collimating mirror and redirected on the diffraction grating. The radiations with energies  $k\tilde{\nu}_d$  (where  $k$  is the diffraction order and  $\tilde{\nu}_d$  the wavenumber in  $\text{cm}^{-1}$ , for  $k = 1$  corresponding to a specific diffraction angle) are focused on the exit slit by a spherical mirror identical to the collimating mirror. An optical filter is inserted in the beam just after the exit slit to allow radiation corresponding to only a single value of  $k$ , in order to get a nearly monochromatic radiation. Sequential scanning of the spectrum at the exit slit is realized by rotating the grating about an axis parallel to the grooves of the grating, which changes the useful diffraction angle.<sup>2</sup> It can be shown that the theoretical resolving power  $\mathcal{R} = \tilde{\nu}_d/\delta\tilde{\nu}_d$  of a grating monochromator for infinitely small exit slits is the product of the width of the grating effectively illuminated by the number of lines (or grooves) of the grating per unit length. The lines of a reflection diffraction grating are cut to produce a maximum of diffraction efficiency for a given reflection angle (the blaze angle). For common uses, this angle is  $\sim 30^\circ$

<sup>2</sup> In spectrographs, the dispersing element is immobile and the spatially dispersed spectrum is recorded on a photographic plate or on a linear array charge-coupled device (CCD) detector.

and the number of lines per unit length can be chosen as desired, with the proviso that the grating step (the distance between two successive lines) must remain comparable with the diffracted wavelength in the first order for useful diffraction angles near the blaze angle. For instance, in the  $10\text{ }\mu\text{m}$  IR region ( $1000\text{ cm}^{-1}$  or  $0.124\text{ eV}$ ), for a grating with a width of  $100\text{ mm}$  ruled with  $100\text{ lines/mm}$ , the theoretical spectral band-width  $\delta\tilde{\nu}_d$  is  $0.1\text{ cm}^{-1}$  or  $12.4\text{ }\mu\text{eV}$ . This is valid only for a full illumination of the grating, in the absence of optical aberrations and infinitely narrow slits. Practically, with the above parameters, working energy resolution  $\sim 0.3\text{--}0.4\text{ cm}^{-1}$  ( $40\text{--}50\text{ }\mu\text{eV}$ ) were achieved. With a dispersive monochromator, a spectrum is made of  $N$  spectral elements (not necessarily equal) scanned sequentially at the exit slit of the monochromator. The values of these spectral elements, which can be considered as the spectral resolution, depend on  $\delta\tilde{\nu}_d$  and on the actual values of the mechanical widths of the entrance and exit slits. The intensity of the radiation diffracted by a reflection grating is higher for the electric vector of the radiation parallel to the grooves than for electric vector perpendicular to the grooves so that the output of a grating monochromator is always partially polarized.

The dimension of a monochromator is conditioned by the size of the grating. The main reason being, to reduce optical aberrations, the focal length of the collimating mirror must be at least 4–5 times the width of the grating. There exist a few different configurations of grating monochromators intended to reduce optical aberrations for a given optical and volume limitations. The best known are the Czerny-Turner, Ebert-Fastie and Littrow mountings. In the Littrow mounting, the maximum diffraction of the grating is obtained when the diffraction angle is equal to the angle of incidence  $i$ . Under this condition, the wavelength diffracted at angle  $i$  in the  $k^{\text{th}}$  order by a grating with  $N$  lines per unit length is  $\lambda_d = 2 \sin i / kN$  and the spectral domain is scanned by the rotation of the grating.

The idiosyncrasies of the Littrow mounting were found in the Model 99 infrared monochromator, a rather compact prism unit produced at the end of the 1950s by the Perkin-Elmer Corporation, supplemented by Model 99G, equipped with a grating, which has been used in many semiconductor absorption studies. In this mounting, the collimating mirror was an off-axis paraboloid mirror with a focal length of  $264\text{ mm}$  (an off-axis paraboloid mirror is corrected for optical aberrations for a given off-axis angle while a spherical mirror is not). For radiation detection by the lock-in technique and also to discriminate between the dispersed and background radiations, the beam from the source is time-modulated by a rotating chopper also providing an electric reference signal at  $13\text{ Hz}$  for a phase-locked amplification, adapted to the time constant of the radiation thermocouple. With the use of photoconductive detectors with smaller time constants, an electrically driven tuning fork with soldered blades, tuned at  $400\text{ Hz}$  and located close to the entrance slit has also been used.

In the above Littrow mounting, internal modulation of the dispersed beam and an appropriate optical mounting allowed a second dispersion of the beam

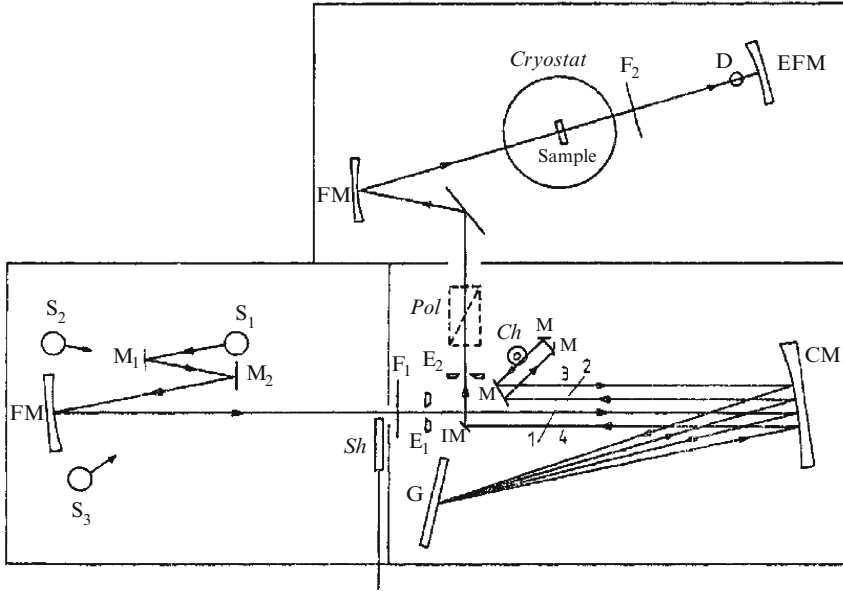


**Fig. 4.1.** Schematic of an experimental set-up for absorption measurements at low temperature incorporating a Perkin-Elmer Model 99G monochromator.  $S_1$ ,  $S_2$  and  $S_3$  are IR sources selectable with plane mirrors  $M_1$  and  $M_2$ . FM: focusing spherical mirrors.  $E_1$  and  $E_2$ : entrance and exit slits. CM: off-axis paraboloid collimating mirror. G: plane reflection grating. Beam 1 from  $S_1$  is converted by CM into a parallel beam dispersed by G. One wavelength is diffracted in a direction where it can be intercepted by first mirror M as beam 2 and focused on the internal chopper Ch. Modulated beam 2 is redirected toward G as beam 3 and re-dispersed a second time as beam 4. Beam 4 intercepted by IM is focused on  $E_2$  and re-focused on the sample by FM. The divergent monochromatic beam is finally focused on thermocouple D by ellipsoidal mirror EFM.  $F_1$ ,  $F_2$  and Pol are locations for transmission filters and a polarizer. Beam 1 can be blocked by shutter Sh (after [37]). With permission from the Institute of Physics

on the grating before reaching the exit slit (the so-called Walsh double pass system). With the same mechanical slit width, this allowed a reduction of the spectral band-width by a factor of  $\sim 2$  with respect to single pass. In the double-pass mode, the 99G monochromator allowed a practical resolution of  $\sim 20 \mu\text{eV}$  near  $0.124\text{eV}$  using  $64 \times 64 \text{ mm}$  diffraction gratings ruled with 100 lines/mm. A full experimental set-up for low-temperature absorption measurements of solid samples used in the 1960s is shown in Fig. 4.1.

The Czerny-Turner mounting and the Ebert-Fastie mounting, an elegant variant of the Czerny-Turner mounting, that allows the use of long slits without additional aberrations, have been used for the design of commercial and custom-made monochromators in a broad spectral range, from UV to the far IR, with grating as large as 300 mm, requiring focal lengths of the collimating

mirrors between 1 and 2 m. Many commercial grating spectrometers were designed to produce two separate modulated optical beams, which recombined on the detector. These double-beam spectrometers were used to directly measure the ratio of the absorption of a sample, inserted in one beam, with respect to that of a reference sample in the other beam. In compact monochromator designs, the plane grating was sometimes replaced by a spherical concave grating, which replaces both the collimating mirror and the grating. For more details on the dispersive monochromators, see [15].

Presently, grating monochromators are used every time a sample must be illuminated with quasi-monochromatic radiations that are tunable in a broad spectral range or for experiments in the visible–UV range. Another interest of dispersive monochromators is the possibility of wavelength modulation of the output of these monochromators in order to get the first derivative of the transmission spectrum. This has the advantage of increasing the sensitivity, and this technique is also used in laser spectroscopy.

#### 4.2.3.2 Fourier Transform Spectrometers

The heart of the FTS is a two-arm Michelson interferometer equipped with a light source and a detector. The optical beam from the source is divided into two beams by a semi-reflecting beam splitter, and these beams are reflected back to the beam splitter by two plane mirrors  $M_1$  and  $M_2$  (a compensator parallel to the beam splitter is inserted in one arm of the interferometer to ensure identical transmission). In the classical mounting, one of the mirrors  $M_1$  or  $M_2$  moves perpendicularly to its plane and the signal from the beam recombined on the beam splitter/compensator is recorded by the detector as a function of the path difference between the two mirrors. This signal constitutes an interferogram, and the energy spectrum of the source is obtained by calculating the Fourier transform in the time domain of the interferogram. In one alternative, the beam splitter/compensator unit and the two mirrors parallel to it can rotate about an axis perpendicular to the interferometer mounting while  $M_1$  and  $M_2$  are immobile, providing a path difference between the two optical beams [44]. The corollary is the pendulum interferometer, where mirrors  $M_1$  and  $M_2$ , mounted at  $90^\circ$ , are at the end of two linked identical mechanical arms mounted at  $90^\circ$ . These two arms (and mirrors  $M_1$  and  $M_2$ ) can move as a whole like a pendulum about a common point, providing again a path difference between the two optical beams. Small and large FTSs with this pendulum design are now commercially available.

A commercial high-resolution FTS is depicted in Fig. 4.2. The output of the broadband source is focused on a circular aperture (entrance iris). As in the dispersive set-up, the optical beam is made parallel by a collimating mirror, and it intercepts a beam splitter at a non-normal incidence (usually  $45^\circ$  or  $60^\circ$ ). One part of the beam is transmitted towards a fixed plane mirror while the other part towards a plane mirror, which can be translated continuously or in steps at a given distance (scan mirror). The beams reflected back by



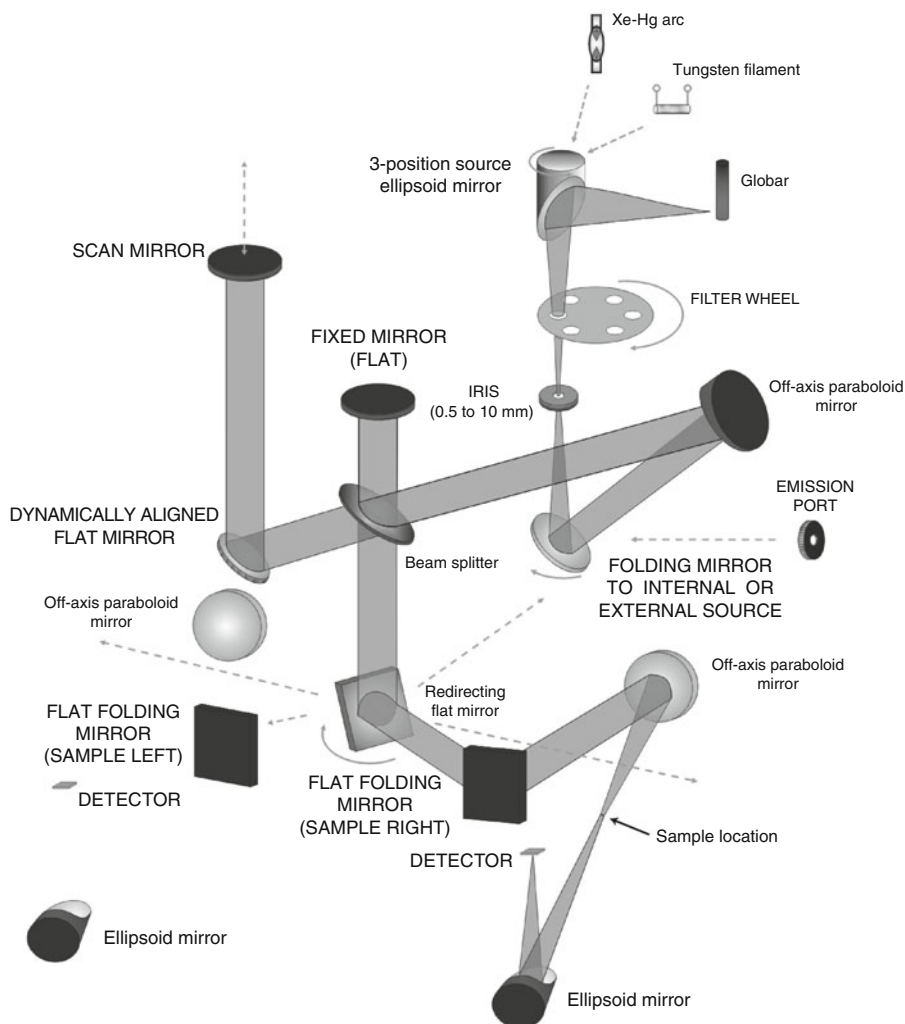


**Fig. 4.2.** Schematic of a commercial FTS (BOMEM DA8, discontinued). The two ellipsoid mirrors and the two paraboloid mirrors are identical so that the mounting is symmetric (the image of the entrance iris is at the sample location). The scan mirror tube is vertical. The two symmetrical sample locations allow the permanent mounting of two different detectors and the redirecting mirror to transfer the modulated beam to external experimental set-ups

these two mirrors recombine on the beam splitter and form an unique beam carrying phase information of both beams. This resultant beam is focused by an appropriate optical element on the virtual exit iris aperture and directed toward a detector. Some FTS are provided with adjustable iris apertures which can accommodate small samples with an intercepting area less than  $1 \text{ mm}^2$ .

When a monochromatic source (a laser line, for instance) with wavenumber  $\tilde{\nu}_0$ , taken as a Dirac function, is used, the interferogram is a sine function with period  $1/\tilde{\nu}_0$  and the Fourier transform of this sine wave in the time domain is close to the initial monochromatic line. In the practical cases, the interferogram of a broadband source is recorded from a path difference prior to the optical contact between the two plane mirrors (zero path difference or zpd) to a maximum value optical path difference  $\delta_{\max}$ , equal to two times the maximum mechanical path difference  $x_{\max}$ , defined by experimental conditions. In an ideal case, this interferogram should present a peak at the zpd, where all the optical frequencies are in phase. Strong oscillations near zpd, and farther away, result in an average signal close to  $I_0/2$ , but still containing information. Practically, the small remaining dispersion of the beam splitter and the response time of the detector and of the associated electronics produce an asymmetry of the recorded interferogram, visible near the zpd. This asymmetry has to be corrected before the symmetrization of the interferogram from  $-\delta_{\max}$  to  $+\delta_{\max}$ . This is the role of the phase correction process, where the correction is calculated from a small double-sided interferogram from  $-\varepsilon$  to  $+\varepsilon$ , with  $\varepsilon$  typically  $\sim 20\ \mu\text{m}$ , which can be taken from the large singly-sided interferogram, or recorded separately. It can be shown that the Fourier transform of the symmetrized interferogram is the power spectrum of the source.

A notable difference exists between the Michelson interferometer and the dispersive monochromator. While recording a spectrum made from  $N$  spectral elements with the first, each spectral element is measured during the whole recording time of the interferogram, but with the second, each spectral element is recorded only during  $1/N$  times the whole recording time. Therefore, for the same recording time of a spectrum of  $N$  spectral elements, the gain in the signal over noise (S/N) ratio for the interferometer is  $\sqrt{N}$  (Felgett or multiplex advantage). A second difference lies in the use of a circular iris, allowing a larger radiation input than a slit (Jacquinot advantage). In FTSs, the path difference between the two mirrors is indexed from zero by the fringes of a single-mode laser (stabilized He–Ne for high-resolution FTSs), whose emission wavelength is accurately known. This provides an accurate internal wavenumber calibration of the Fourier transform spectrum, which does not require an external calibration with absorption lines of reference molecular gases, as for the non-commercial grating monochromators (Connes advantage). The FTSs require a better mechanical stability than the dispersive systems because a very good parallelism between the two plane mirrors is required. Hence, the plane mirrors of the interferometer are sometimes replaced by corner cube reflectors, as in the high-resolution Bruker IFS125, or by cat's eyes, which are insensitive to small differences of optical parallelism between the two mirrors, or are provided with a dynamic alignment system which controls and maintains the parallelism between the two mirrors (Fig. 4.2). For interferometers with a mirror moving in steps (when very large values of  $\delta_{\max}$  are required), the signal is recorded when the mirror is at rest and this requires a time modulation of the optical beam as for dispersive spectrometers. In most com-

mercial FTSs, the mirror moves continuously at a constant (adjustable) velocity  $v_m$ . In this case, using again the example of a monochromatic source, a radiation with wavenumber  $\tilde{\nu}_0$  is modulated in time with frequency  $f_0 = v_m \tilde{\nu}_0$ . For a broadband spectrum containing optical frequencies between  $\tilde{\nu}_{\min}$  and  $\tilde{\nu}_{\max}$ , the input is time-modulated at frequencies between  $f_{\min}$  and  $f_{\max}$ , and this frequency domain must be compatible with the response time of the detector. The ultimate spectral bandwidth or spectral resolution of a FTS depends on the maximum path difference that can be achieved by the machine and on the apodization function used. The fact that the interferogram is practically recorded or symmetrized between  $-\delta_{\max}$  and  $+\delta_{\max}$  corresponds to the multiplication of an infinite interferogram by a boxcar function, equal to unity between  $-\delta_{\max}$  and  $+\delta_{\max}$ , and to zero outside this interval. Therefore, the calculated spectrum is the product of the original spectrum and a function  $\sin(x)/x$  whose FWHM is  $\sim 1.207/2\delta_{\max}$ , and this value constitutes the maximum resolution achievable for a given spectrum. For instance, for the BOMEM DA8.2 FTS, the maximum mechanical path difference is 25 cm and its ultimate resolution is  $0.012 \text{ cm}^{-1}$  or  $1.5 \mu\text{eV}$ . The spectral resolution of the Bruker IFS 125 HR is slightly better than  $0.001 \text{ cm}^{-1}$  or  $125 \text{ neV}$ . For a given value of  $\delta_{\max}$ , the spectral lines with natural FWHM smaller than that of the  $\sin(x)/x$  function will reproduce in their profile the side lobes of this function. To attenuate or suppress these oscillations, the raw interferogram can be multiplied by various apodization functions, which produce actual FWHM or apodized resolutions larger than  $1.207/2\delta_{\max}$ , the unapodized resolution. For the frequently used apodization functions, the practical resolution is reduced to  $\sim 1/\delta_{\max}$ . This loss of resolution compared to that obtained with the boxcar apodization has the advantage of improving the S/N ratio of the computed spectrum.

The beam splitter is made from a transparent material with a good optical homogeneity. In the near and medium IR regions, quartz,  $\text{CaF}_2$  and KBr are used, and in the far IR, mylar films with different thicknesses. An alternative to the classical Michelson interferometer at very low energy (typically below  $40 \text{ cm}^{-1}$  or  $5 \text{ meV}$ ) is the lamellar-grating interferometer, which obviates the need for a beam splitter. The wave-front incident from the radiation source is divided into two parts by reflection on a lamellar mirror consisting of two sets of parallel interleaved facets. One set is fixed while the other can move perpendicular to the plane of the fixed facets, producing an adjustable path difference between the two reflected beams (see for instance [32]). The lowest energy measured with such a FTS is  $1.5 \text{ cm}^{-1}$  or  $0.2 \text{ meV}$ , while the highest energy rarely exceeds  $150 \text{ cm}^{-1}$  or  $18 \text{ meV}$ . In the 1970s, one lamellar grating interferometer was sold by Beckman RIIC, but due to the small market for experiments in this spectral region, no instrument of this type is commercially available now.

When discussing the methods of measurement of the refractive index, we had mentioned in Chap. 3 the recording of periodic interference fringes in the transmission spectra of dielectric plane parallel samples with a spectral bandwidth smaller than the fringe spacing. This situation is often encountered

involuntarily in high-resolution spectroscopy of solids or when measuring the transmission of a thin sample. It is found to interfere with the measurement of the parameters of weak absorption lines. With thick samples, wedging can circumvent this drawback, but for very-high resolution spectra in the far IR, the wedging becomes excessive. Moreover, this is not possible when measuring thin wafers. As these fringes originate from constructive interferences between successive beams reflecting at the sample interface, these fringes disappear when the radiation is incident on the sample at the Brewster angle  $i_B$  defined by  $\tan i_B = n$ , where  $n$  is the refractive index. In this geometry, the output beam is polarized in the plane of incidence and there is no reflection loss at the interface [27, 39]. In experiments performed with a FTS, an alternative consists in replacing the points of the peaked zone corresponding to the fringes in the FT spectrum by zero in the primary interferogram. This is not a panacea, however, as, if the channelled spectrum is efficiently removed by this procedure, the wings of sharp absorption lines can show oscillations. A more general, but more time-consuming method, consists in subtracting from the spectral regions of interest a suitable sine function with adequate dispersion and attenuation.

In absorption spectroscopy, and more specially at high resolution, one must take into account the fact that carbon dioxide and water vapour found in atmosphere give rise to vibrational absorption lines in the infrared which can turn effective transmittance to zero in some spectral regions. Before the advent of spectrometers operating in vacuum, this parasitic absorption was reduced by flushing the optical path of the IR spectrometers and monochromators with dry nitrogen or desiccated air. Presently, all the FTSs are operated under primary vacuum, but in some critical cases, it can still be necessary to use sorption pumps cooled with liquid nitrogen to reduce the residual absorption of atmospheric gases. Evidently, the vacuum-operated machines can also be alternatively operated flushed with dry nitrogen.

With a high-resolution FTS, it is in principle possible to get an estimation of the true line width by decreasing the spectral resolution  $\delta\tilde{\nu}_s$  until the observed FWHM stays constant. In the experiments performed with tunable lasers, this condition is generally met. There are also experimental situations where the profile of an absorption or PL spectral feature containing several unresolved individual lines cannot be further resolved by increasing the resolution because of the combination of the intrinsic FWHMs of the components and of their separations. It is possible to artificially decrease the FWHMs of the components in order to determine accurately their positions by a method known as self-deconvolution [19].

The uncertainty (or accuracy) on the measured position of an absorption line depends on the noise in the spectrum, but for negligible noise, as a rule of thumb, it can be considered to be ultimately limited to one tenth of the FWHM.

### 4.3 Filtering and Polarization

Optical filters are necessary with grating monochromators to retain only one diffraction order, usually the first, and with FTSs to limit the spectral domain and the radiant power incident on the detector. This can be obtained with low-frequency pass absorption filters with a high-frequency cut-off above which the filter is opaque. From their optical properties, semiconductors are adequate substrates as they already provide a high-frequency cut-off corresponding to their band gap energy, but the reflection losses due to the high refractive indices have to be compensated by anti-reflection coatings. Silicon, germanium, indium arsenide or indium antimonide substrates have been used and the list is not limitative. The low-frequency cut-off of compound crystals due to the onset of the one-phonon absorption can be used when simple high-frequency pass absorption filters are required (note that these compounds become transparent again at frequencies below the one-phonon absorption region). It is also possible to grow on transparent substrates interference filters with different spectral bandwidths and peak transmissions energies. Before the advent of FTS machines, filtering for far and very far IR experiments was a very serious problem. A decrease of the high-frequency radiation contribution was obtained by using mirror substrates polished with 10 or 20  $\mu\text{m}$  diameter alumina powder grit. The scattering properties of these mirrors for high-frequency radiation made them acceptable reflection filters for the far IR. Similarly, materials transparent in the far IR, but translucent or opaque in the near IR like polyethylene or black polyethylene were and are still used as optical components and filters in the far IR. The selective near-metallic reflection of the alkali halides and alkaline earth halides, due to their strong absorption near the TO absorption region (see Sect. 3.2.1), has also been used by replacing in the far IR set-ups the metallic mirrors by “*reststrahlen*” plate made from these compounds, adapted to the spectral range being investigated, but this is very rarely used presently.

For some absorption experiments on dichroic or anisotropic samples, it is desirable to use radiation where the orientation of the electric vector with respect to crystal axes is known (linearly polarized radiation). This can be obtained with dispersive monochromators as well as with FTS by inserting a transmission polarizer in the optical path. The most popular ones are the wire grid polarizers made from a metallic wire grid (Au or Al) evaporated on a transparent substrate (ZnSe, AgBr, KRS5 and polyethylene have been used). For wire spacing smaller than the wavelength of the radiations of interest, this array acts as a metallic mirror for electric vector of the radiation parallel to the wires of the grid, but the electric vector component perpendicular to the wires is transmitted with an overall efficiency depending on the metallized area and on the refractive index of the substrate. These polarizers are mounted on a rotating holder so that the orientation of the transmitted electric vector can easily be selected. Before the advent of wire grid polarizers, linear polarization of IR radiation was obtained by reflection of a natural parallel beam on a

silicon or germanium slab at Brewster angle. For germanium, this angle is  $\sim 75^\circ$ . The component of the electric vector  $\mathbf{E}$  perpendicular to the plane of incidence is totally reflected and the transmitted beam is polarized in the plane of incidence. For the far IR, several plates of polyethylene were used.

## 4.4 Radiation Detection

A radiation detector is a device in which the photons absorbed are transformed ultimately into electrical energy. The efficiency with which the photons are transformed into electrical power is described by the responsivity of the detector, and it is expressed as the voltage generated by one watt of incident radiant power. The average time required for the incident power to be transformed and dissipated by the detector characterizes the response time, or time constant of the detector. To be specific, the electrical response of a detector to a radiation beam time-modulated at frequency  $f$  is similar to the frequency response  $R(f)$  of a low-pass electrical filter with time constant  $\tau$ :

$$R(f) = \frac{R_0}{(1 + 4\pi^2 f^2 \tau^2)^{1/2}}$$

where  $R_0$  is the response at zero frequency. For a detector with time constant  $\tau_d$ , the modulation frequency or its average value can be considered as  $4\pi^2 f^2 \tau^2 = 1$ . Fluctuations in the detector generate an electrical signal known as noise, and as will be seen later, noise in radiation detectors can have different origins. The ultimate performance of a detector is determined by a quantity directly related to noise: the noise equivalent power (NEP), discussed also later in this chapter.

Radiation detectors can be separated into two categories. The first one comprises devices called thermal detectors that detect a radiation-induced variation of the temperature of the sensor; the second one includes all the semiconductor-based devices where a photon is used to make an energy-dependent electronic transition producing a free electron-hole pair or a free carrier of a given type (photoconductivity), and also the photo-emissive detectors. In thermal detectors, the photon energy is transformed into thermal energy and these detectors display, therefore, a flat spectral response independent of the photon energy. In the detectors belonging to the second category, the photon energy must be larger than a threshold value below which the absorption coefficient for the relevant transition is zero. These latter detectors are called the photoconductive detectors. Note that the detectors discussed here are those used with laboratory spectrometers. In space research, very sophisticated thermal and photoconductive detectors are used, but they are not discussed here.

### 4.4.1 Thermal Detection

Among the thermal detectors, the thermocouple has been extensively used in the 1960s with broadband commercial spectrometers and IR monochromators,

but it is no longer or rarely used now in infrared spectroscopy. In this device, one of the thermocouple junctions is heated by the radiation while the other is kept at a constant temperature, producing a thermoelectric voltage due to the Seebeck effect. The actual devices include several pairs of junctions and a blackened radiation absorber. The responsivity of the best of these radiation thermocouples was in the  $25 \text{ VW}^{-1}$  range, with a time constant  $\sim 30 \text{ ms}$ , allowing a time modulation frequency of  $\sim 10 \text{ Hz}$ . The infrared spectral response of these small thermal detectors, operated under vacuum, was limited by the optical window (above  $\sim 25 \text{ meV}$  or below  $\sim 50 \mu\text{m}$  when fitted with a CsI window), but mainly limited by the input signal with a diamond window.

The Golay cell uses the distortion of a reflecting Sb-coated collodion membrane, closing one of the ends of a so-called pneumatic chamber. This distortion is caused by the thermal expansion of a gas heated by the radiation incident in the cell, and produces the deflection of a beam of visible light, which is detected by a photocell. The Golay cell was used, fitted with a diamond window, with the first far IR FTS and its responsivity and response time were comparable to those of the radiation thermocouple. For more details on these detectors, see [15].

A thermal detector still in use in commercial spectrometers is the pyroelectric detector. The materials of these detectors are ferroelectric compounds used at temperatures not far below their Curie point. In this temperature range, they display a pronounced temperature dependence of their spontaneous polarization, and the induced change of their dielectric constant produces a capacitance change in an electric circuit. The frequently used dielectric (ferroelectric) materials in these RT-operated detectors are triglycine sulphate (TGS), deuterated TGS (DTGS), and L- $\alpha$ -alanine-doped DTGS (DLATGS). The ones with the broadest spectral band in the near IR are fitted with KRS5 windows, which makes them useful in the  $\sim 30\text{--}620 \text{ meV}$  range ( $\sim 40\text{--}2 \mu\text{m}$ ). Those in the far IR are fitted with polyethylene windows and can be used for energies in the  $50\text{--}700 \text{ cm}^{-1}$  ( $200\text{--}14 \mu\text{m}$ ). These detectors have larger responsivities ( $\sim 5 \text{ kWV}^{-1}$ ) and noise than the radiation thermocouple, and a smaller time constant ( $\sim 3 \text{ ms}$ ), allowing slightly higher modulation frequency of the radiation beam.

The simplest thermal detector, the bolometer was invented by Langley [25]. It is based on the change in the electrical resistance of an appropriate thermometer when heated by the radiation through a radiation absorber. The first thermometers were blackened platinum strip resistances held at room temperature; they were used as radiometers rather than as detectors coupled with spectrometers. The extended use of physical measurements near LHeT led to investigate new materials for the conception of low-temperature radiation bolometers, with the objective of a low heat capacity and a large temperature dependence of the electrical resistance, possibly coupled with a large absorption coefficient. One example is the superconducting bolometer described in [31], a tin film deposited on a mica substrate and maintained at a temperature within the superconducting transition domain of tin ( $\sim 3.74 \text{ K}$ ),

where its equilibrium resistance is about half the value in the normal state. Such detectors require an accurate temperature control ( $\sim 10^{-4}$  K), and this is one of the reasons why the commercial low-temperature bolometers used today with IR spectrometers are of the semiconductor type. They are based on the absorption of radiation by the free carriers in heavily-doped non-metallic germanium or silicon crystalline samples and the temperature rises from the coupling of the free-carriers with the crystal lattice. It must be pointed out that this electron–lattice coupling is not always operative: in direct band gap semiconductors like InSb, the coupling of small effective-mass electrons with the lattice in n-type crystals can be weak when the accelerating electric field is raised (Ohm’s law is no longer valid). Such electrons are called the hot electrons, and they can be characterized by a hot-electron temperature higher than the lattice temperature. They can absorb electromagnetic radiation to increase their temperature and as the electron mobility goes as  $T^{3/2}$ , a net increase of the electrical conductivity is obtained. This effect has been used by Kinch and Rollins [22] to develop a low-temperature free electron bolometer (FEB), characterized by a time constant much smaller ( $\sim 10^{-7}$  s) than that of the classical bolometers, but the FEB has been used only for very specific applications.

Depending on the doping level, the electrical compensation and the operating temperature, the temperature dependence of the resistance of the silicon and germanium bolometers may be larger than  $T^5$  in the best cases. A prototype of these bolometers has been described by Low [30]. The simplest bolometer is a semiconductor element supported in vacuum by electrical wires providing also the thermal link to the cooled substrate (the heat sink). The sensitivity and time constant of the detector are improved by using a sensing element with the smallest possible size, and this is usually detrimental to an efficient absorption of radiation. The situation can be improved by placing the sensing element in an integrating gold-coated cavity with a small aperture to admit external radiation. Another possibility is to use a distinct heat collector glued to the sensing element. This absorber is made from a metallic film (Bi or Nichrome is often used) deposited on a dielectric substrate with low heat capacity and high thermal conductivity (sapphire or diamond). Such bolometers are known as composite bolometers. The time constant of a bolometer is determined by the heat capacity of the sensing element, but it can be reduced (at the expense of sensitivity) by increasing the thermal conductance with the heat sink. Inversely, a high sensitivity requires a lower thermal conductance to the heat sink through thin lead wires, resulting in a time constant in the 10 ms range. Accidental mechanical vibration of these wires can be a source of microphonics for bolometers, which are more sensitive to this problem than photoconductive detectors. Practically, the low-temperature bolometers used with IR spectrometers down to about 10 meV (up to 120–130  $\mu$ m) are operated at a nominal temperature of 4.2 K. In the very far IR, down to and below 1 meV, they are operated at the lowest temperature that can be obtained by pumping liquid He ( $\sim 1.3$ – $1.6$  K depending on the performance of



the pumping system). The performances of the bolometers used with IR spectrometers depend on the surrounding thermal radiation. This is discussed in the section devoted to noise in detectors. For a review on IR bolometers, see [38]. Slightly different configurations have also been used where, for instance, the temperature rise of a sample due to optical absorption is detected by a bolometer located close to the sample [48]. One of the advantages of the Si and Ge bolometers is that they are relatively insensitive to the effects of magnetic fields. They can, therefore, be used very close to the superconducting solenoid without much change in their response.

The measurement of very small absorption coefficients (down to  $\sim 10^{-5} \text{ cm}^{-1}$ ) of optical materials has been carried out by laser calorimetry. In this method, the temperature difference between a sample illuminated with a laser beam and a reference sample is measured and converted into an absorption coefficient at the laser energy by calibration [13]. Photoacoustic spectroscopy, where the thermal elastic waves generated in a gas-filled cell by the radiation absorbed by the sample are detected by a microphone, has also been performed at LHeT [34]. Photoacoustic detection using a laser source allows the detection of very small absorption coefficients [14]. Photoacoustic spectroscopy is also used at smaller absorption sensitivity with commercial FTSs for the study of powdered or opaque samples. Calorimetric absorption spectroscopy (CAS) has also been used at LHeT and at mK temperatures in measurement using a tunable monochromatic source. In this method, the temperature rise of the sample due to the non-radiative relaxation of the excited state after photon absorption by a specific transition is measured by a thermometer in good thermal contact with the sample [34, 36].

## 4.4.2 Photoconductive Detection

### 4.4.2.1 Intrinsic Photoconductors

The main advantage of photoconductors over thermal detectors is their higher sensitivity and a much smaller time constant. The materials used to make photoconductive detectors are semiconductors chosen for their band-gap energies or for the ionization energies of specific impurities that fit a given spectral range. Photons with energies above  $E_g$  are absorbed by semiconductors (see Sect. 3.3.1). This intrinsic absorption produces photoconductivity when ohmic contacts are made to such a crystal, and an electric field applied to the crystal. An alternative to these simple photoconductors is a p-n junction. Subsequently, even without a polarizing field, the electron of a free electron-hole pair photo-created at the junction is drifted by the electric field to the n-region and the hole to the p-region, thus contributing to the photocurrent. The detectors based on this latter principle are called photovoltaic detectors and most of the modern intrinsic semiconductor photon detectors are of this type. The sensitivity of intrinsic photoconductors is increased when cooled at liquid nitrogen temperature (77 K). They are characterized by time constants of the order of

1  $\mu\text{s}$  or less, and the order of magnitude of the intrinsic absorption coefficients allows for small-sized detectors. The lowest-energy detection limit of detectors made from HgTe–CdTe alloys corresponds to a band gap of  $\sim 55$  meV at LNT, and this seems to be the low-energy limit of use of commercially-available intrinsic photoconductors. Some direct band gap InSb detectors or those made with the HgTe–CdTe alloys, known generically as mercury cadmium telluride (MCT) detectors, when optimized for high-resolution measurements, are very sensitive (see [49]). Consequently, when the radiation density incident on these detectors is too large, they show saturation effects (the signal is sublinear with the radiation power input). This can be corrected by reducing the spectral band width of the input signal by optical filtering or by using, when possible, a smaller iris aperture for a FTS.

#### 4.4.2.2 Extrinsic Photoconductors

In the 1960s, when the intrinsic detector technology had not reached today's maturity, the extrinsic Ge:Ga photoconductor operating at 77 K was very popular for high sensitivity detection down to about 0.16 eV ( $\sim 8 \mu\text{m}$ ), and Ge:Hg cooled below  $\sim 30$  K with liquid  $\text{H}_2$  was used for detection down to  $\sim 92$  meV ( $\sim 13 \mu\text{m}$ ). Currently, different liquid  $\text{N}_2$ -cooled intrinsic MCT detectors are available for photon energies above  $\sim 55$  meV ( $\sim 23 \mu\text{m}$ ), but when radiation detection is required below this energy together with a short time constant, extrinsic photoconductors are continued to be used. These detectors are based on the photoionization of an impurity centre of relatively low energy. The shallow acceptor centres in germanium (mainly Ga) are well suited for this purpose, but are limited to energies above  $\sim 10$  meV (below  $\sim 120 \mu\text{m}$ ). As a consequence, these detectors must be operated at LHeT to prevent thermalization of the ground state, from which photoionization occurs. Their sizes are larger than those of the intrinsic detectors because the extrinsic absorption coefficient is smaller than the intrinsic one. An attempt to increase the optical path within the detector volume is the rooftop detector geometry allowing internal reflections. In germanium, a decrease of the ionization energies of acceptors has been observed under a uniaxial stress [20], and this property has been applied to the Ge:Ga photoconductor, whose normal low frequency detection limit is  $\sim 90 \text{ cm}^{-1}$  (11 meV), down to about  $50 \text{ cm}^{-1}$  ( $\sim 6$  meV) with good detecting properties observed by applying a stress of 660 MPa along a  $\langle 100 \rangle$  axis [21]. No commercially available extrinsic photoconductor seem to exist for lower energies. If a short time constant is necessary, an InSb FEB can be used, or else, a semiconductor bolometer must be used.

There are cases where, in absorption measurements, the sample itself can be used as an extrinsic photoconductor, once provided with electrical contacts. This is illustrated in the specific case of germanium co-doped with acceptor couples (Ga, Zn), (Zn, Cu) and (Cu, Hg). The ionization energy of Ga is 11.3 meV, and those of the double acceptors, when neutral, are 32.9 meV (Zn), 43.2 meV (Cu) and 91.6 meV (Hg). The continuous photoconductivity

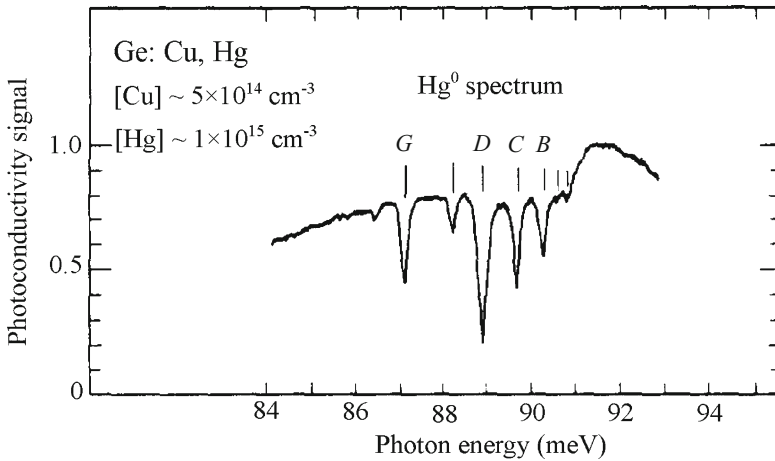


**Fig. 4.3.** Absorption lines of the neutral Hg acceptor detected by the photoconductivity signal of Cu<sup>0</sup> in germanium at LHeT. The photoconductivity increase near 91–92 meV is due to the Hg<sup>0</sup> contribution to the photoconductivity after [33]. Copyright 1965, with permission from Elsevier

of the acceptor with the lowest energy of the pair can then be used to detect the discrete absorption spectrum of the one with the highest energy and Fig. 4.3 shows the line spectrum of Hg<sup>0</sup> (see Table 7.15) detected in the photoconductive signal of Cu<sup>0</sup> [33].

Another possibility which does not require co-doping can be used with crystals containing impurities whose excited states are separated from the continuum by energies  $E_i$  of the order of  $k_B T$  at the temperature of the measurement. Normally, an electron or a hole in such an excited state de-excites directly into the ground state by phonon creation. But in this situation, low-energy acoustic phonons present in the crystal can annihilate by promoting the photoexcited electrons or holes into the continuum. This results in photoconductivity peaks for photons absorbed at energies of discrete transitions. This effect, presently termed as PTIS, was discovered by Lifshits and Nad [28], who called it photoelectric spectroscopy. At the lowest temperatures, PTIS detects the excited levels close to the continuum, but increasing temperature also allows detection at deeper levels. In germanium, a temperature of  $\sim 8 \text{ K}$  allows the observation of the entire shallow impurity spectrum, and in silicon a temperature of  $\sim 16 \text{ K}$  is required. This rises to values between 70 and 140 K for boron in diamond. PTIS measurements require, in principle, electrical contacts on the sample. These contacts have to be ohmic at low temperature, and they must not contribute to additional noise in the measuring circuit or to the introduction of additional shallow impurities in the sample. In silicon and germanium, the best contacts are obtained by ion implantation of P in n-type material and of B in p-type material. The problem of reproducible ohmic contacts on high-resistivity materials can be avoided by

a contactless PTIS method where the sample is inserted between the plates of one of the capacitors of a high-frequency capacitance bridge. When properly analyzed, the changes in the complex admittance of the capacitor containing the sample under photon absorption can yield a spectrum comparable to the one obtained traditionally [1]. The PTI spectra of Fig. 4.4 were obtained by this contactless method.

Illuminating the sample with a band gap radiation allows detection of lines of neutralized minority impurities as negative peaks.

PTIS is not quantitative as the relative intensities of the photoconductivity peaks depend on temperature, but it is very sensitive as can be inferred from Fig. 4.4, since, in the best cases, the peaks emerge from a zero background, and impurity concentrations as low as  $10^7 \text{ cm}^{-3}$  can be detected and identified by this technique.

The samples used in PTIS measurements are, however, characterized by an effective optical thickness which can be much larger than their physical thickness because of internal reflections or scattering, or of their lateral dimensions. For relatively “large” impurity concentrations ( $\sim 10^{12} \text{ cm}^{-3}$ ), the internal transmission of a line can tend to zero in such samples, producing saturation effects which are not as obvious as in classical absorption spectroscopy. The result is an apparent FWHM larger than the FWHM measured at the same resolution by classical optical absorption [1, 2].

#### 4.4.3 Limits to Detectors Sensitivity

The spontaneous fluctuations at the output of any detector may have several origins, and they produce what is called noise. For a general presentation, see [41]. The statistical nature of radiation emission and absorption is the origin of radiation noise, a fundamental process sometimes called thermal noise in thermal detectors and photon noise in photoconducting detectors (note that the Johnson noise arising from thermal fluctuations in voltage occurring at the resistor output is sometimes also called a thermal noise). We introduce here the term background radiation noise (BRN). For a thermal detector, the BRN can be derived from the temperature fluctuations of a black body with a heat capacity  $C$  in an environment at temperature  $T$ . The average value of the radiation exchange power  $W_{\text{therm}}$  between a thermal detector and its surroundings, at temperature  $T$  in an electrical frequency range  $\Delta f$  can be expressed as:

$$\langle W_{\text{therm}}^2 \rangle^{1/2} = 2T(Gk_B\Delta f)^{1/2} \quad (4.2)$$

where  $G$  is the thermal conductance of the detector to its surroundings. When considering only coupling by radiation, for an absorbing medium of area  $A$ ,  $G$  derived from Stefan’s radiation law is  $4A\epsilon\sigma T^3$  where  $\sigma = \pi^2 k_B^4 / 15 \hbar^3 c^2$  is Stefan’s constant ( $5.6704 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$ ) and  $\epsilon$  the emissivity of the medium. Hence, for a field of view of  $2\pi$  steradians:

$$\langle W_{\text{BRN}}^2 \rangle^{1/2} = 4(Ak_B\sigma T^5 \Delta f)^{1/2} \quad (4.3)$$

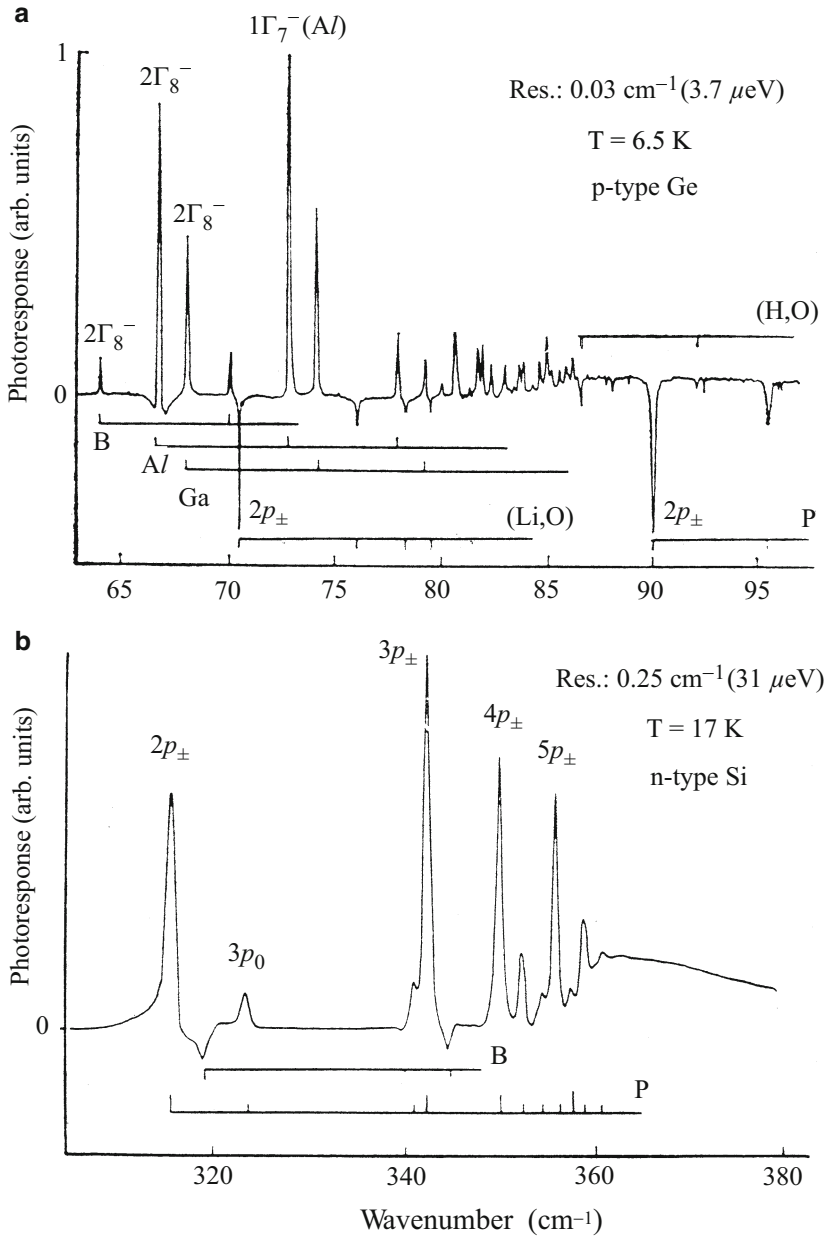


**Fig. 4.4.** PTI spectra obtained by a contactless method: (a) p-type germanium between  $\sim 7.9$  and  $12.0$  meV ( $N_A$  and  $N_D$  are  $6.0$  and  $0.9 \times 10^{10} \text{ cm}^{-3}$ ). Lines  $2\Gamma_8^-$  and  $1\Gamma_7^-$  correspond to acceptor lines  $D$  and  $C$  of Fig. 7.10b n-type silicon between  $\sim 38$  and  $47$  meV, with  $N_D$  and  $N_A \sim 1$  and  $< 1 \times 10^{12} \text{ cm}^{-3}$ , respectively (compare with Fig. 6.1). The negative peaks are due to compensating boron after [1]. Reproduced, with permission from Trans Tech Publications

It must be noted that this radiative power, called the BRN equivalent power, noted here as  $\text{NEP}_{\text{BR}}$ , is frequency-independent and varies with  $T^{5/2}$ . Assuming an ideal absorbing medium with  $\epsilon = 1$ , for  $A = 1 \text{ cm}^2$ ,  $T = 300 \text{ K}$  and  $\Delta f = 1 \text{ Hz}$ ,  $\text{NEP}_{\text{BR}} (\text{cm}, 300 \text{ K}, 1 \text{ Hz})$  is  $6 \times 10^{-11} \text{ W}$ .

When a thermal detector is at a temperature  $T_{\text{det}}$  different from that of the background,  $T_{\text{back}}$ , the total mean square of the radiation power is given by:

$$\langle W_{\text{BRN}}^2 \rangle = 8Ak_{\text{B}}\sigma(T_{\text{det}}^5 + T_{\text{back}}^5)\Delta f \quad (4.4)$$

When a detector is cooled to 4.2 K with a background temperature of 300 K, it produces a reduction in the room-temperature  $\text{NEP}_{\text{BR}}$  by a factor of  $1/\sqrt{2}$ , while  $\text{NEP}_{\text{BR}} (\text{cm}, 4.2 \text{ K}, 1 \text{ Hz})$  deduced from expression (4.3) is  $1.4 \times 10^{-15} \text{ W}$ . This is the reason why, under laboratory conditions, the background radiation (BR) incident on low-temperature thermal detectors is strongly attenuated by filters cooled at the detector temperature, which cut the medium IR background and provide a low value of  $T_{\text{back}}$ . An improvement is also observed by reducing the field of view of the incident radiation.

Expression (4.3) is actually derived by integration from the more general expression

$$\langle W_{\text{BRN}}^2 \rangle = \frac{8A\pi h^2 \Delta f}{c^2} \int_0^\infty \frac{\nu^4 \exp(h\nu/k_{\text{B}}T)}{[\exp(h\nu/k_{\text{B}}T) - 1]^2} d\nu \quad (4.5)$$

where the integrand involves the temperature derivative of the spectral emissivity per unit of area and solid angle at frequency  $\nu$  of a black body at temperature  $T$ , known as the Planck function

$$B(\nu, T) = 2h\nu^3 / [c^2 (\exp(h\nu/k_{\text{B}}T) - 1)]$$

Currently, a photoconductor does respond to the number of photons that produce an electronic excitation in the detector. When defining  $q_\nu$  as the photon quantum efficiency at frequency  $\nu$  and  $\nu_0$  as the frequency of interest, it can be shown (see [15] for the derivation) that if the photodetector temperature is much less than the temperature  $T$  of the surroundings, the radiation background NEP for a photoconductor is given by:

$$(\text{NEP}_{\text{BR}})^2 = 4\pi A (\Delta f) \frac{h^2 \nu_0^2}{c^2} \int_0^\infty \frac{q_\nu \nu^2 \exp(h\nu/k_{\text{B}}T)}{[\exp(h\nu/k_{\text{B}}T) - 1]^2} d\nu \quad (4.6)$$

At a difference with thermal detectors, the background noise of photoconducting detectors is frequency-dependent. If it is assumed that the photoconductor is used to detect radiation at a frequency just above its cut-off frequency  $\nu_c$ , the detectors with a cut-off in the near IR display a much smaller background noise than those with a cut-off at lower energies. This is because in the near IR, the black body emissivity contribution at room temperature and below is very small.

Besides the BRN, there are additional sources of noise due to the physical nature and operation method of the detectors. Most bolometers and photoconducting detectors are basically resistors, and they display at their terminals voltage fluctuations due to the random motion of the electric charges within this resistor. The corresponding noise is called Johnson noise or thermal noise. The voltage fluctuations  $V_n$  at the terminal of a resistor  $R$  at temperature  $T$  for an electrical band width  $\Delta f$  is:

$$\langle V_n^2 \rangle^{1/2} = (4k_B TR \Delta f)^{1/2} \quad (4.7)$$

known also as the Nyquist's formula. The associated open-circuit noise equivalent power, which is independent of  $R$  is:

$$\text{NEP}_n = 4k_B T \Delta f \quad (4.8)$$

At 300 K and for  $\Delta f = 1\text{Hz}$ ,  $\text{NEP}_n$  is  $4.14 \times 10^{-21}\text{ W}$ . Under the same conditions, the thermal noise voltage  $V_n$  in a  $1\ \Omega$  resistor is  $1.21 \times 10^{-10}\text{ V}$ . It decreases to  $1.7 \times 10^{-12}\text{ V}$  at LHeT, but for a detector with a  $1\text{ M}\Omega$  resistance, one must keep in mind that it is  $1.7\ \mu\text{V}$ . Johnson's noise is frequency-independent and for this reason, it is referred to as a "white" noise.

In thermal detectors and especially in bolometers, the energy exchange between the sensing element and the heat sink through a thermal link of conductance  $G$  results in a thermal noise known as phonon noise. The NEP associated with this phonon noise, which is a white (frequency-independent) noise, is given by:

$$\text{NEP}_{\text{phon}} = (4k_B T^2 G \Delta f)^{1/2} \quad (4.9)$$

For a bolometer with  $G = 10^{-5}\text{ WK}^{-1}$ , operated at 4.2 K,  $\text{NEP}_{\text{phon}}$  is about  $10^{-15}\text{ W}$  for  $\Delta f = 1\text{Hz}$ ; this is comparable with  $\text{NEP}_{\text{BR}}$  when the detector and its surroundings are both at 4.2 K. The bolometer time constant can be reduced by increasing  $G$ , but this results both in a sensitivity loss, as mentioned above, and also in an increase of the phonon noise.

Deep centres are often present in photoconductors and they can trap the photo-generated carriers. The statistical trapping (recombination or capture) and subsequent release (generation or emission) of these carriers leads to an extra source of noise called generation-recombination (g-r) noise. The presence of this noise depends on the purity of the material used as a photoconductor, but in some cases, it is inherent to the deliberate technological process as recombination centres can be added to reduce the time constant of the detector for specific applications. The time constant  $\tau$  of a single trap is related to its capture and emission time constants  $\tau_c$  and  $\tau_e$  by  $\tau^{-1} = \tau_c^{-1} + \tau_e^{-1}$ , and when the g-r noise arises from a trap with a definite value of  $\tau$ , the observed noise spectrum has a Lorentzian dependence on the modulation frequency  $f$ , peaking at  $f_0 = 1/2\pi\tau$ .

The time constant of a trap in a photoconductor is temperature-dependent: it depends on the energy position of the corresponding level in the band gap

and on the position of the Fermi level of the photoconductor in the dark region. At low temperature, when the Fermi level is above the trap level, it can be shown that  $\tau$  is essentially a constant.

Low-frequency noise, referred to as  $1/f$  noise, has been observed in both thermal and photon detectors. Current noise that appears when an electrical current is passed through a resistor has this approximate spectral dependence. This noise has several origins, some of them technological, other more fundamental and its contribution can vary in different detectors. Besides the fact that the amplification of electric signals can be made more selective at high frequencies, the existence of this noise is an incentive to use, when possible, high modulation frequencies.

The performance of the radiation detectors depends on their intrinsic properties, temperature and external conditions of use. They can be compared by using a factor of merit  $D^*$ , known as the detectivity, equal to the inverse of the NEP for a detector with unit area used with an electrical band-width  $\Delta f$  of 1 Hz and expressed in  $\text{cm Hz}^{1/2} \text{W}^{-1}$ . When a value of  $D^*$  is indicated for a thermal detector, it is considered to be independent of the radiation frequency and the time modulation frequency is assumed to be adapted to the intrinsic time constant  $\tau_d$  of the detector. For a photoconductive detector,  $D^*$  peaks at a radiation frequency very close to the band gap for an intrinsic detector or to the ionization energy of the relevant centre for an extrinsic detector and decreases steadily at lower energies.

## 4.5 Conditioning the Samples

First, there are valuable samples, like cut gemstones or diamonds, which must be measured as they are, and where conditioning is out of question. The best absorption measurements are made on samples cut from crystals or polycrystals in orthogonal parallelepipeds shapes. The surfaces of the samples intercepting the radiation beam must be reasonably plane and optically polished to prevent scattering of the incident radiation by the surface inhomogeneities, with dimensions of the order of the wavelength. This condition becomes less drastic with increasing wavelengths and in the very far IR, samples with ground surfaces are acceptable. However, mechanical cutting and polishing leave uneven surfaces at the microscopic scale; therefore, as a function of the mechanical properties of the crystals and of the kind of experiment envisaged, it can be necessary to remove the perturbed layer by adequate chemical etching. The surface of cleaved samples has a good optical quality and this is also generally true for the epitaxied samples, with the possible exception being the back surface of the substrate, and these samples do not usually require further mechanical treatment. The absorption measurements on commercial silicon wafers with etched back surfaces are usually performed in the as-received surface state. This surface state reduces the transmission because of the scattering of the back surface and expression (3.8) is no longer valid. A discussion



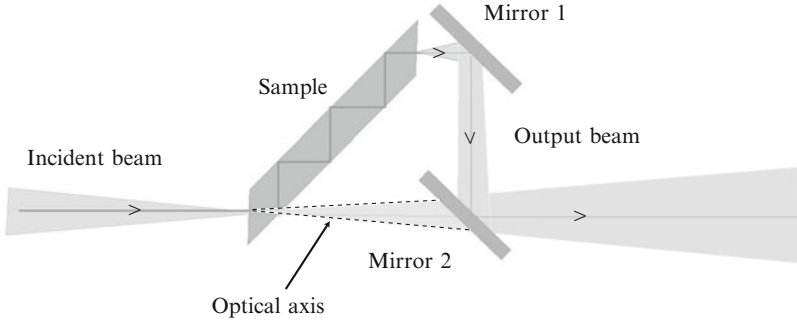


**Fig. 4.5.** Schematic side view of the positioning in a spectrometer beam of a sample cut with a  $45^\circ$  geometry allowing for multiple internal reflections, and of the two mirrors of the sample holder (not shown) redirecting the output beam along the optical axis. The beam delimited by dashes is the normal beam (courtesy C. Naud)

of the methods used to deal with this situation, centred on the vibrational absorption of  $O_i$ , can be found in [4].

The spectral transmission of a plane parallel sample of thickness  $d$  and refractive index  $n$  is modulated by equal-thickness fringes with spacing  $\Delta\tilde{\nu}$  in wavenumber, approximately equal to  $1/2nd$ . When the spectral bandwidth  $\delta\tilde{\nu}_d$  is larger than this spacing, the fringes are averaged out, but they become visible at higher resolution. Solutions to this problem have been discussed in Sect. 4.2.3.2.

The optical thickness of a sample must be adapted to the peak absorption of the impurities to avoid saturation of the lines, and this can lead to very thin samples when the impurity concentration is large and cannot be reduced, and when the OS is also large. Inversely, the measurement of small impurity concentrations can require thick samples and this limits the spectroscopic measurements of impurities. In some cases, as an alternative to the increase of the thickness of the sample, it can be cut with a geometry allowing multiple internal reflections, which increases the optical path, as shown schematically in Fig. 4.5.

## 4.6 Cooling the Samples

Many absorption experiments on impurities and defects are performed at low temperature or as a function of temperature, especially for the observation of discrete spectra. This is a necessity when the population of the ground state level of a transition or of a series of transitions is thermalized at room temperature. Another reason for using low temperatures is the decrease of the widths of spectral lines with temperature due to the reduced coupling of the levels with lattice phonons. The samples have to be, therefore, cooled in optical cryostats.

Presently, the most convenient cryostats, when liquid helium is not available, are the commercial closed-cycle cryostats based on Joule–Thomson cooling, with a reservoir of compressed He gas and a Gifford–McMahon type regenerator. These refrigerators do not require manipulation of cryogenic liquids, and standard units allow a temperature of 6 K with useful dissipation power. Recently, temperatures as low as 3 K have been achieved with such cryostats. The cold head of these refrigerators can be fitted with an optical cryostat, and mechanical vibrations reduced to a point where optical measurements are possible. When liquid He is available, the most useful cryostats to cool the small samples down to about 5 K are the continuous flow cryostats, through which liquid He is continuously pumped from a container and vaporized in a small exchanger cell. The exchanger cell can eventually be filled with liquid He and pumping on it can allow temperatures near 2 K to be obtained for a short time. For other purposes, cryostats with a liquid He reservoir are preferable, for instance in experiments where the sample must be processed (implanted or irradiated) at LHeT before optical measurements without breaking the low-temperature conditions, or when measurements between the temperatures of the boiling points of liquid He at atmospheric pressure and at the lambda point are needed with samples mounted in vacuum. When the sample is directly immersed in liquid He, bubbling of the liquid induces a strong scattering of the transmitted radiation. To overcome this, reducing the pressure over the liquid is then necessary to reach temperatures below the lambda point of  $^4\text{He}$  (50 kPa or 38.3 torr for  $T \sim 2.18$  K) where the liquid becomes superfluid with no subsequent bubbling. The cryostats with a liquid He reservoir are thus widely used for transmission and PL experiments between  $\sim 2$  and 1.2 K.

Below 1.2 K, the cryostats using natural He are replaced by  $^3\text{He}/^4\text{He}$  dilution refrigerators. Such refrigerators are commonly used to cool the bolometer/radiation detectors in the mK range (typically  $\sim 30$ – $60$  mK range). They are used, for instance, in the detection of the weakly interacting massive particles (WIMP). They have only been used in a limited number of cases for optical studies of impurities in semiconductors [36].

When temperatures  $\sim 80$ – $100$  K are required regularly, liquid nitrogen (boiling point: 77 K) is a convenient cryogenic liquid.

Cooling a sample in vacuum can be obtained by gluing it to a part of the cryostat called a sample holder (cold finger) generally made of copper. This requires gluing a material with good thermal conductance and mechanical strength. In the 1960s, type N or H Apiezon grease eventually mixed with copper powder, or GE low-temperature varnish 7031, both with a low vapour pressure, were used for this dual purpose, but silicon grease has later been used. Accurate temperature measurement also necessitates a temperature sensor glued to the sample. This kind of cooling can be useful for measurements between 2 and  $\sim 5$  K as bubbling prevents measurements with the sample immersed in liquid He in this temperature range. However, with such mounting, the sample itself must have a good thermal conductance to avoid thermal

gradients, and it must not be easily cleaved as inhomogeneous mechanical strains are inevitably produced within the sample (mounting of very thin samples is problematic). The presence of these inhomogeneous strains can also lead to inhomogeneous broadening of sharp electronic absorption lines with high piezospectroscopic coefficients.

The best way to avoid some of the above problems is to use a cryostat like the one shown in Fig. 4.6, with an extra sample compartment, which can be

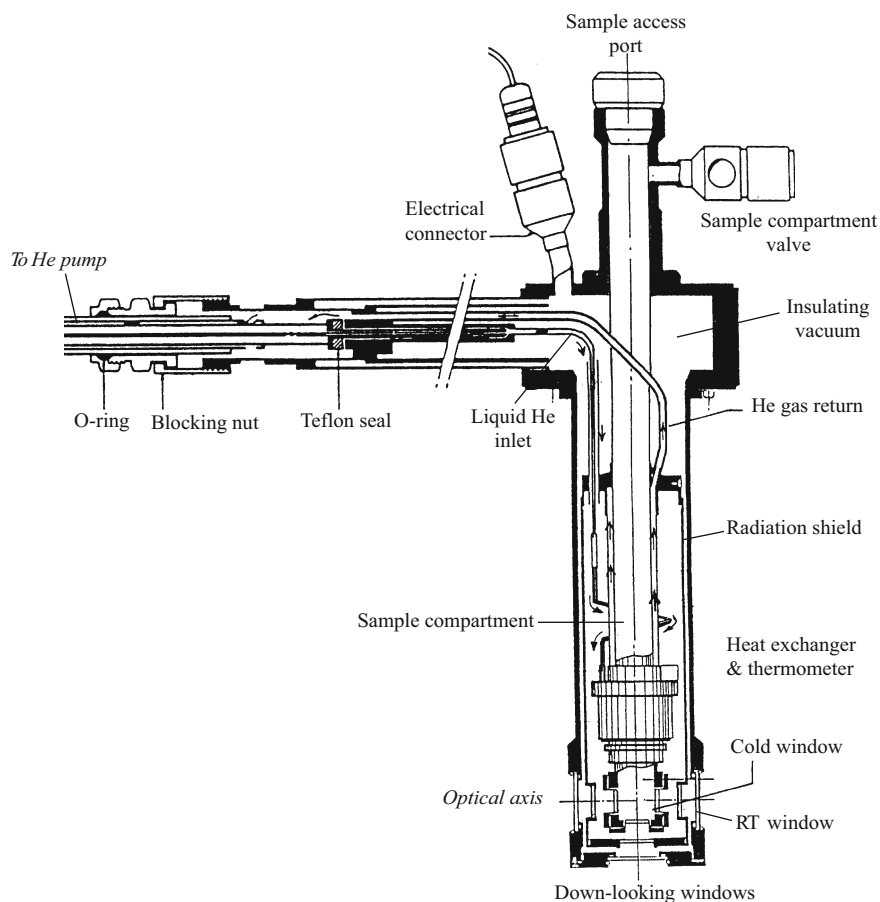


**Fig. 4.6.** Cross-section of an optical continuous-flow cryostat (CF 204 of Oxford Instruments), with the extremity of the removable transfer tube inserted, but without sample holder. The evacuation valve at the top is masked by the sample port. The optional windows on the radiation shield can be replaced by metallic irises to reduce the field of view. This cryostat can be fitted with one or two more optical windows at  $90^\circ$  from the main optical axis for additional excitation, and also with a down-looking window. The arrows indicate the direction of the flow of liquid or gaseous helium. Reproduced with permission from Oxford Instruments

filled independently with He gas at low pressure from a clean He gas supply with a small oil-free pumping system. Since cooling is insured by gas, the mechanical contact between the sample and the holder can be made loose as long as the sample is immobile during the measurement (for instance, by loosely fitting the sample in an aluminium paper holder fixed to the sample holder by aluminium Scotch ® tape, which retains sticking properties down to LHeT). Temperature can be measured by a sensor located close to the sample. The temperature of the sample can be varied easily by controlling the temperature of the gas with an additional heater. Another advantage of gas cooling is that the positions of the samples can be changed or varied with respect to the radiation beam by using sample holders with a thin intermediate tubular section and an extremity at RT. When several samples are mounted on the low-temperature side of such a holder, the use of an appropriate spacer on the RT side of the holder allows adjustment of the position of a given sample on the radiation beam. Thin spacers coupled with small cross-sections of the optical beam (down to  $0.2\text{ mm}^2$  with some FTSs) allow measurement of the low-temperature absorption at different points of a sample. Axial rotation of the holder is possible through its RT O-ring. The use of spacers allows cooling of the sample in a position above that of the sample beam, avoiding its illumination with room temperature BR during cooling-down. This configuration corresponds to a true thermal equilibrium configuration while the usual one (sample in the optical beam) is called the pseudo-thermal equilibrium configuration. The entire holder can even be removed and replaced by a new one by temporarily limiting the liquid He flow and over-pressurizing the sample compartment with He gas at RT.

The price to pay for these advantages is the necessity of cold windows on the exchange gas compartment, in addition to the RT windows of the cryostat. Cold windows are, of course, mandatory in cryostats with a liquid He reservoir, where the sample is immersed in liquid He. These windows must not be hygroscopic and be resistant to thermal shocks. From the UV to  $\sim 0.25\text{ eV}$ , corundum with the *c*-axis perpendicular to the window surface (to avoid polarization effects) is a good option. Polycrystalline ZnSe can be used from about  $2.7\text{ eV}$  in the visible region of the spectrum down to  $\sim 0.03\text{ eV}$ . Such windows, already mounted on metal flanges, are commercially available and the whole unit can be mounted on the exchange gas as well as liquid He compartments (they are tight for superfluid He) with standard In seals or, for some flanges, with Cu gaskets. KRS5 (thallium bromo-iodide) cold windows are also proposed and this material has the advantage of a relatively extended spectral range (down to  $\sim 25\text{ meV}$  or up to  $\sim 50\text{ }\mu\text{m}$ ) compared to ZnSe, but its reflection losses are higher and its high frequency cut-off is near  $2.1\text{ eV}$ . For the far IR, thin polypropylene films ( $\sim 30\text{ }\mu\text{m}$ -thick) can be used [24]. These films are slightly permeable to He gas at RT, but become He-tight at lower temperatures. Below the one-phonon absorption, the compound insulating materials again become transparent: at LHeT, corundum and ZnSe windows can again be used below  $\sim 23\text{ meV}$  (above  $\sim 55\text{ }\mu\text{m}$ ). Diamond, which

is transparent from the UV region to the far IR, with only a few spectral regions showing absorption, presents good optical and mechanical properties, and synthetic diamond windows are commercially available.

## 4.7 Compressing the Samples

Important information on the atomic properties of impurity centres and defects are obtained by recording the transmission of a sample while subjected to an external pressure. The pressure can be hydrostatic and it can be applied to amorphous as well as monocrystalline samples. This is usually performed by inserting the sample in a diamond anvil cell (DAC). When the samples are monocrystalline, the stress can be applied along one symmetry axis of the crystal. In the following section, the set-ups with which a uniaxial stress can be applied to a sample are described.

### 4.7.1 Uniaxial Stresses

Most of the uniaxial stress experiments are performed at LHeT because the mechanical properties of the crystals improve when temperature is lowered. For this purpose, continuous flow cryostats are often used because they allow a rather large temperature gradient between the room temperature and LHeT sides using thin stainless steel tubes for the force-transmitting jig. Force is applied to the room-temperature side of the piston by a spring or by pressurized gas, and the sample is inserted between the piston and a base, as shown in Fig. 4.7. With such a set-up, the heat load is larger than with a classical sample holder, and hence, it is difficult to cool the samples under stress at temperatures below 8 K. The value of the force applied is measured either by a force transducer when using a spring or by a manometer reading the gas pressure. The pressure is the ratio of the applied force to the cross-section of the sample.

The maximum pressure that can be applied to the samples depends on their mechanical strength and cleaving properties. Qualitatively, the mechanical strength of crystals increases with covalent bonding and higher pressures can be applied to group IV crystals than to III-V compounds. To apply very high pressures, the pressurized gas set-ups are superior to those with a spring-loaded piston. Under good experimental conditions, silicon and diamond crystals can withstand at low temperature uniaxial pressures in the 0.5–1 GPa range.

In addition to accurate crystalline orientation, the sample must be cut with a very good parallelism between opposite sides to avoid crushing when applying stress. A combination of cardboard, Cu or In spacers are placed between the sample and the metallic surfaces to avoid edge effects and minimize the effect of possible misalignment. It is usual to consider that the ratio between

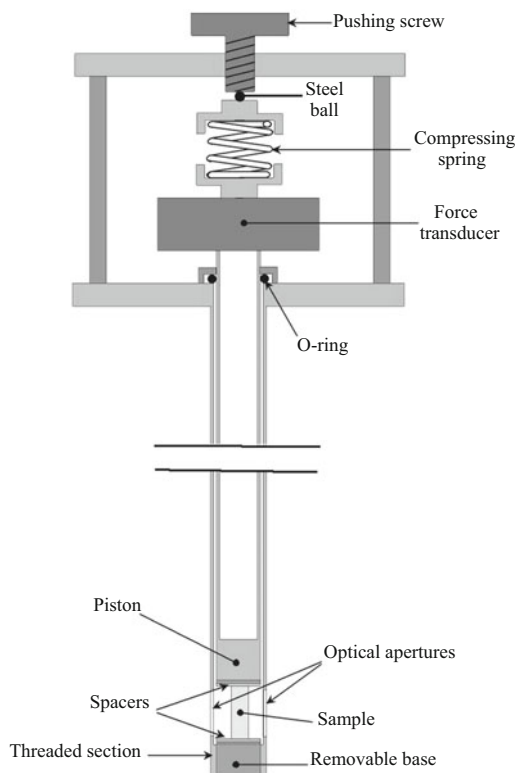


**Fig. 4.7.** Schematic of a stress apparatus of the compressing-spring type devised by C. Naud to be inserted in a continuous-flow optical cryostat for measuring the absorption of a sample under uniaxial stress. Extra optical apertures are indicated. The height adjustment system to the top of the cryostat is not shown (after [6])

the sample length and the largest side of the base section must be  $\geq 3$  in order to obtain a reasonable uniaxial stress within the central region of the sample.

Centering of the samples is delicate and it can be made easier by accurate lapping of the sample ends into pyramidal shapes (Fig. 4.8a) which fit into corresponding hopper-shaped slots in the brass parts of the stress rig, as shown in Fig. 4.8b [47].

#### 4.7.2 Hydrostatic Stresses

The optical absorption of small samples subjected to a hydrostatic pressure is usually measured in a diamond anvil cell (DAC). There are several types of DACs, differing mainly in the way in which the pressure is transmitted to the cell [17]. Some of these cells, like the so-called Merrill-Basset one, have been modified for absorption spectroscopy at low temperature [12]. The basic part of a DAC is shown in Fig. 4.9. It is made of two diamonds separated by an

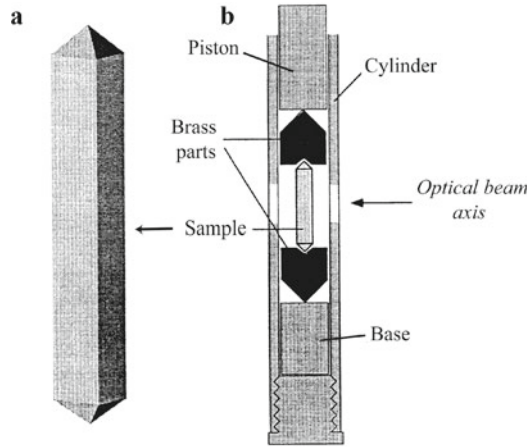


**Fig. 4.8.** (a) Sample cut for uniaxial stress measurements with ends lapped into a pyramidal shape. (b) Detail of the stress rig showing the sample mounted between the two brass parts [47]

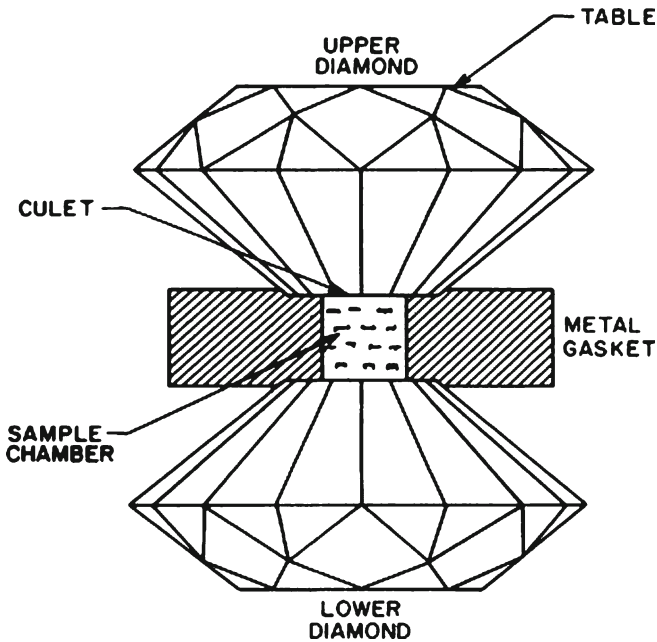


**Fig. 4.9.** Basic part of a diamond anvil cell. Pressure is exerted on the diamond tables by the metallic plates (not shown) [17]. Copyright 1983 by the American Physical Society

indented metal plate, at the centre of which a hole has been drilled to form the sample chamber. The resulting metal gasket acts as a seal when pressure is applied.

The diamonds used in DACs are brilliant-cut type with the bottom part of the gem (the culet) removed by grinding to obtain another flat surface, or standard cut octagonal diamonds, better suited for very high pressure experiments [16]. These diamonds have a small size and the largest dimension of their tables does not exceed 1 mm, requiring a concentrating optics. Type I diamonds show absorption in the  $1100\text{--}1400\text{cm}^{-1}$  spectral region due to nitrogen under different forms, but they are more common (and less expensive!) than the purer IIa ones. They are, therefore, used for DACs except in situations where access to the above spectral region is needed. Note that the 2- and 3-phonon absorption of diamond between about  $1900$  and  $3900\text{cm}^{-1}$  limits its transparency in this region. The gasket is made of a metal or alloy (inconel, different varieties of stainless steel, BeCu, rhenium) adapted to the intended experiment, with a thickness in the  $0.1\text{--}0.2\text{ mm}$  range. Pressure is exerted on the diamond tables by two metallic plates with apertures for admitting radiation. The largest size of the crystalline samples is of the  $0.3\text{ mm}$  order of magnitude, with thicknesses in the  $50\text{ }\mu\text{m}$  range. One of the metallic plates is stationary and the other pushed by a movable mechanical device, for instance through a lever arm [35], but for low-temperature measurements, screws mounted directly on the plates exerting pressure on the metallic tables are preferred [43].

The use of relatively large sapphire anvil cells has also been reported for PL measurements at LHeT in the near IR. This allows chamber volume for the sample about one order of magnitude larger than the one of DACs at reasonable cost, at the expense of a smaller hydrostatic stress [42].

The sample chamber of a DAC is filled with a medium that is able to transfer to the sample a homogeneous pressure, and is transparent in the spectral region of interest. At low temperatures, He, Ne and Xe and also homonuclear molecules ( $\text{H}_2$ ,  $\text{D}_2$ ,  $\text{N}_2$  or  $\text{O}_2$ ) have been used as pressure-transmitting media. The hydrostatic behaviour of He and  $\text{H}_2$  allows experiments at low temperature up to 60 GPa (The kbar unit, traditionally used in many experiments with DACs, is close to 0.1 GPa) and  $\text{N}_2$  can be used up to 13 GPa. Loading the sample chamber with the sample and the pressure transmitting medium is usually performed by the liquid-immersion technique [40]. Hydrostatic pressure measurements in absorption experiments can be obtained from a calibration of the DAC using the pressure-induced shift of  $\text{R}_1$  and  $\text{R}_2$  fluorescence lines of  $\text{Cr}^{3+}$  of a ruby chip near 694 nm, developed by [8]. However, this calibration is performed at RT and it must be extrapolated at low temperatures. It has been shown by Hsu [16] that the shift of the vibrational lines of the  $\text{CO}_2$  impurities contained in  $\text{N}_2$  used for pressure transmission could be used to measure pressure at low temperature.



## 4.8 Magneto-optical Measurements

The measurement of absorption by impurities and defects in crystalline solids under magnetic fields is mainly intended to observe the Zeeman splitting and shift of their levels or of bound excitons. As for a uniaxial stress, magnetic field is applied along the main symmetry axes of the crystal. When the propagation vector  $\mathbf{k}$  of the radiation is parallel to the magnetic field  $\mathbf{B}$ , one refers to Faraday configuration, allowing only  $\mathbf{E} \perp \mathbf{B}$  polarization, and when  $\mathbf{k}$  is perpendicular to  $\mathbf{B}$ , to Voigt configuration, allowing both  $\mathbf{E} \perp \mathbf{B}$  and  $\mathbf{E} // \mathbf{B}$  polarizations.

Minimizing the line widths and preventing thermalization implies that most of the optical experiments on impurities under a magnetic field are performed at LHeT. In the first experiments of this kind, the tail of an optical cryostat was inserted in the gap between the poles of a dc electromagnet, and samples could be subjected to effective magnetic fields up to near 4 T ( $1\text{T} = 10^4\text{ G}$ ) [52]. Larger values of the magnetic field ( $\sim 10\text{ T}$ ) could also be obtained in some cases like the Francis Bitter National Magnet Laboratory (Cambridge, Massachusetts) using a Bitter solenoid operated at RT. The first commercially available magneto-optical cryostats incorporating superconducting solenoids consisted in a solenoid made from Nb–Ti alloy or  $\text{Nb}_3\text{Sn}$  wire (later cable), whose horizontal bore allowed insertion of a sample holder with the sample glued to it. With good thermal contacts, the temperature of the sample was about 8 K. The Faraday configuration was standard, but with a bore diameter of 20 mm, a sample holder with two parallel mirrors at  $45^\circ$  could be used to allow Voigt configuration. Later, the solenoids were wound into a split-coil configuration or even replaced by two close solenoids (split pair) with the magnetic field along a vertical axis and a standard geometry in Voigt configuration. They were provided with an exchange-gas cryostat in which the sample could be rotated and its temperature adjusted, or with an anti-cryostat for measurements at RT. A magnetic field homogeneity of  $10^{-3}$  at the centre of the solenoids combination is sufficient for standard optical measurements. For magnetic resonance measurements, an improvement of at least two orders of magnitude in the field homogeneity is necessary, and it requires design modifications of the overall solenoid structure.

The value of  $B$  at the centre of a standard solenoid of length  $L$ , made from  $N$  turns of conducting or superconducting material produced by an electric current of intensity  $I$  circulating in the solenoid is  $\mu_0 N I L^{-1}$ . As  $N$  and  $L$  are generally known, the value of  $B$  can be deduced from the value of the intensity of the low-voltage dc current. However, the relationship between the current intensity and the magnetic field is provided by the supplier for commercial solenoids, irrespective of their structure. The maximum allowable value of  $I$  must be kept below a limit corresponding to the transition field  $B_s$  above which the material of the solenoid returns to the normal resistive state. The most widely used superconductors in commercial solenoid magnets are the Nb–Ti alloys (40–60% Ti) with a transition temperature  $T_s$  between 10 and

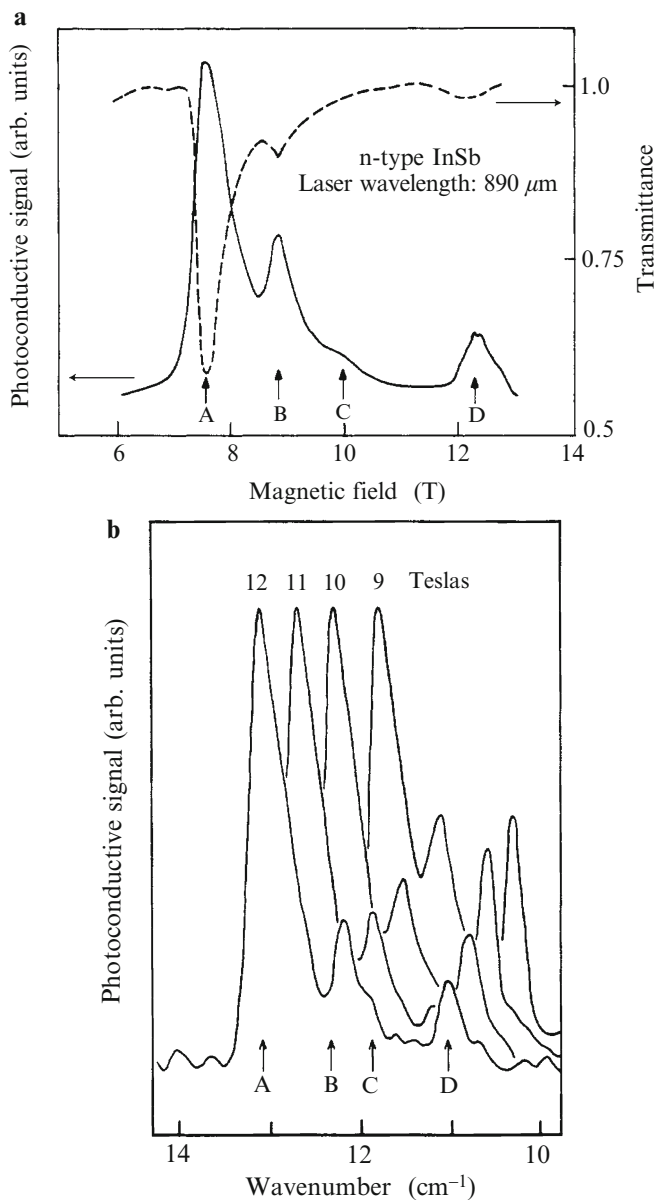


**Fig. 4.10.** LHeT spectra of the transition of donors in InSb samples obtained (a) at a laser wavelength of  $890\ \mu\text{m}$  ( $11.24\ \text{cm}^{-1}$  or  $1.393\ \text{meV}$ ) as a function of the magnetic field. The broken curve gives the transmittance and the full curve the photoconductivity. The features labelled A, B, C and D are due to electronic transitions of different chemical donors ( $N_D - N_A = 8 \times 10^{13}\ \text{cm}^{-3}$ ). (b) FTS photoconductivity spectra at a resolution of  $0.2\ \text{cm}^{-1}$  ( $\sim 25\ \mu\text{eV}$ ) for different values of the magnetic field of a sample with  $N_D - N_A = 5 \times 10^{13}\ \text{cm}^{-3}$  after [23]. Reproduced with permission from the Institute of Physics

12 K and  $B_s$  values near 12 T and  $\text{Nb}_3\text{Sn}$ , with  $T_s = 18$  K and  $B_s = 22$  T. The set-up of large current intensities in the magneto-optical cryostats leads to non-negligible Joule heating of the ohmic metallic leads and electrical contacts with the solenoid, and a corresponding increase of liquid He evaporation. To reduce this evaporation, the manufacturers of magneto-optical cryostats connect the solenoid with a parallel circuit made from the same superconductor. During the set-up of current, a part of this circuit (the so-called superconducting switch) is kept resistive by an external heater so that current flows in the solenoid, but when the desired current intensity is reached, the heater is switched-off and the whole circuit becomes superconducting. The intensity of the current source can then be set to zero while the solenoid operates in closed loop. This type of operation is called persistent mode.

In magneto-optical experiments, and especially in the ones performed in the very-far IR, two methods can be used. In the first one, the transmission or photoconductivity of a sample subjected to a constant magnetic field is analyzed in energy with a spectrometer. In the second one, the transmission or photoconductivity of the sample at the energy of a laser line is measured as a function of the magnetic field. This allows a better S/N ratio than the first method because of the low emissivity of the IR sources in the very-far IR. However, the thermal population of the different impurity levels may change when the magnetic field is swept, so that the relative intensities of the lines associated with different centres do not truly reflect their relative concentrations. Furthermore, the change in the magnetoresistance of the sample with the magnetic field can also modify the sensitivity with PTI detection. An example is shown in Fig. 4.10.

Figure 4.10a shows the  $1s \rightarrow 2p_m = -1$  transition  $((000) \rightarrow (0\bar{1}0))$  in the high-field limit of donors in high-purity InSb at LHeT obtained by the field-sweeping method. This can be compared in Fig. 4.10b with the same spectrum obtained by the “classical” method for different values of the magnetic field, where spectral noise is clearly visible [23].

## References

1. B.A. Andreev, V.B. Ikonnikov, E.B. Koslov, T.M. Lifshits, V.B. Shmagin, in *Defects in Semiconductors 17*, eds. H. Heinrich, W. Jantsch. Trans Tech, Mater. Sci. Forum **143–147**, 1365 (1994)
2. B.A. Andreev, E.B. Kozlov, T.M. Lifshitz, Sov. Phys. Semicond. **25**, 532 (1991)
3. M. Budde, G. Lüpke, C. Parks Cheney, N.H. Tolk, L.C. Feldman, Phys. Rev. Lett. **85**, 1452 (2000)
4. W.M. Bullis, in *Oxygen Concentration Measurements*, ed. by F. Shimura Oxygen in Silicon, Semicond. Semimetals, vol. 42 (Academic, San Diego, 1999), pp. 95–152
5. A.R. Chraplyvy, W.E. Moerner, A.J. Sievers, Opt. Lett. **6**, 254 (1981)
6. D. Côte, Doctoral Thesis, Université Pierre et Marie Curie, Paris, 1988
7. W. Eisenmenger, in *Physical Acoustics* 12, ed. by W.P. Mason, R.N. Thurston (Academic, San Diego, 1976), pp. 79–153

8. R.A. Forman, G.J. Piermarini, J.D. Barnett, S. Block, *Science* **176**, 284 (1972)
9. E.M. Gershenson, G.N. Gol'tsman, N.G. Ptisina, *Sov. Phys. JETP* **37**, 299 (1974)
10. J. Golka, J. Mostowski, *Phys. Rev. B* **18**, 2755 (1978)
11. M. Göppert-Mayer, *Ann. Phys. (Leipzig)* **9**, 273 (1931)
12. E.E. Haller, L. Hsu, J.A. Wolk, *Phys. Stat. Sol. B* **198**, 153 (1996)
13. M. Hass, J.W. Davisson, H.B. Rosenstock, J. Babinski, *Appl. Opt.* **14**, 1128 (1975)
14. A. Hordvik, H. Schlossberg, *Appl. Opt.* **16**, 101 (1977)
15. J.T. Houghton, S.D. Smith, *Infrared Physics* (Oxford University Press, London, 1966)
16. L. Hsu, Ph. D. Thesis, E.O. Lawrence Berkeley National Laboratory, University of California, Berkeley, 1997
17. A. Jayaraman, *Rev. Mod. Phys.* **55**, 65 (1983)
18. W. Kaiser, C. Garrett, *Phys. Rev. Lett.* **7**, 229 (1961)
19. J.K. Kauppinen, D.J. Moffatt, H.H. Mantsch, D.G. Cameron, *Appl. Spectrosc.* **35**, 271 (1981)
20. A.G. Kazanskii, P.L. Richards, E.E. Haller, *Solid State Commun.* **24**, 603 (1977)
21. A.G. Kazanskii, P.L. Richards, E.E. Haller, *Appl. Phys. Lett.* **31**, 496 (1977)
22. M.A. Kinch, B.V. Rollin, *Br. J. Appl. Phys.* **14**, 672 (1963)
23. F. Kuchar, R. Kaplan, R.J. Wagner, R.A. Cooke, R.A. Stradling, P. Vog, *J. Phys. C* **17**, 6403 (1984)
24. D. Labrie, I.J. Booth, M.L.W. Thewalt, B.P. Clayman, *Appl. Opt.* **25**, 171 (1986)
25. S.P. Langley, *Nature* **57**, 620 (1898)
26. K. Lassmann, in *Advances in Solid State Physics*, vol. 37, ed. by R. Helbig (Springer, Berlin, 1995), pp. 79–98
27. J. Lerouille, *Appl. Spectrosc.* **36**, 153 (1982)
28. T.M. Lifshits, F.Ya. Nad, *Sov. Phys. Dokl.* **10**, 532 (1965)
29. S.P. Love, K. Muro, R.E. Peale, A.J. Sievers, W. Lo, *Phys. Rev. B* **36**, 2950 (1987)
30. F.J. Low, *J. Opt. Soc. Am.* **51**, 1300 (1961)
31. D.H. Martin, D. Bloor, *Cryogenics* **1**, 159 (1961)
32. R.C. Milward, *Infrared Phys.* **9**, 59 (1969)
33. W.J. Moore, *Solid State Commun.* **3**, 385 (1965)
34. A. Nakib, S. Houbloss, A. Vasson, A.M. Vasson, *J. Phys. D* **21**, 478 (1988)
35. G.J. Piermarini, S. Block, *Rev. Sci. Instrum.* **46**, 973 (1975)
36. L. Podlowski, H. Hoffman, I. Broser, *J. Cryst. Growth* **117**, 698 (1992)
37. A.K. Ramdas, S. Rodriguez, *Rep. Prog. Phys.* **44**, 1297 (1981)
38. P.L. Richards, *J. Appl. Phys.* **76**, 1 (1994)
39. H. Saito, H. Shirai, *Jpn. J. Appl. Phys.* **34**, L1097 (1995)
40. D. Schiferl, D.T. Cromer, R.L. Mills, *High Press.* **10**, 493 (1978)
41. R.A. Smith, F.E. Jones, R.P. Chasmar, *The Detection and Measurement of Infra-red Radiation* 2nd edn. (Clarendon Press, Oxford, 1968)
42. T.W. Steiner, M.K. Nissen, S.M. Wilson, Y. Lacroix, M.L.W. Thewalt, *Phys. Rev. B* **47**, 1265 (1993)
43. E. Sterer, M.P. Pasternak, R.D. Taylor, *Rev. Sci. Instrum.* **61**, 1117 (1990)
44. R.S. Sternberg, J.F. James, *J. Sci. Instrum.* **41**, 225 (1964)
45. A. Szabo, *Phys. Rev. B* **11**, 4512 (1974)

46. T. Theiler, H. Navarro, R. Till, F. Keilmann, Appl. Phys. A **56**, 22 (1993)
47. A. Thilderkvist, Doctoral Dissertation, Lund University, pp. 41–42, 1994
48. A. Vasson, A.M. Vasson, N. Tebbal, M. El Metoui, C.A. Bates, J. Phys. D **26**, 2231 (1993)
49. R.K. Willardson, A.C. Beer (eds.), *Semiconductors and Semimetals*, vol. 18. Mercury cadmium telluride (Academic, New York, 1981)
50. A. Yang, M. Steger, D. Karaiskaj, M.L.W. Thewalt, M. Cardona, K.M. Itoh, H. Riemann, N.V. Abrosimov, M.F. Churbanov, A.V. Gusev, A.D. Bulanov, A.K. Kaliteevskii, O.N. Godisov, P. Becker, H.-J. Pohl, J.W. Ager III, E.E. Haller, Phys. Rev. Lett. **97**, 227401 (2006)
51. F. Zenitani, S. Minami, Jpn. J. Appl. Phys. **12**, 379 (1973)
52. S. Zwerdling, B. Lax, L.M. Roth, K.J. Button, Phys. Rev. **114**, 80 (1959)

---

## Effective-Mass Theory and its Use

### 5.1 Initial Assumptions

A historical perspective of the early developments on the theory of impurity levels in semiconductors can be found in the review by Pantelides [47]. The measurement of the IR absorption of p-type silicon at low temperature in the mid-1950s revealed broad features, which could be attributed to the electronic absorption of dopants, and a correlation between the chemical nature of the dopant and the spectra was established [15]. They provided spectroscopic estimations of the ionization energies of the dopant atoms, which were earlier derived from electrical measurements. The results thus derived stimulated theoretical developments aimed at calculating the ionization energies of shallow dopants in silicon and germanium [28], and later of the discrete spectrum [32–34], which demonstrated the significance of the free-carrier effective masses and of the static dielectric constant to explain the experimental results. The generalization of these ideas led to the concept of effective-mass (EM) centres and to the development of effective-mass theory (EMT), which was proved to be successful in predicting the energy of the excited levels of some donors and acceptors in many materials, and the relative intensities of the lines of the spectra of many acceptor or donor centres.

A brief introduction to the EM centres in semiconductors has been provided in Sect. 1.3.1. The EM centres are defined as isolated atoms or complexes with bound electrons (donors) or holes (acceptors) whose excited states can be described by a formalism known as the EMT or effective-mass approximation (EMA). They are best represented by substitutional donor atoms of groups IV and VI of the Periodic Table in III-V compounds like GaAs and InP, and by the group-III and group-V substitutional atoms and interstitial Li in silicon and germanium. The deepest energy levels of the electron or hole bound to the positive or negative ion are discrete, and their spacings decrease with their binding energy. They converge towards the ionization energy limit, which is actually the ground state energy. Macroscopically, above this limit, one speaks of the free carriers, but quantum mechanically, one rather

speaks of continuum states. Below the ionization energy, the photon absorption spectrum is discrete while above this, it is continuous and known as the photoionization spectrum.

The main assumption of the EMA is that the effective mass of an electron or a hole bound to an ionic core in a semiconductor crystal can be taken as the effective mass tensor of a *CB* electron or of a hole in the *VB* (see Sect. 3.3.1). This assumption is valid when the electronic probability density extends over the volume of the crystal and is large compared to the ionic core. This condition is met for the excited states of many centres. The EMA should, therefore, describe correctly the donor and acceptor excited states and still more precisely, the states characterized by a pseudo-orbital quantum number  $\ell$ , for which parity  $P = (-1)^\ell$  is odd. For an electronic state with wave function  $\psi(r)$ , the electronic probability density is  $|\psi(r)|^2$  and for a hydrogenic  $1s$  ground state, this probability is maximum at the ionic core. In this case, screening by the static dielectric constant is no longer effective and the local atomic potential must be considered. The logical conclusion is that unless the EM is very small, the ground state cannot be properly described within the EMA and hence, except for donor centres in direct-gap semiconductors with small electron EMs, EMT usually fails to quantitatively account for the ground state energies. As a matter of fact, the ground state energies of centres with EM excited states can cover a broad range: the value for the B acceptor in silicon is 45.7 meV, but it rises to 602 meV for the P donor in diamond. There are even impurity atoms with a very deep ground state with respect to the band gap of the host crystal, whose excited states display an EM behaviour: this is the case for interstitial isolated donor-like Fe (a TM with several ground-state configurations) in silicon, with ground state energies between 788.71 and 795.63 meV. By comparison, the ground state of interstitial Li (a nearly perfect EM donor centre) in silicon is 31 meV. Among the substitutional impurity atoms in elemental crystals, one can identify those with only one more or less electron in their electronic configuration than the host atom (e.g. P and Al in silicon or As and Ga in germanium). Their ionic core is the same as that of the host atom, and they are singled out as isocoric. For these impurities, the electronic potential near the core is close to a pure Coulombic one.

Since the first energy level calculations of the EM centres in silicon and germanium [28, 34], many calculations have been undertaken to explain quantitatively the absorption and photoluminescence (PL) spectra associated with these centres in many semiconductors. The first part of this chapter is devoted to the presentation of the energy level calculations of EM donors and it is followed by the results of the calculations for EM acceptors. The modification to EMA, which is independent of the chemical nature of the centres, is also discussed. The chapter concludes with results of calculations of the oscillator strength (OS) for transitions between the ground states and the acceptor or donor states.

### 5.1.1 Selection Rules

Optical absorption in a medium can take place because of the existence of electric or magnetic dipole moments associated with atomic, molecular or crystal entities. Unless otherwise specified, only electric dipoles are considered here. In quantum mechanics, the condition related to the dipole moment for discrete optical absorption appears in terms of transition probability between the initial and final states. It can be formally expressed as the modulus squared of a matrix element involving the wave functions  $\Psi_i$  and  $\Psi_f$  of the initial and final states and the electric dipole operator, which reduces, within a proportionality factor to the general displacement coordinate  $r_\alpha$ :

$$\langle i | r_\alpha | f \rangle = \int \psi_i^* r_\alpha \psi_f d\tau \quad (5.1)$$

where  $\Psi_i^*$  is the complex conjugate of  $\Psi_i$ . The actual value of the general displacement coordinate depends on both the physical situation and the polarization conditions.

The symmetry of an isolated atom is that of the full rotation group  $R^+(3)$ , whose irreducible representations (*IRs*) are  $D^{(j)}$ , where  $j$  is an integer or half an odd integer. An application of the fundamental matrix element theorem [22] tells that the matrix element (5.1) is non-zero only if the *IR*  $D^{(i)}$  of  $\Psi_i$  is included in the direct product  $D^{(\alpha)} \times D^{(f)}$  of the *IRs* of  $r_\alpha$  and  $\Psi_f$ . The components of the electric dipole transform like the components of a polar vector, under the *IR*  $D^{(1)}$  of  $R^+(3)$ . Thus, when the initial and final atomic states are characterized by angular momenta  $J_1$  and  $J_2$ , respectively, the electric dipole matrix element (5.1) is non-zero only if  $D^{(J_1)}$  is contained in  $D^{(1)} \times D^{(J_2)} = D^{(J_2+1)} + D^{(J_2)} + D^{(J_2-1)}$  for  $J_2 \geq 1$ . This condition is met for  $J_1 = J_2 + 1$ ,  $J_2$ , or  $J_2 - 1$ . However, it can be seen that a transition between two states with the same value of  $J$  is allowed only for  $J \neq 0$  as  $D^{(1)} \times D^{(0)} = D^{(1)}$  ( $D^{(0)}$  is the unit *IR* of  $R^+(3)$ ). For a hydrogen-like centre, when an atomic state is defined by an orbital quantum number  $\ell$ , this can be reduced to the Laporte selection rule  $\Delta\ell = \pm 1$ . This is of course formal, as it will be shown that an impurity state is the weighted sum of different atomic-like states with different values of  $\ell$  but with the same parity  $P = (-1)^\ell$ . These states are represented by an atomic spectroscopy notation, with lower case letters for the values of  $\ell$  (0, 1, 2, 3, 4, 5, etc. correspond to *s*, *p*, *d*, *f*, *g*, *h*, etc.). The impurity states with  $P = 1$  and  $-1$  are called even- and odd-parity states, respectively. For the one-valley EM donor states, this quasi-atomic selection rule determines that the parity-allowed transitions from  $1s$  states are towards  $np$  ( $n \geq 2$ ),  $nf$  ( $n \geq 4$ ),  $nh$  ( $n \geq 6$ ), or  $nj$  ( $n \geq 8$ ) states. For the acceptor states in cubic semiconductors, the even- and odd-parity states labelled by the double *IRs*  $\Gamma_i$  of  $O_h$  or  $T_d$  are indexed by  $+$  or  $-$ , respectively, and the parity-allowed transition take place between  $\Gamma_i^+$  and



$\Gamma_j^-$  states.<sup>1</sup> As already mentioned, these series of donor and acceptor transitions are somewhat analogous to the Lyman series for the H atom, and hence the corresponding impurity spectra are sometimes called Lyman spectra.

When the degeneracy of the EM levels due to the symmetry of the *CB* of the material is included, a donor state is represented by different *IRs* of the symmetry point group of the donor centre. For instance, for centres with  $T_d$  point group symmetry, the  $1s$  and  $nd_0$  even-parity states correspond to the six-dimensional reducible representation  $A_1 + E + T_2$  in silicon and by the four-dimensional  $A_1 + T_2$  representation in germanium. The corresponding degeneracy of the  $1s$  state is partially lifted by the valley-orbit interaction, which is discussed later in this chapter. When considering these *IRs* and those associated with the components of the electric dipole for the same symmetry point group, the rule derived from the fundamental matrix-element theorem stated above can be used to determine the symmetry-allowed transitions that are independent of the parity-allowed transitions. It can be verified that for donors with  $T_d$  symmetry, this procedure allows transitions between states with  $A_1$  and  $T_2$  symmetries. When they are not parity-allowed, the intensities of these symmetry-allowed transitions depend on the chemical nature of the donors and on their lattice sites. The possibility for such transitions explains why the  $1s(A_1) \rightarrow 1s(T_2)$  and  $1s(A_1) \rightarrow 3d_0$  transitions can be observed in some donor spectra. The  $1s(A_1) \rightarrow 1s(E)$  transition is IR parity and symmetry-forbidden, but it is Raman-allowed and has been observed for donors in silicon by Raman scattering. As for donors, the optical transitions between the acceptor states take place with a change of parity. One transition without a change of parity has also been observed by Raman scattering. For donors as well as for acceptors, two-electron or two-hole transitions involving even-parity excited states can be observed in PL. The experimental results for donors and acceptors are presented in Chaps. 6 and 7.

## 5.2 Donor Centres

### 5.2.1 The One-Valley Approximation

Formally, the Hamiltonian  $H_e$  of an electron with effective mass  $m^*$  and wave vector  $\mathbf{k}$  in the *CB* of a semiconductor crystal lattice is:

$$H_e = -\frac{\hbar^2}{2m^*} \nabla^2 + V(r) \quad (5.2)$$

where  $V(r)$  is an effective periodic potential and the eigenfunctions of  $H_e$  are Bloch functions  $\varphi_{\mathbf{nk}}(r)$  that are products of periodic functions  $u_{\mathbf{nk}}(r)$  and  $e^{i\mathbf{k}r}$ , and  $-\hbar^2 \nabla^2$  is the operator  $p^2 = \hbar^2 k^2$ . The classical Hamiltonian  $H_{ed}$  of a donor electron in a such a lattice is derived from (5.2) by adding a potential

<sup>1</sup> The different notations for the *IRs* of  $O_h$  and  $T_d$  are given in Appendix B. For the acceptors, the Bethe-Koster notation is used and for donors, the Mulliken's one.

energy term arising from the Coulomb interaction between an electron and the positive donor ion screened by the static dielectric constant  $\varepsilon_s$  of the crystal:

$$H_{\text{ed}} - \frac{\hbar^2}{2m^*} \nabla^2 + V(r) - \frac{e^2}{4\pi\varepsilon_0\varepsilon_s r} \quad (5.3)$$

It can be shown [33] that the eigenfunctions  $\psi(r)$  of (5.3) are the products of Bloch functions and hydrogen-like envelope functions  $F(r)$ . It can be further demonstrated that the envelope functions are eigenfunctions of a so-called EM equation:

$$H_{\text{EM}} = -\frac{\hbar^2}{2m^*} \nabla^2 - \frac{e^2}{4\pi\varepsilon_0\varepsilon_s r} \quad (5.4)$$

and this Hamiltonian can be used with the above-mentioned limitations on the effective screening provided by  $\varepsilon_s$ .

The anisotropy of the electron effective masses at the energy minima of the *CB* reflects its symmetry. For indirect-band-gap semiconductors, like group-IV crystals (see Table 3.4), the *CB* has equivalent energy minima along the six equivalent  $\langle 100 \rangle$  directions for  $\text{C}_{\text{diam}}$  and silicon, and along the four equivalent  $\langle 111 \rangle$  directions for germanium (these directions are the same for the reciprocal and direct lattices). There are as many total donor wave functions  $\psi^{(i)} = F^{(i)}(r) \varphi_{\mathbf{k}^{(i)}}(r)$  as equivalent *CB* minima. We first consider a bound donor electron, with an effective mass equivalent to that of a free electron along one of the *CB* minima. This is often qualified as one-valley approximation because of the shape of the energy dispersion vs.  $\mathbf{k}$  curve at the *CB* minima. The neglect of the *CB* degeneracy will be *a posteriori* justified by comparison with the spectroscopic results. The EM energy levels of the bound electron are eigenvalues of  $H_{\text{EM}}$ , where  $z$  is the main axis of the constant-energy ellipsoid,  $m_{\text{nt}}$  the transverse effective mass of a conduction electron and  $\gamma$  the effective mass ratio  $m_{\text{nt}}/m_{\text{nl}}$  of the transverse and longitudinal effective masses (see Sect. 3.3.1 for the definition of the effective masses), viz.:

$$H_{\text{EM}} - \frac{\hbar^2}{2m_{\text{nt}}} \left[ \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) + \gamma \frac{\partial^2}{\partial z^2} \right] - \frac{e^2}{4\pi\varepsilon_0\varepsilon_s r} \quad (5.5)$$

This Hamiltonian is invariant under a rotation about the  $z$  axis. The corresponding symmetry group is the axial rotation group  $D_{\infty\text{h}}$ , whose *IRs* are characterized by the integral values of quantum number  $|m|$ , which is a projection of the quantized angular momentum  $\ell$  on the symmetry axis. The net result of this symmetry is the splitting of a hydrogenic  $n$  state into  $n$  ( $n, \ell$ ) sublevels, characterized by quantum number  $\ell$  and varying from 0 to  $n - 1$ . Each ( $n, \ell$ ) sublevel is, in turn, split into ( $n, \ell, |m|$ ) sublevels with  $|m_{\text{max}}| = \ell$ . This splitting is analogous to that observed for a H atom placed in an external electric field (Stark effect). These levels are represented by an atomic spectroscopy notation, with lower case letters for the values of  $\ell$  (0, 1, 2, 3, 4, 5, etc. correspond to *s*, *p*, *d*, *f*, *g*, *h*, etc.) and an index for  $m$ : a hydrogenic state with  $n = 2$  is for instance, split into *2s* and *2p* states, and the *2p* state is in turn split into *2p* ( $m = 0$ ) and *2p* ( $|m| = 1$ ) substates. It is usual to replace the

whole expression for  $|m|$  by index 0,  $\pm 1$ ,  $\pm 2$ , etc., depending on the value of  $\pm m$ , e.g.,  $2p_0$  and  $2p_{\pm 1}$ . The continuous symmetry group  $D_{\infty h}$  of Hamiltonian (5.5) is useful when studying the effect of external perturbations, considering that the wave functions for the ns,  $np_0$  and  $np_{\pm 1}$  states correspond, respectively, to  $IRs$   $\Sigma_g^+$ ,  $\Sigma_u^+$  and  $\Pi_u$  of this group. By choosing the atomic units of length and energy for donors, an effective Bohr radius  $a_{0d}^* = a_0 \varepsilon_s / m_{nt}$  and an effective Rydberg  $R_{\infty d}^* = (m_{nt} / \varepsilon_s^2) R_{\infty}$ , with  $m_{nt}$  expressed in units of  $m_e$ ,  $H_{EM}$  can be rewritten as:

$$H_{EM} = - \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \gamma \frac{\partial^2}{\partial z^2} \right) - \frac{2}{r} \quad (5.6)$$

For  $\gamma < 1$ , no eigenvalue of this Hamiltonian can be found analytically and a variational method, like the one initiated by Faulkner [17], is used in most cases [13, 26]. However, a non-variational method has also been used by the Kogan group in the late Soviet Union (see [7, 8], and references therein). This method is facilitated by transforming Hamiltonian (5.6) using a deformed new coordinate frame  $X = \gamma^{1/6} x / a$ ,  $Y = \gamma^{1/6} y / a$ ,  $Z = \gamma^{1/3} z / a$ , where  $a = \gamma^{1/3} a_{0d}^*$ . From  $\cos \theta = Z / R$  with  $R = (X^2 + Y^2 + Z^2)^{1/2}$ , Hamiltonian (5.5) can be rewritten as:

$$H_{EM} = - \frac{\nabla_R^2}{2} - \frac{q(\theta)}{R} \quad (5.7)$$

where  $q(\theta) = [1 - (1 - \gamma) \cos^2(\theta)]^{1/2}$ . Expression (5.7) differs from (5.6) in the transfer of anisotropy of the problem from the kinetic energy term to the potential energy term, which further simplifies the calculations.

In the variational method, the calculation principle is to define a  $N \times N$  matrix whose elements are  $\langle \phi_j | H_0 | \phi'_j \rangle$ , and to obtain its eigenvalues by proper diagonalization under minimization conditions with respect to variational parameters [17]. The basis hydrogen-like wave functions used in this calculation are:

$$\phi_{n\ell m}(x, y, z) = (\beta / \gamma)^{1/4} \psi_{n\ell m}(x, y (\beta / \gamma)^{1/2} z) \quad (5.8)$$

where  $\psi_{n\ell m}(x, y, (\beta / \gamma)^{1/2} z)$  corresponds to hydrogenic wave functions:

$$\psi_{n\ell m}(x, y, z) = R_{n,\ell}(r) Y_{\ell,m}(\theta, \phi) \quad (5.9)$$

and  $\beta$  is an adjustable parameter that depends only on parity  $P = (-1)^\ell$  and  $m$ . The spherical harmonics  $Y_{\ell,m}(\theta, \varphi)$  are orthogonal for different values of  $(\ell m)$  and the normalized radial wave functions  $R_{n,\ell}(r)$  are orthogonal for different values of  $n$ . The radial wave functions used are:

$$R_{n,\ell}(r) = \frac{2\alpha^{3/2}}{n^2} \sqrt{\frac{(n - \ell - 1)!}{[(n + \ell)!]^3}} \left( \frac{2\alpha r}{n} \right)^\ell e^{-\alpha r / n} L_{n-\ell-1}^{2\ell+1} \left( \frac{2\alpha r}{n} \right) \quad (5.10)$$

where  $L_p^k(u) = \sum_{s=0}^p (-1)^s u^s [(p-k)!]^2 / [(p-s)!(k-s)!s!]$  is a Laguerre polynomial of order  $p$ . In the hydrogen radial wave function,  $\alpha = 1/a_0$ , but in the variational calculations, it is taken as a variable parameter that is the same for a given value of  $(\ell, m)$  and different values of  $n$ . Invariance of Hamiltonian (5.5) with respect to inversion implies that the matrix elements involving wave functions with a change of parity are zero, and it can be shown that the angular part  $\langle \ell, m | H_0 | \ell', m' \rangle$  of the matrix element  $\langle \phi_j | H_0 | \phi_{j'} \rangle$  is non-zero for

$$\Delta\ell = 0, \pm 2 \quad \text{and} \quad \Delta m = 0$$

where  $|\ell, m\rangle$  stands for  $Y_{\ell, m}(\theta, \varphi)$ . In [13], for the even parity states  $ns, nd, ng, \dots$ , the states considered were those with  $|m| = 0, 1, 2, 3$  and 4, and for the odd parity states  $np, nf, nh, \dots$ , the states with  $|m| = 0, 1, 2, 3, 4$  and 5. The results obtained in this reference are derived from the diagonalization of matrices between  $70 \times 70$  for the  $h_{\pm 4}$  and  $h_{\pm 5}$  states and  $105 \times 105$  for the  $s$  states. Therefore, the eigenfunctions of (5.6) are linear combinations of the basis functions (5.8) with a given parity and a given value of  $|m|$ , viz.:

$$F_{n\ell} = \sum_{n', \ell'} C_{n'\ell'} \phi_{n'\ell'} \quad (5.11)$$

and they are called the envelope wave functions [33, 49]. For the deepest states like  $2p_0$  or  $2p_{\pm 1}$ , the contributions of the corresponding basis functions are predominant, but for more excited states, it decreases drastically. Also, the contributions of other basis functions become more important than the one corresponding to the  $\ell$  value of the state and this can be seen in Tables 2 and 3 of [6]. Thus, it can be understood that an attempt to calculate energy levels by a variational method applied only to the diagonal matrix element for each basis function gives results with little or no relationship with the eigenvalues of the EM Hamiltonian except for the very first states [62].

The eigenvalues of Hamiltonian (5.4) where a simple Coulomb potential is used are independent of the chemical nature of the donor. This situation corresponds to experiment for the odd-parity levels, but not for the even-parity ones and especially for the  $1s$  ground state. There have been many attempts to use impurity-dependent potentials in Hamiltonian (5.4) in a generalized effective mass theory to provide realistic ground-state energies (see [47]).

For  $\gamma < 1$ , it has been said that a hydrogenic  $n$  state is split into states  $(n, \ell, |m|)$  with definite parity  $P = (-1)^\ell$ . For instance, the odd-parity states for  $n = 6$  are  $6h, 6f$ , and  $6p$  corresponding to  $\ell = 5, 3$ , and 1, respectively. In his ordering of the levels, Faulkner assumed that, in the limit of  $\gamma < 1$ , near from 1, for a given value of  $|m|$ , the energies of the states decreased with increasing  $\ell$ , that is, for odd-parity states with  $|m| = 1$ ,  $E(6p_{\pm 1}) > E(6f_{\pm 1}) > E(6h_{\pm 1})$ . Each state corresponds to a linear combination of basis eigenfunctions (5.8). [13] considered the calculated contributions of these coefficients near from

$\gamma = 1$  and labelled each state by a hydrogen-like state with the largest coefficient in the expansion (5.11). This results in an ordering of states different from that of Faulkner: in the above example, with this new ordering,  $E(6h_{\pm 1}) > E(6f_{\pm 1}) > E(6p_{\pm 1})$  and the  $6p_{\pm 1}$  state becomes the  $6h_{\pm 1}$  state. However, as Faulkner's labelling is widely used, we stick to its notations. The EM donor levels have been calculated for values of the physical parameter  $\gamma^{1/3} = (m_{nt}/m_{nl})^{1/3}$  with a step of 0.1 between 0.1 and 1 [17] and 0.2 and 1 [13]. Results for an oblate ellipsoid ( $\gamma > 1$ ) are also presented in [13], relevant to the calculation of the acceptor levels in the limit of a very high applied uniaxial stress.

For  $\gamma^{1/3}$  between 0.5 and 1, the differences between the energy levels obtained from the two calculations are within  $\pm 5\%$ , but for larger anisotropy, significant differences occur for a number of excited states. This is explained by the larger value of  $\ell_{\max}$  used by Broeckx et al. in their calculations, providing good convergence of the energies (the claimed precision is between  $10^{-4} R^*_{\infty d}$  for all the calculated energies when  $\gamma^{1/3} > 0.35$  and  $10^{-3} R^*_{\infty d}$  in the range  $0.15 < \gamma^{1/3} < 0.35$ ) and from the instabilities in Faulkner's calculations for large anisotropies, in relation to the interactions between closely-spaced levels. The binding energies of the EMT donor states for a prolate ellipsoid in units of  $R^*_{\infty d}$  are given in Tables 5.1 and 5.2. They allow to obtain by interpolation, the energies of EM one-valley donor states in any indirect-gap cubic semiconductor with prolate *CB* minimum constant-energy surfaces.

For a known value of  $\gamma$ , the values of the levels in physical units (usually meV) require a determination of the value of  $R^*_{\infty d}$ . When there is a doubt on the value of  $\varepsilon_s$  at low temperature,<sup>2</sup> this can be done in a self-consistent way by comparison with experimental spectroscopic data [17]. In this method, the experimental  $3p_{\pm 1} - 2p_{\pm 1}$  spacings of the donor spectra are used because they are the largest, ensuring the best accuracy, and because they depend marginally on the chemical nature of the donors, it is assumed that they are given correctly by EMT (as a matter of fact the calculated spacings in physical units are used in the identification of unknown lines). Subsequently,  $R^*_{\infty d}$  is derived from the ratio of the experimental and calculated spacings. In fact, any experimental  $np_{\pm 1} - n'p_{\pm 1}$  spacing can be used for this purpose and any combination with a  $nf_{\pm 1}$  line can be used as well. The spacings given in Table 5.3 for  $C_{\text{diam}}$ , Si and Ge are those for the P donor, and for 3C-SiC, the one for the N donor on a C site [43]. The values of  $\gamma$  are obtained from Table 3.4, and the calculated  $3p_{\pm 1} - 2p_{\pm 1}$  spacings interpolated from Table 5.2. Values of low-temperature static dielectric constants and refractive indices of Si and Ge are self-consistent from  $\varepsilon_s^2 = m_{nt} R_{\infty}/R^*_{\infty d}$ , with the values of  $m_{nt}$  given in Table 3.4 in good agreement with those derived from refractive index measurements at 1.5 K in the far IR [39].

For diamond, the low-temperature value of  $\varepsilon_s$  has been measured independently [19, 50] to be 5.697. From  $m_{nt} \sim 0.30m_e$  deduced from the Zeeman

<sup>2</sup> In [13],  $\varepsilon_s$  is noted  $\varepsilon_{\infty}$ .

**Table 5.1.** Binding energies of the first EM even-parity donor states for  $\gamma < 1$  in effective Rydberg units [13]

| $\gamma^{1/3}$ :                   | 0.20  | 0.30  | 0.40   | 0.50   | 0.60   | 0.70   | 0.80   | 0.90   | 1.00   |
|------------------------------------|-------|-------|--------|--------|--------|--------|--------|--------|--------|
| 1s                                 | 2.694 | 2.321 | 2.0116 | 1.7604 | 1.5530 | 1.3796 | 1.2329 | 1.1077 | 1.0000 |
| 2s                                 | 1.327 | 0.958 | 0.7051 | 0.5436 | 0.4375 | 0.3656 | 0.3151 | 0.2782 | 0.2500 |
| 3s (3d <sub>0</sub> )              | 0.888 | 0.602 | 0.4143 | 0.3034 | 0.2354 | 0.1905 | 0.1577 | 0.1319 | 0.1111 |
| 3d <sub>0</sub> (3s)               | 0.643 | 0.427 | 0.2841 | 0.2202 | 0.1857 | 0.1582 | 0.1374 | 0.1223 | 0.1111 |
| 4s (4d <sub>0</sub> )              | 0.481 | 0.322 | 0.2447 | 0.1900 | 0.1432 | 0.1125 | 0.0911 | 0.0750 | 0.0625 |
| 4d <sub>0</sub> (4s)               | 0.365 | 0.280 | 0.2028 | 0.1395 | 0.1056 | 0.0879 | 0.0763 | 0.0682 | 0.0625 |
| 5s (5d <sub>0</sub> )              | 0.312 | 0.245 | 0.1571 | 0.1174 | 0.0950 | 0.0748 | 0.0598 | 0.0486 | 0.0400 |
| 5d <sub>0</sub> (5g <sub>0</sub> ) | 0.277 | 0.193 | 0.1382 | 0.1030 | 0.0762 | 0.0636 | 0.0542 | 0.0465 | 0.0400 |
| 5g <sub>0</sub> (5s)               | 0.213 | 0.166 | 0.1207 | 0.0876 | 0.0718 | 0.0566 | 0.0484 | 0.0434 | 0.0400 |
| (3d <sub>±1</sub> )                | 0.344 | 0.300 | 0.2584 | 0.2225 | 0.1921 | 0.1665 | 0.1449 | 0.1266 | 0.1111 |
| (4d <sub>±1</sub> )                | 0.263 | 0.217 | 0.1735 | 0.1403 | 0.1156 | 0.0969 | 0.0826 | 0.0714 | 0.0625 |
| (5d <sub>±1</sub> )                | 0.211 | 0.168 | 0.1288 | 0.1000 | 0.0798 | 0.0654 | 0.0548 | 0.0466 | 0.0400 |
| (5g <sub>±1</sub> )                | 0.172 | 0.135 | 0.1009 | 0.0812 | 0.0701 | 0.0604 | 0.0522 | 0.0455 | 0.0400 |
| (3d <sub>±2</sub> )                | 0.153 | 0.148 | 0.1424 | 0.1370 | 0.1316 | 0.1262 | 0.1210 | 0.1160 | 0.1111 |
| (4d <sub>±2</sub> )                | 0.126 | 0.113 | 0.0995 | 0.0878 | 0.0790 | 0.0729 | 0.0687 | 0.0653 | 0.0625 |
| (5d <sub>±2</sub> )                | 0.104 | 0.092 | 0.0772 | 0.0683 | 0.0631 | 0.0572 | 0.0510 | 0.0452 | 0.0400 |
| (5g <sub>±2</sub> )                | 0.088 | 0.076 | 0.0710 | 0.0635 | 0.0544 | 0.0481 | 0.0443 | 0.0418 | 0.0400 |
| (5g <sub>±3</sub> )                | 0.074 | 0.070 | 0.0649 | 0.0601 | 0.0555 | 0.0512 | 0.0471 | 0.0434 | 0.0400 |
| (5g <sub>±4</sub> )                | 0.047 | 0.047 | 0.0464 | 0.0454 | 0.0444 | 0.0433 | 0.0422 | 0.0411 | 0.0400 |

The state labels are those used by [17]. Those of [13] are indicated in parentheses when they differ

splitting of  $2p_{\pm 1}(\text{P})$  in  $\text{C}_{\text{diam}}$  (see Sect. 8.3.1.3), a value of effective Rydberg  $R^*_{\infty \text{d}} = (m_{\text{nt}}/\epsilon_{\text{s}}^2) R_{\infty}$  of 125.8 meV is obtained. The experimental  $3p_{\pm 1} - 2p_{\pm 1}$  spacing of the P donor spectrum in diamond is 20.2 meV (Table 6.11), or 0.1606 a.u. Using Table 5.2, this spacing is found to correspond<sup>3</sup> to  $\gamma^{1/3} \sim 0.56$ , giving a longitudinal effective mass  $m_{\text{nl}} = 1.7m_{\text{e}}$  close to the value of  $1.8m_{\text{e}}$  derived by Gheeraert et al. [21] on the basis of a self-consistent fit with EMT.

A value of the energy corresponding to the Coulomb term  $e^2/(4\pi\epsilon_0\epsilon_{\text{s}}a_{\text{0d}}^*)$  for a value of  $r$  equal to the effective Bohr radius  $a_{\text{0d}}^*$  is also given for comparison in Table 5.3. For H, this energy is 27.2 eV.

A non-variational method of calculation has been used for the determination of eigenvalues of EM-donor Hamiltonian [31]. It is based on the finite boundedness method. A review of this method can be found in [1]. This

<sup>3</sup> In Table 5.2, a  $2p_{\pm 1} - 3p_{\pm 1}$  spacing of 0.1606 a.u. corresponds also to  $\gamma^{1/3} \sim 0.72$ , but this latter value of  $\gamma^{1/3}$  does not fit the experimental  $2p_{\pm 1} - 4p_{\pm 1}$  spacing of  $\sim 0.22$  a.u.

**Table 5.2.** Same as 5.1 for the first odd-parity EM donor states

| $\gamma^{1/3}$ :          | 0.20  | 0.30  | 0.40   | 0.50   | 0.60   | 0.70   | 0.80   | 0.90   | 1.00   |
|---------------------------|-------|-------|--------|--------|--------|--------|--------|--------|--------|
| $2p_0$                    | 1.682 | 1.251 | 0.9386 | 0.7214 | 0.5661 | 0.4520 | 0.3664 | 0.3009 | 0.2500 |
| $3p_0$                    | 1.040 | 0.718 | 0.4977 | 0.3594 | 0.2694 | 0.2083 | 0.1653 | 0.1342 | 0.1111 |
| $4p_0$                    | 0.738 | 0.488 | 0.3221 | 0.2234 | 0.1622 | 0.1223 | 0.0953 | 0.0763 | 0.0625 |
| $4f_0$                    | 0.552 | 0.360 | 0.2296 | 0.1547 | 0.1158 | 0.0985 | 0.0843 | 0.0724 | 0.0625 |
| $5p_0$                    | 0.423 | 0.278 | 0.1736 | 0.1364 | 0.1094 | 0.0811 | 0.0622 | 0.0492 | 0.0400 |
| $5f_0$                    | 0.328 | 0.220 | 0.1623 | 0.1143 | 0.0797 | 0.0629 | 0.0535 | 0.0461 | 0.0400 |
| $6p_0$                    | 0.255 | 0.194 | 0.1359 | 0.0906 | 0.0746 | 0.0580 | 0.0440 | 0.0344 | 0.0278 |
| $6f_0 (6h_0)$             | 0.224 | 0.176 | 0.1113 | 0.0880 | 0.0606 | 0.0453 | 0.0382 | 0.0325 | 0.0278 |
| $6h_0 (6f_0)$             | 0.196 | 0.139 | 0.1081 | 0.0702 | 0.0544 | 0.0436 | 0.0366 | 0.0317 | 0.0278 |
| <hr/>                     |       |       |        |        |        |        |        |        |        |
| $2p_{\pm 1}$              | 0.405 | 0.384 | 0.3615 | 0.3399 | 0.3195 | 0.3003 | 0.2823 | 0.2656 | 0.2500 |
| $3p_{\pm 1}$              | 0.297 | 0.253 | 0.2106 | 0.1782 | 0.1549 | 0.1387 | 0.1272 | 0.1183 | 0.1111 |
| $2p_{\pm 1} - 3p_{\pm 1}$ | 0.108 | 0.131 | 0.1509 | 0.1617 | 0.1646 | 0.1616 | 0.1551 | 0.1482 | 0.1389 |
| $4p_{\pm 1} (4f_{\pm 1})$ | 0.233 | 0.190 | 0.1499 | 0.1237 | 0.1086 | 0.0956 | 0.0833 | 0.0721 | 0.0625 |
| $4f_{\pm 1} (4p_{\pm 1})$ | 0.189 | 0.151 | 0.1260 | 0.1114 | 0.0938 | 0.0805 | 0.0721 | 0.0666 | 0.0625 |
| $5p_{\pm 1} (5f_{\pm 1})$ | 0.156 | 0.135 | 0.1132 | 0.0876 | 0.0718 | 0.0620 | 0.0538 | 0.0464 | 0.0400 |
| $5f_{\pm 1} (5p_{\pm 1})$ | 0.142 | 0.122 | 0.0909 | 0.0726 | 0.0624 | 0.0529 | 0.0464 | 0.0425 | 0.0400 |
| $6p_{\pm 1} (6h_{\pm 1})$ | 0.129 | 0.101 | 0.0810 | 0.0666 | 0.0529 | 0.0447 | 0.0383 | 0.0326 | 0.0278 |
| $6f_{\pm 1}$              | 0.106 | 0.092 | 0.0738 | 0.0578 | 0.0496 | 0.0423 | 0.0367 | 0.0319 | 0.0278 |
| $6h_{\pm 1} (6p_{\pm 1})$ | 0.100 | 0.083 | 0.0649 | 0.0540 | 0.0439 | 0.0375 | 0.0324 | 0.0295 | 0.0278 |
| <hr/>                     |       |       |        |        |        |        |        |        |        |
| $(4f_{\pm 2})$            | 0.138 | 0.128 | 0.1157 | 0.1045 | 0.0942 | 0.0849 | 0.0466 | 0.0691 | 0.0625 |
| $(5f_{\pm 2})$            | 0.113 | 0.101 | 0.0866 | 0.0740 | 0.0639 | 0.0559 | 0.0495 | 0.0443 | 0.0400 |
| $(6f_{\pm 2})$            | 0.095 | 0.083 | 0.0688 | 0.0568 | 0.0480 | 0.0416 | 0.0363 | 0.0318 | 0.0278 |
| $(6f_{\pm 2})$            | 0.080 | 0.069 | 0.0578 | 0.0515 | 0.0453 | 0.0394 | 0.0345 | 0.0326 | 0.0278 |
| <hr/>                     |       |       |        |        |        |        |        |        |        |
| $(4f_{\pm 3})$            | 0.079 | 0.077 | 0.0753 | 0.0732 | 0.0711 | 0.0689 | 0.0667 | 0.0646 | 0.0625 |
| $(5f_{\pm 3})$            | 0.068 | 0.063 | 0.0576 | 0.0522 | 0.0479 | 0.0450 | 0.0430 | 0.0414 | 0.0400 |
| $(6f_{\pm 3})$            | 0.058 | 0.053 | 0.0469 | 0.0434 | 0.0410 | 0.0378 | 0.0343 | 0.0309 | 0.0278 |
| $(6h_{\pm 3})$            | 0.049 | 0.045 | 0.0448 | 0.0404 | 0.0355 | 0.0320 | 0.0300 | 0.0288 | 0.0278 |
| <hr/>                     |       |       |        |        |        |        |        |        |        |
| $(6h_{\pm 4})$            | 0.045 | 0.043 | 0.0413 | 0.0389 | 0.0365 | 0.0341 | 0.0319 | 0.0298 | 0.0278 |
| <hr/>                     |       |       |        |        |        |        |        |        |        |
| $(6h_{\pm 5})$            | 0.039 | 0.029 | 0.0312 | 0.0309 | 0.0303 | 0.0297 | 0.0291 | 0.0284 | 0.0278 |

The  $2p_{\pm 1} - 3p_{\pm 1}$  energy difference can be used to determine the effective Rydberg when  $\gamma$  is known, or inversely, a value of  $\gamma$  when the effective Rydberg is known

method generally gives results comparable to those obtained by the variational method, as can be evaluated from Tables 5.4 and 5.5.

A non-variational method has also been used by [25] to determine the donor energy levels in uniaxial crystals, with an application to  $4H$ -SiC. It considers first a constant-energy ellipsoid with three different electron effective masses  $m_X$ ,  $m_Y$  and  $m_Z$  along three mutually orthogonal axes, which

**Table 5.3.** Anisotropy parameters and EMT donor parameters for group IV crystals. The calculated values of the  $3p_{\pm 1} - 2p_{\pm 1}$  spacings are in units of  $R^*_{\infty d}$ . The values of  $\varepsilon_s$  in parentheses are derived self-consistently from the calculations. For diamond, the experimental value of  $\varepsilon_s$  in brackets is used to determine  $\gamma$

|                                                         | C <sub>diam</sub>   | 3C-SiC | Si             | Ge             |
|---------------------------------------------------------|---------------------|--------|----------------|----------------|
| $\gamma^{1/3} = (m_{nt}/m_{nl})^{1/3}$                  | 0.56 <sup>†</sup>   | 0.7181 | 0.5924         | 0.3718         |
| $3p_{\pm 1} - 2p_{\pm 1}$ (calc) (a.u.)                 | 0.1606 <sup>†</sup> | 0.1604 | 0.1645         | 0.1462         |
| $3p_{\pm 1} - 2p_{\pm 1}$ (exp) (meV)                   | 20.2                | 5.59   | 3.282          | 0.687          |
| $R^*_{\infty d}$ (meV)                                  | 125.8 <sup>†</sup>  | 34.85  | 19.95          | 4.70           |
| $e^2 / (4\pi\varepsilon_0\varepsilon_s a_{0d}^*)$ (meV) | 251.5               | 69.70  | 39.89          | 9.31           |
| $\varepsilon_s$ at LHeT                                 | 5.697 <sup>†</sup>  | (9.82) | (11.40) 11.40a | (15.36) 15.44b |
| $n = \sqrt{\varepsilon_s}$                              | 2.387               | 3.15   | 3.38           | 3.91           |

<sup>†</sup> See text, <sup>a</sup> [61], <sup>b</sup> [39]

is more general than the constant-energy revolution ellipsoid considered in Hamiltonian (5.5), and dielectric constants that can be different along the anisotropy axis ( $\varepsilon_{//}$ ) and perpendicular to it ( $\varepsilon_{\perp}$ ). To facilitate the computation, generalized masses  $m_1 = m_X$ ,  $m_2 = m_Y$ , and  $m_3 = \frac{\varepsilon_{//}}{\varepsilon_{\perp}} m_Z$  are considered, where the largest one defines the Oz axis and the smallest one the Oy axis. For convenience, these two generalized masses are relabelled  $m_z$  and  $m_y$ , respectively. A coordinate transformation similar to the one used to derive Hamiltonian (5.7) is:

$$\xi = \sqrt{\frac{m_x}{m_y}} x, \quad \eta = y, \quad \zeta = \sqrt{\frac{m_z}{m_y}} z$$

With spherical coordinates  $\xi = r \cos \varphi \sin \vartheta$ ,  $\eta = r \sin \varphi \sin \vartheta$  and  $\zeta = r \cos \vartheta$ , and atomic units of length  $a$  and energy  $R^*_{\infty}$  as defined below, the effective-mass Hamiltonian for a donor electron in the uniaxial crystal takes the form:

$$-\nabla^2 - \frac{2}{r \sqrt{1 - \alpha \cos^2 \vartheta - \beta \sin^2 \vartheta \cos^2 \varphi}} \quad (5.12)$$

comparable to the Hamiltonian (5.7). The atomic units of length (effective Bohr radius) and energy (effective Rydberg) are defined here as  $a = a_0 \varepsilon / m_y$  and  $R^*_{\infty} = (m_y / \varepsilon^2) R_{\infty}$ , where  $\varepsilon = \sqrt{\varepsilon_{//} \varepsilon_{\perp}}$ . In (5.11)  $\alpha = 1 - m_y / m_z \leq 1$  and  $\beta = 1 - m_y / m_x \leq \alpha$  are the two parameters describing the anisotropy (note that parameter  $\beta$  used here is different from the one of expression (5.8)). In the general case, it can be verified that the symmetry group of Hamiltonian (5.12) is  $D_{2h}$ , but for  $\beta = 0$ , it reduces to  $D_{\infty h}$ , the symmetry group of (5.7) (in that case,  $(1 - \alpha) m_y / m_z$  is identical to  $\gamma$  in Hamiltonian (5.5)). The calculations



**Table 5.4.** Calculated energies (meV) of the first odd-parity EM donor states in silicon for  $|m| = 0$  and 1. The values of the last column are obtained by a non-variational method and the corresponding states are denoted by  $nP_0$  for  $m = 0$  and  $nP_{\pm}$  for  $|m| = 1$

| State <sup>a</sup> | Energy              |                      | State <sup>b</sup> | Energy <sup>b</sup> |
|--------------------|---------------------|----------------------|--------------------|---------------------|
| $2p_0$             | 11.492 <sup>c</sup> | (11.51) <sup>a</sup> | $2P_0$             | 11.491              |
| $2p_{\pm 1}$       | 6.402               | (6.40)               | $2P_{\pm}$         | 6.401               |
| $3p_0$             | 5.485               | (5.48)               | $3P_0$             | 5.485               |
| $4p_0$             | 3.309               | (3.33)               | $4P_0$             | 3.309               |
| $3p_{\pm 1}$       | 3.120               | (3.12)               | $3P_{\pm}$         | 3.120               |
| $4f_0$             | 2.339               | (2.33)               | $5P_0$             | 2.339               |
| $5p_0$             | 2.235               | (2.23)               | $6P_0$             | 2.235               |
| $4p_{\pm 1}$       | 2.187               | (2.19)               | $4P_{\pm}$         | 2.187               |
| $4f_{\pm 1}$       | 1.894               | (1.89)               | $5P_{\pm}$         | 1.894               |
| $5f_0$             | 1.630               | (1.62)               | $7P_0$             | 1.631               |
| $6p_0$             | 1.510               | (1.52)               | $8P_0$             | 1.510               |
| $5p_{\pm 1}$       | 1.449               | (1.44)               | $6P_{\pm}$         | 1.449               |
| $5f_{\pm 1}$       | 1.260               | (1.27)               | $7P_{\pm}$         | 1.259               |
| $6f_0$             | 1.241               | (1.20)               | $9P_0$             | 1.243               |
| $6h_0$             | 1.102               | (1.10)               |                    |                     |
| $6p_{\pm 1}$       | 1.070               | (1.04)               | $8P_{\pm}$         | 1.071               |
| $7p_0$             | 1.004               |                      |                    |                     |
| $6f_{\pm 1}$       | 1.002               |                      | $9P_{\pm}$         | 1.002               |
| $7f_0$             | 0.980               | (0.98)               |                    |                     |
| $6h_{\pm 1}$       | 0.886               | (0.88)               | $10P_{\pm}$        | 0.886               |
| $7h_0$             | 0.842               |                      |                    |                     |
| $7p_{\pm 1}$       | 0.822               |                      | $11P_{\pm}$        | 0.823               |
| $8p_0$             | 0.764 <sup>d</sup>  |                      |                    |                     |
| $7f_{\pm 1}$       | 0.750               |                      | $12P_{\pm}$        | 0.750               |
| $8f_0$             | 0.733 <sup>d</sup>  |                      |                    |                     |
| $7h_{\pm 1}$       | 0.676               |                      | $13P_{\pm}$        | 0.678               |
| $8p_{\pm}$         | 0.636 <sup>d</sup>  |                      | $14P_{\pm}$        | 0.637               |
| $8f_{\pm 1}$       | 0.596 <sup>d</sup>  |                      | $15P_{\pm}$        | 0.596               |
| $8h_{\pm 1}$       | 0.566 <sup>d</sup>  |                      | $16P_{\pm}$        | 0.566               |

<sup>a</sup> [17], <sup>b</sup> [7], <sup>c</sup> [26], <sup>d</sup> Broeckx and Clauws, unpublished results

for  $\beta = 0$  have been performed in [25] by the same non-variational method as that used in [51] for the acceptors in cubic semiconductors, with  $\gamma^{1/3}$  as a parameter. The obtained energy levels are close to those defined of [13], given in Tables 5.1 and 5.2.

The energies of the odd-parity states of donors in silicon calculated by variational and non-variational methods are given in Table 5.4.

**Table 5.5.** Comparison of the calculated energies (meV) of odd-parity EM donor states in germanium. The values of the last column are obtained by a non-variational method and the corresponding states are denoted by  $nP_0$  for  $m = 0$  and  $nP_{\pm}$  for  $m = \pm 1$

| State <sup>a</sup> | Energy <sup>b</sup> |                     | State <sup>c</sup> | Energy <sup>c</sup> |
|--------------------|---------------------|---------------------|--------------------|---------------------|
| $2p_0$             | 4.776               | (4.74) <sup>a</sup> | $2P_0$             | 4.750               |
| $3p_0$             | 2.586               | (2.56)              | $3P_0$             | 2.573               |
| $2p_{\pm 1}$       | 1.729               | (1.726)             | $2P_{\pm}$         | 1.720               |
| $4p_0$             | 1.696               | (1.67)              | $4P_0$             | 1.689               |
| $4f_0$             | 1.220               | (1.16)              | $5P_0$             | 1.217               |
| $3p_{\pm 1}$       | 1.042               | (1.03)              | $3P_{\pm}$         | 1.037               |
| $5p_0$             | 0.93                | (0.84)              | $6P_0$             | 0.928               |
| $5f_0$             | 0.80                | (0.80)              | $7P_0$             | 0.800               |
| $4p_{\pm 1}$       | 0.753               | (0.73)              | $4P_{\pm}$         | 0.750               |
| $6p_0$             | 0.73                | (0.61)              | $8P_0$             | 0.735               |
| $4f_{\pm 1}$       | 0.609               | (0.61)              | $5P_{\pm}$         | 0.607               |
| $6f_0$             | 0.58                | (0.55)              |                    |                     |
| $5p_{\pm 1}$       | 0.573               | (0.53)              | $6P_{\pm}$         | 0.573               |
| $6h_0$             | 0.55                |                     |                    |                     |
| $5f_{\pm 1}$       | 0.465               | (0.41)              | $7P_{\pm}$         | 0.467               |
| $6p_{\pm 1}$       | 0.397               | (0.38)              | $8P_{\pm}$         | 0.399               |
| $6f_{\pm 1}$       | 0.379               | (0.32)              | $9P_{\pm}$         | 0.384               |
| $6h_{\pm 1}$       | 0.318               | (0.29)              | $10P_{\pm}$        | 0.328               |
| $7p_{\pm 1}$       | 0.308               |                     | $11P_{\pm}$        | 0.313               |
| $7f_{\pm 1}$       | 0.29                |                     | $12P_{\pm}$        | 0.290               |
| $7h_{\pm 1}$       |                     |                     | $13P_{\pm}$        | 0.282               |

<sup>a</sup> [17], <sup>b</sup> [13, 16], <sup>c</sup> [7]

One can note the good agreement between the values obtained by the variational and non-variational methods. The difference between Faulkner's and Janzén et al.'s values is only a matter of accuracy.

The energies of the odd-parity levels of donors in germanium calculated by variational and non-variational methods are given in Table 5.5.

The energy levels from  $13P_{\pm}$  (0.282 meV) to  $17P_{\pm}$  (0.207 meV) have also been calculated in [7].

For the odd-parity levels of donors in germanium, the difference in the values obtained by the two methods never exceed a few percent, but the discrepancies with Faulkner's values are larger for the shallowest excited states. They can reach the values of the spacings between excited levels (see for instance,  $6h_{\pm 1}$ ), and their origins have already been discussed. For  $n > 2$ , one observes a slight difference between silicon and germanium in the ordering of the  $np_0$  and  $nf_0$  levels with respect to the odd-parity levels with  $|m| = 1$ .

As will be seen later, the calculations of the donor levels based on the one-valley approximation give values of the energy levels in good agreement with the experimental ones as long as the impurity potential can be fitted to a Coulomb potential screened by the static dielectric constant of the crystal, and as long as the actual symmetry of the donor wave functions related to the point group symmetry of the crystal is ignored. This conjunction was met for the odd-parity states, but the situation is different for the even-parity states, at least for the first ones and the degeneracy of the  $CB$  electrons needs to be introduced in that case. For further comparisons, Table 5.6 gives the one-valley values of the first even-parity donor levels for silicon and germanium.

The experimental ionization energies of all the substitutional group-V donors in silicon and germanium are larger than the energies of the  $1s$  levels calculated in the one-valley EMA, as shown from the comparison with the  $1s$  ( $A_1$ ) values of Table 5.9. For shallow donors in diamond, with  $\gamma^{1/3} = 0.56$  and  $R^*_{\infty d} = 125.8 \text{ meV}$  taken from Table 5.3, the  $1s$  and  $2s$  EM energies interpolated from Table 5.1 are 205.8 and 60.4 meV, respectively.

For double donors, a scaling with the  $\text{He}^0$  and  $\text{He}^+$  energy levels of helium can be used to obtain the one-valley energy levels for the ground state. The ratios of the ground-state energy levels of  $\text{He}^0$  and  $\text{He}^+$  with that of H are 1.808 and 4.002, respectively and we assume that the same ratios also hold for EM donors. For silicon, with a calculated H-like donor ground state of 31.26 meV, the corresponding one-valley ground states for  $\text{He}^0$ -like and  $\text{He}^+$ -like donors are 56.52 and 125.10 meV, respectively.

**Table 5.6.** One-valley energies (meV) of the first even-parity donor states in silicon and germanium [13], extrapolated to states with  $\ell > 0$ . The values in parentheses are those of [26] for silicon and those of [17] for germanium

| State label <sup>a</sup> | Silicon            |          | Germanium         |        |
|--------------------------|--------------------|----------|-------------------|--------|
| $1s$                     | 31.26 <sup>b</sup> | (31.262) | 9.84 <sup>b</sup> | (9.81) |
| $2s$                     | 8.86               | (8.856)  | 3.60              | (3.52) |
| $3s$                     | 4.78               | (4.777)  | 2.15              | (2.01) |
| $3d_{\pm 1}$             | 3.87               | (3.874)  | 1.27              |        |
| $3d_0$                   | 3.75               | (3.751)  | 1.48              | (1.34) |
| $4s$                     | 2.91               | (2.911)  | 1.21              | (1.17) |
| $3d_{\pm 2}$             | 2.63               | (2.632)  | 0.68              |        |
| $4d_{\pm 1}$             | 2.34               | (2.338)  | 0.87              |        |
| $4d_0$                   | 2.14               | (2.141)  | 1.07              |        |
| $5s$                     | 1.93               | (1.929)  | 0.83              | (0.72) |
| $5d_{\pm 1}$             | 1.62               | (1.617)  | 0.65              |        |
| $4d_{\pm 2}$             | 1.59               | (1.587)  |                   |        |
| $5d_0$                   | 1.55               | (1.546)  | 0.69              | (0.61) |
| $5g_0$                   | 1.46               | (1.458)  | 0.64              | (0.53) |

<sup>a</sup> [17], <sup>b</sup> [16]

The experimental ionization energies of P in diamond and of N in 3C-SiC are 604 and 51.19 meV, respectively, compared with the one-valley  $1s$  energies of 206 and 47.2 meV, respectively. For N at the hexagonal site in 4H-SiC, the measured ionization energy is 61.4 meV, and it can be compared with the general value derived from the one-valley Hamiltonian, which is just discussed below.

In 4H-SiC, the  $CB$  minimum is at the M point on the surface of the BZ of the hexagonal lattice, along one of the three equivalent directions  $[\bar{1}100]$ ,  $[0\bar{1}10]$  and  $[10\bar{1}0]$  (Figure B.1 of Appendix B), and it is thus triply degenerate. The three electron effective masses at this point are different: in units of  $m_e$ , their values by decreasing order are  $m_{\Gamma M} = 0.58$ ,  $m_{ML} = 0.33$  and  $m_{MK} = 0.31$ , along the  $\Gamma$ -M, M-L and M-K directions, respectively. The relevant values of the dielectric constants are  $\varepsilon_{//} = 10.36$  and  $\varepsilon_{\perp} = 9.55$ , such that the parameters  $\alpha = 1 - m_{MK}/m_{\Gamma M}$  and  $\beta = 1 - (\varepsilon_{\perp}/\varepsilon_{//}) (m_{MK}/m_{ML})$  of Hamiltonian (5.12) are 0.466 and 0.098, respectively. In the general case, the donor energy levels have to be calculated with Hamiltonian (5.12), with no assumption made on the site of the donor atom. As for  $D_{\infty h}$  symmetry, the eigenfunctions of (5.12) are expanded for the point group  $D_{2d}$  in the series of normalized spherical harmonics  $\frac{U_{\ell,n}^m(r)}{r} Y_{\ell,m}(\theta, \varphi)$ , where  $\frac{U_{\ell,n}^m(r)}{r}$  are the coefficients in the expansion [25]. They involve linear combinations of spherical harmonics whose parities  $(-1)^\ell$  and parities of quantum number  $m$  depend on the  $IR$  of  $D_{2d}$  considered. Each wave function has a definite parity, but different values of  $m$ . The basis wave functions for the  $\Gamma_1^+$   $IR$  of  $D_{2d}$  involve spherical harmonics with both  $\ell$  and  $m$  even and within the one-valley approximation,  $\Gamma_1^+$  is the  $IR$  corresponding to the  $nS$  states. The parity- and symmetry-allowed electric dipole transitions from the  $1S$  ground state are only possible towards levels whose wave functions transform as basis functions of the  $IRs$   $\Gamma_2^-$ ,  $\Gamma_3^-$ , and  $\Gamma_4^-$  of  $D_{2d}$ . The spherical harmonics that are basis functions for  $\Gamma_2^-$ ,  $\Gamma_3^-$ , and  $\Gamma_4^-$   $IRs$  involve only  $(\ell \text{ odd}, m \text{ odd})$ ,  $(\ell \text{ odd}, m \text{ even})$ , and  $(\ell \text{ odd}, m \text{ odd})$  values of  $\ell$  and  $m$ , respectively. For  $\Gamma_3^-$ , these basis functions correspond to  $nP_0$  states, for  $\Gamma_2^-$ , to  $nP_-$  states, and for  $\Gamma_4^-$ , to  $nP_+$  states [25]. The main difference with the  $D_{\infty h}$  symmetry is the splitting of the  $np_{\pm 1}$  states. The calculated binding energies of the deepest EM donor levels in 4H-SiC corresponding to the four  $IRs$  of  $D_{2d}$  of interest are displayed in Table 5.7 (see [25] for the details of the calculation). A table including the first ten binding energies of the states associated with all the  $IRs$  can be found in the above reference. The levels are labelled considering the value of  $\ell$  with the largest weight in the term  $Y_{\ell,m}(\theta, \varphi) \pm Y_{\ell,-m}(\theta, \varphi)$  in the expansion of the wave function, and the subscript indicates the corresponding value of  $|m|$  (1 is omitted). The “+” and “-” subscripts of the  $P$  states are used only in a somewhat arbitrary fashion to indicate  $P_+$  as the state with the highest energy.

The one-valley ionization energies of the donors are a relatively small fraction of the energy gaps of the semiconductors: their ratios are 0.028, 0.015,

**Table 5.7.** Calculated binding energies (meV) of the five deepest donor states in 4H-SiC for each of the *IRs* involved in the optical transitions after [25]

| <i>S</i> -like ( $\Gamma_1^+$ ) |       | <i>P</i> <sub>0</sub> -like ( $\Gamma_3^-$ ) |       | <i>P</i> <sub>+</sub> -like ( $\Gamma_4^-$ ) |       | <i>P</i> <sub>-</sub> -like ( $\Gamma_2^-$ ) |       |
|---------------------------------|-------|----------------------------------------------|-------|----------------------------------------------|-------|----------------------------------------------|-------|
| 1 <i>S</i>                      | 53.99 | 2 <i>P</i> <sub>0</sub>                      | 15.67 | 2 <i>P</i> <sub>+</sub>                      | 12.79 | 2 <i>P</i> <sub>-</sub>                      | 12.25 |
| 2 <i>S</i>                      | 13.72 | 3 <i>P</i> <sub>0</sub>                      | 7.046 | 3 <i>P</i> <sub>+</sub>                      | 5.735 | 3 <i>P</i> <sub>-</sub>                      | 5.504 |
| 3 <i>D</i> <sub>0</sub>         | 6.781 | 4 <i>P</i> <sub>0</sub>                      | 4.044 | 4 <i>F</i> <sub>+</sub>                      | 3.672 | 4 <i>F</i> <sub>-</sub>                      | 3.559 |
| 3 <i>S</i>                      | 5.998 | 4 <i>F</i> <sub>0</sub>                      | 3.649 | 4 <i>P</i> <sub>+</sub>                      | 3.238 | 4 <i>P</i> <sub>-</sub>                      | 3.114 |
| 3 <i>D</i> <sub>2</sub>         | 5.386 | 4 <i>F</i> <sub>2</sub>                      | 3.358 | 4 <i>F</i> <sub>+3</sub>                     | 2.979 | 4 <i>P</i> <sub>-3</sub>                     | 2.978 |

0.022, and 0.035 for silicon, germanium, 3C-SiC, and diamond, respectively and they are dominated by the influence of the effective masses and dielectric constant, justifying the initial assumptions of the model.

### 5.2.2 Conduction Band Degeneracy

The absolute *CB* minima of the indirect-band-gap crystals show an orientational degeneracy in *k*-space (see Table 3.4) which translates on the EM donor levels in these crystals. The donor optical spectra show that in the case of the first *ns* donor states, this multi-valley degeneracy is broken and the resultant splitting of the levels must be accounted for satisfactorily by theory. This degeneracy is also of fundamental importance in explaining the splitting of the donor spectra when an external uniaxial perturbation, like a magnetic field or a uniaxial stress, is applied to a crystalline sample.

When all the equivalent minima of the *CB* are considered, the wave functions  $\psi^{(j)}(r)$  where index *j* corresponds to a given *CB* minimum are degenerate eigenfunctions of a Hamiltonian corresponding to (5.5). In this case, the total wave functions of an eigenstate span as a basis for a representation of the symmetry point group *T<sub>d</sub>* of the tetrahedrally bonded substitutional donor. In silicon, for instance, there are six equivalent one-valley wave functions that transform as *x*, *-x*, *y*, *-y*, *z* and *-z* under the symmetry operations of *T<sub>d</sub>* (the character table of this group is given in Table B.4 of appendix B). The values of the characters of this representation for the different symmetry operation classes of *T<sub>d</sub>* are 6 (*E*), 0 (8*C*<sub>3</sub>), 2 (3*C*<sub>2</sub>), 0 (6*S*<sub>4</sub>) and 2 (6σ<sub>*d*</sub>). This representation then reduces into the *IRs* *A*<sub>1</sub> + *E* + *T*<sub>2</sub> (or  $\Gamma_1 + \Gamma_3 + \Gamma_5$ , in Koster's notations) of *T<sub>d</sub>* for the states with  $|m| = 0$  (*ns*, *np*<sub>0</sub>, *nd*<sub>0</sub>, etc.). For the states with  $|m| = 1$ , it can be shown [49] that because of the additional twofold degeneracy associated with  $|m|$ , the *IRs* associated with these states are 2*T*<sub>1</sub> + 2*T*<sub>2</sub> (or 2*Γ*<sub>4</sub> + 2*Γ*<sub>5</sub>). For donors in germanium, with four equivalent ellipsoids along the  $\langle 111 \rangle$  axes, the *IRs* for the states with  $|m| = 0$  and  $|m| = 1$  are *A*<sub>1</sub> + *T*<sub>2</sub> and *E* + *T*<sub>1</sub> + *T*<sub>2</sub>, respectively. The wave functions including degeneracy are thus expressed as:

$$\psi_{n\ell} = \sum_{j=1}^N \alpha^{(j)} F_{n\ell}^{(j)}(r) \varphi_{k(j)}(r) = \sum_{j=1}^N \alpha^{(j)} \psi_n^{(j)}(r) \quad (5.13)$$

**Table 5.8.** Coefficients  $\alpha^{(j)}$  of the one-valley wave functions in the total donor electron wave functions corresponding to different  $IRs$  in silicon, diamond and germanium for levels with  $m = 0$ . They include the normalization coefficient

|                       |                |                                      |
|-----------------------|----------------|--------------------------------------|
| Si, C <sub>diam</sub> | A <sub>1</sub> | $(1, 1, 1, 1, 1, 1)/\sqrt{6}$        |
|                       | E              | $((-1, -1, -1, -1, 2, 2)/\sqrt{12})$ |
|                       |                | $(1, 1, -1, -1, 0, 0)/2$             |
|                       |                | $((1, -1, 0, 0, 0, 0)/\sqrt{2})$     |
|                       | T <sub>2</sub> | $(0, 0, 1, -1, 0, 0)/\sqrt{2}$       |
|                       |                | $(0, 0, 0, 0, 1, -1)/\sqrt{2})$      |
| Ge                    | A <sub>1</sub> | $(1, 1, 1, 1)/2$                     |
|                       |                | $((1, 1, -1, -1)/2$                  |
|                       | T <sub>2</sub> | $(1, -1, -1, 1)/2$                   |
|                       |                | $(1, -1, 1, -1)/2)$                  |

where  $N$  is the number of equivalent valleys. For the  $ns$  and  $np_0$  donors states in silicon, there are six different linear combinations similar to (5.13) corresponding to the dimensions of the  $IRs$  (one for  $A_1$ , two for  $E$  and three for  $T_2$ ) and four in the case of germanium (one for  $A_1$  and three for  $T_2$ ). The symmetry-dependent coefficients  $\alpha^{(j)}$  of the wave functions (5.13) are given in Table 5.8.

The combined effect of the multi-valley degeneracy and the interactions of the donor electron at and near from the donor ion site are generally called valley-orbit coupling. Logically, the result of this coupling is the valley-orbit splitting. The  $ns$  envelope wave functions are non-zero for  $r = 0$ , and because the wave function associated with the different  $CB$  minima are in phase for the  $ns$  ( $A_1$ ) states, the interaction between the substitutional donor electron and the donor ion is expected to be more significant for this configuration than for  $ns(E)$  and  $ns(T_2)$ . The expected result is the lifting of degeneracy, more pronounced for  $1s$  because of the relatively stronger localization of the wave function near from and at  $r = 0$ , where the screened potential assumption no longer holds. A qualitative estimate of the  $1s$  donor splitting in silicon has been made by Kohn and Luttinger [34] using a tight-binding approximation for the functions  $\psi_{1s}^{(i)}(r)$  in the vicinity of the donor ion. It consists in taking for these functions a linear combination of  $s$  and  $p$  radial atomic donor wave functions with adequate coefficients, and to express the wave functions (5.13) accordingly. Within this approximation, the  $\psi(1s(A_1))$  wave function is a linear combination of atomic  $s$  wave functions (the terms with the  $p$  wave functions cancel out because of the symmetry of the coefficient of the  $p$  atomic functions). As a consequence, the interaction between the electron and the donor is the largest for this  $1s(A_1)$  state and it is thus expected to be the deepest in energy. Similarly, as the two  $\psi(1s(E))$  wave functions are identically zero, they should be the less perturbed of the  $1s$  wave functions in the vicinity of the donor, and the  $1s(E)$  state should be the shallowest of the

1s states. The three  $\psi(1s(T_2))$  include only the  $p$  wave functions, and the  $1s(T_2)$  level should be somewhat deeper than the  $1s(E)$  state. This is borne out by experiments, with the energy of the  $1s(E)$  state not too different from the one calculated using the one-valley approximation, and the  $1s(T_2)$  ground state slightly higher in energy.

The value of  $\psi(1s)$  at  $r = 0$  for a given donor can be estimated from the splitting of the ESR line due to the interaction between the electronic and nuclear spins mentioned in Sect. 1.3.5, and this point is discussed in the review [33]. This property distinguishes between donors whose ground state has  $1s(A_1)$  symmetry, with values of  $|\psi(1s)(0)|^2$  much larger than those with  $1s(T_2)$  symmetry.

A quantitative treatment of the splitting of the degenerate  $1s$  donor state considering intervalley coupling was provided by Baldereschi [2]. The coupling terms between equivalent valleys, that can be ignored for odd-parity states, must be considered and they contain a  $\mathbf{k}$ -dependent dielectric constant  $\varepsilon_{ij} = \varepsilon(\mathbf{k}_i - \mathbf{k}_j)$  where the wave vectors correspond to the minima of the equivalent valleys. When coupling is neglected,  $\mathbf{k}_i = \mathbf{k}_j$  and  $\varepsilon_{ij}$  reduces to  $\varepsilon_s$ , but for  $\mathbf{k}_i \neq \mathbf{k}_j$ , this  $\mathbf{k}$ -dependent dielectric constant, calculated earlier for silicon and germanium [44], must be used. For instance, in silicon, the EM equation of a donor electron for valley 1 with a wave vector  $\mathbf{k}_1$ , taken along the  $x$  axis can be written as:

$$\left[ \frac{(p_x - \hbar k_1)^2}{2m_l} + \frac{p_y^2 + p_z^2}{2m_t} - \frac{e^2}{4\pi\varepsilon_0\varepsilon_s r} \right] f_1(r) - \sum_{j \neq 1}^5 \frac{e^2}{4\pi\varepsilon_0\varepsilon(\mathbf{k}_1 - \mathbf{k}_j)} f_j(r) = E f_1(r) \quad (5.14)$$

together with five similar equations for the other valleys. Equation (5.14) has the symmetry of the silicon host crystal, and depends on the valley wave vectors for both the kinetic and potential energy terms. The values of  $\varepsilon(\mathbf{k})$  decrease with increasing  $k$  and this takes partially into account the change from a fully screened potential far from the impurity ( $\mathbf{k} = 0$ ) to a bare potential for higher values of  $k$ . Baldereschi performed the calculations for silicon by considering for the valley a minimum located at  $\mathbf{k}_x = (2\pi/a)(x, 0, 0)$  along the  $\Delta$  direction of the  $BZ$  (actually  $\mathbf{k}_x = 0.84\mathbf{k}_X$ ) and a  $1s$  state with the classical anisotropic one-valley wave function with two variational parameters. The coupling term in (5.14), including the dielectric functions with  $\mathbf{k} = (2\pi/a)(2x, 0, 0)$  and  $(2\pi/a)(x, x, 0)$  calculated from the values of [45] was treated as a perturbation. As expected from the experimental results, a splitting of the  $T_2$  and  $A_1$  levels from the  $E$  level was found for the domain of variation of  $x$  investigated ( $\sim 0.55-1$ ). Moreover, the magnitude of the  $1s(E) - 1s(A_1)$  splitting for  $x = 0.84$  was about one order of magnitude larger than the one for  $1s(E) - 1s(T_2)$  observed experimentally. More accurate values of these splittings, that are also dependent on the chemical nature of the donors, have been obtained by calculations involving the atomic potential near from and at the donor site and they will be discussed in due time. A similar result was also

**Table 5.9.** Comparison between the experimental values and spacings (meV) of the  $1s$  manifold energy levels showing the amplitude of the valley-orbit/chemical splittings of the group-V donors in silicon and germanium and the calculated values of [2], where no chemical effect is included. More accurate experimental values of the  $E(1s(A_1))$  are given in Tables 6.3 and 6.7

|    |                     | P     | As    | Sb               | Bi                | Calc.              |
|----|---------------------|-------|-------|------------------|-------------------|--------------------|
| Si | $1s(A_1)$           | 45.58 | 53.76 | 42.77            | 70.88             | 31.26 <sup>a</sup> |
|    | $1s(A_1) - 1s(T_2)$ | 11.70 | 21.1  | 9.8 <sup>b</sup> | 38.4 <sup>b</sup> | 10.6               |
|    | $1s(T_2) - 1s(E)$   | 1.33  | 1.4   | 1.4 <sup>b</sup> | 2.6 <sup>b</sup>  | 1.1                |
| Ge | $1s(A_1)$           | 12.89 | 14.19 | 10.32            | 12.81             | 9.84 <sup>a</sup>  |
|    | $1s(A_1) - 1s(T_2)$ | 2.81  | 4.12  | 0.32             | 2.85              | 0.6                |

<sup>a</sup> One-valley values of Table 5.6, <sup>b</sup> Average of spin-split levels

obtained for germanium, but the splitting by a smaller order of magnitude is to be correlated with a smaller intervalley coupling. This difference can be understood in view of the larger spread of the donor ground state wave function in the real space in germanium, compared to silicon. A comparison between the experimental values and the calculations of [2] is given in Table 5.9. The valley-orbit/chemical splittings  $1s(A_1) - 1s(T_2)$  of germanium and  $1s(A_1) - 1s(E)$  of silicon are sometimes denoted by  $4\Delta_c$  and  $6\Delta_c$ , respectively, after [48].

For P in diamond, the experimental value for  $1s(A_1)$  is 604.0 meV. The calculated one-valley  $1s$  energy is 205.8 meV, and this value should be close to the energy of the  $1s(E)$  level, while the  $1s(T_2)$  level could be 5–10 meV deeper. A lifting of the degeneracy is, in principle, possible for the odd-parity states, but the envelope functions of these states are zero at  $r = 0$  and they are spread out in a large volume of the crystal so that multi-valley effects expected for these states are very small. It will be seen later that for the odd-parity states, there is indeed a very good agreement between experiment and the results of the calculations with the one-valley approximation. Quantitatively, the experimental energies of the  $ns$  states other than  $ns(A_1)$  are not too different from the ones obtained in the one-valley calculations, and this also includes the  $1s$  state.

Calculations of realistic ground state energies of donors and of the valley-orbit splitting have been undertaken (see [47], and references therein). Ground state energies have been calculated by considering a more appropriate dielectric screening and taking into account the lattice distortion at the donor atom site, and they will be compared with the experimental results. The above results concerning the ordering of the valley-orbit split of  $1s$  levels are valid for substitutional donors as it turns out that for interstitial Li in silicon and germanium, it has been found experimentally that the  $1s(A_1)$  state was the shallowest one.

The question of the long-range changes in the eigenvalues of the one-valley Hamiltonian (5.5) produced by the lattice deformation arising from



the introduction of the donor atom in an otherwise perfect lattice has been addressed by Stoneham [58]. The basis of the method is to derive the perturbation potential induced by the foreign atom as a function of the  $CB$  deformation potentials  $\Xi_d$  and  $\Xi_u$ , assumed to be the same as those for weakly bound electrons, and of the actual strain at the donor site. The diagonal terms of this perturbation, when added to (5.5), can be computed as a function of the actual strains at the donor site. The results can be obtained by numerical integration and expressed in terms of a small number of constants (the deformation potentials, elastic constants and effective-mass Bohr radii for the donor electron), a cut-off to describe the short-range variation of the strain, and the volume change  $\Delta V$  induced by the donor atom in a large finite crystal. Every energy level is expected to be shifted by this perturbation; the deeper the level, the stronger is the shift observed. To see if such shifts can be detected in practice, one should compare the splitting between the excited levels calculated from the point-charge Hamiltonian (5.5) with the experimental one.

In the above discussion of the electronic structure of the donor levels, the electron spin has been neglected. It has been, however, proven necessary to introduce the spin-orbit coupling to explain the observation of parity-forbidden transitions for donors with relatively deep  $1s$  ( $A_1$ ) ground states. Using the double group representation of  $T_d$ , it is found (see Table B.4 of appendix B) that the simple representations  $A_1$  and  $E$  transform into the  $\Gamma_6$  and  $\Gamma_8$  double representations, respectively and that  $T_2$  transforms into  $\Gamma_7 + \Gamma_8$ . Electric-dipole transitions are symmetry-allowed between  $A_1$  ( $\Gamma_6$ ) and the two  $T_2$  ( $\Gamma_7$ ) and  $T_2$  ( $\Gamma_8$ ) levels.

Valley-orbit splitting has also been investigated in the case of donors in  $4H$ -SiC. In this material, a donor atom can occupy a hexagonal ( $h$ ) site, with local symmetry  $C_{3v}$ , or a quasi-cubic site with symmetry close to  $T_d$  (see Appendix B). The case when a N donor atom sits on the  $h$  site of the C sublattice has been analyzed by Ivanov et al. [24]. Similarly, for crystals with  $T_d$  symmetry, as a result of the threefold degeneracy of the  $CB$  band of  $4H$ -SiC, the total wave functions of an eigenstate, whose expressions are similar to (5.13), are threefold degenerate. They form a basis for the representation of the  $C_{3v}$  point group, which comprises two 1D IRs  $\Gamma_1$  and  $\Gamma_2$  and one 2D IR  $\Gamma_3$ . Also, in the one-valley approximation, the shallow donor states in  $4H$ -SiC can be separated into  $S$ ,  $P_0$ ,  $P_+$  and  $P_-$  states, respectively, associated with the IRs  $\Gamma_1^+$ ,  $\Gamma_3^-$ ,  $\Gamma_4^-$  and  $\Gamma_2^-$  of the  $D_{2d}$  symmetry group of the one-valley Hamiltonian. At a  $h$  site, the total wave function of the donor electron transforms as a representation of the  $C_{3v}$  point group, which can be deduced from the transformation properties of the one-valley wave functions under the symmetry operations of  $C_{3v}$ . As a result, for the  $S$ ,  $P_0$  and  $P_+$  states, the resulting reducible representation of  $C_{3v}$  is  $\Gamma_2 + \Gamma_3$ , and for the  $P_-$  state, it is  $\Gamma_1 + \Gamma_3$ . For the  $1S$  state, the valley-orbit coupling splits the  $1S$  ( $\Gamma_2 + \Gamma_3$ ) state into the non-degenerate  $1S$  ( $\Gamma_2$ ) and doubly degenerate  $1S$  ( $\Gamma_3$ ) levels, the ground state being  $1S$  ( $\Gamma_2$ ). A fit of the spectroscopic data is less simple than in the case of donors in silicon and germanium, because the experimental

results are scarce. It gives for N at the  $h$  site energies of 61.37 and 53.9 meV for the  $1S(\Gamma_2)$  and  $1S(\Gamma_3)$  states, respectively [25].

For  $C_{3v}$  symmetry, the  $z$  component of the dipole moment transforms as  $\Gamma_1$  and the  $x$  and  $y$  components as  $\Gamma_3$ . As a consequence, for  $\mathbf{E} // c$  ( $z$  component), the parity-allowed transitions from  $1S(\Gamma_2)$  are toward the odd-parity states belonging to the  $\Gamma_2$  IR; from  $1S(\Gamma_3)$ , they are toward the odd-parity states belonging to the  $\Gamma_3$  IR. For  $\mathbf{E} \perp c$  ( $x$  and  $y$  components), the parity-allowed transitions from  $1S(\Gamma_2)$  are toward the odd-parity states belonging to the  $\Gamma_3$  IR, and from  $1S(\Gamma_3)$  toward the odd-parity states belonging to the  $\Gamma_1$ ,  $\Gamma_2$  and  $\Gamma_3$  IRs. Evidently, symmetry-allowed transitions are also possible from the  $1S$  states toward the even-parity states with appropriate symmetry.

### 5.2.3 The Quasi-Hydrogenic Case

In direct-gap semiconductors where the  $CB$  minimum lies at  $\mathbf{k} = 0$ , the donor states are not degenerate in  $k$ -space. This is the case for many III-V and II-VI compounds (GaAs, InP, and ZnTe fall in this category). Another important characteristic of some of these materials is that the electron effective mass can be considered in a first approximation as spherical, corresponding to a parabolic  $CB$ . In semiconductors with an anisotropy axis like the wurtzite-type materials, one usually considers  $m_{n//}$ , corresponding to optical properties measured with  $\mathbf{E}$  parallel to this axis and  $m_{n\perp}$ , corresponding to optical properties measured with  $\mathbf{E}$  perpendicular to this axis, but for a parabolic  $CB$ , these two quantities should be the same. In direct-gap cubic semiconductors, the effective Rydberg for the EM donors  $R^*_{\infty d} = R_{\infty} m_n / \varepsilon_s^2$  can be taken as a reasonable approximation of the ground state energy of the donor electron, but the actual value of  $R^*_{\infty d}$  depends critically on  $\varepsilon_s$ . The energy of the  $n$ th excited state is then  $R^*_{\infty d} / n^2$  and the energies of the  $1s \rightarrow np$  transitions are given by the modified expression  $R^*_{\infty d} (1 - 1/n^2)$  of the Lyman series for the H atom. The calculated energies of the first donor lines in InSb, GaAs, InP, ZnSe and CdTe are given in Table 5.10.

The effective Rydberg values for GaAs and InP in this table differ slightly from the ones 5.74 and 7.33 meV, respectively) given by [56].

Departure from the  $CB$  parabolicity results in a non-isotropic effective mass, whose value depends on the electron energy  $E$  in the  $CB$ . This is the main reason for the spread in the values of  $m_n$  reported for semiconductors with  $CB$  minimum at  $\mathbf{k} = 0$ , another being polaron coupling. Non-parabolicity has been addressed *inter alia* for  $w$ -GaN, without reference to a difference between  $m_{n//}$  and  $m_{n\perp}$ . The most recent results give  $m_{n0} = 0.208 m_e$  at the  $CB$  edge ( $E = 0$ ) and the increase of  $m_n$  with  $E$  is given empirically by  $m_n = m_{n0} (1 + 2KE/E_g)$ , with  $K = 2.5$  for GaN [60].

For  $c$ -GaN, the effective Rydberg value calculated for  $m_n = 0.19 m_e$  and  $\varepsilon_s = 9.5$  is 28.6 meV. For  $w$ -GaN, a difference between  $m_{n//}$  and  $m_{n\perp}$  would produce a splitting of the  $n = 2$  level into  $2s$ ,  $2p_0$  and  $2p_{m=\pm 1}$  states. Calculations including central-cell corrections have been performed by [42], resulting in Table 5.11.

**Table 5.10.** Calculated EM transition energies (meV ( $\text{cm}^{-1}$  in parentheses)) from the  $1s$  state to the first np quasi-hydrogenic donor levels of five compounds with the sphalerite structure.  $E_{np}$  is  $R^*_{\infty d}/n^2$ . For InSb, GaAs, and InP,  $\varepsilon_s$  at low temperature is taken as 17, 12.4, and 12.2, respectively, and  $m_n/m_e$  is taken from Table 3.6. Experimental  $1s \rightarrow 2p$  transition energies are given in Table 6.37

|                       | InSb         | GaAs          | InP           | CdTe                    | ZnSe                    |
|-----------------------|--------------|---------------|---------------|-------------------------|-------------------------|
| $1s \rightarrow 2p$   | 0.491 (3.96) | 4.393 (35.43) | 5.417 (43.69) | 9.87 (79.5)             | 19.3 (155)              |
| $E_{2p}$              | 0.163        | 1.465         | 1.805         | 3.28                    | 6.43                    |
| $1s \rightarrow 3p$   | 0.582 (4.69) | 5.207 (42.00) | 6.420 (51.78) | 11.7 (94.2)             | 22.8 (184)              |
| $E_{3p}$              | 0.073        | 0.651         | 0.802         | 1.46                    | 2.86                    |
| $1s \rightarrow 4p$   | 0.614 (4.95) | 5.492 (44.29) | 6.771 (54.61) | 12.3 (99.4)             | 24.1 (194)              |
| $E_{4p}$              | 0.041        | 0.366         | 0.451         | 0.82                    | 1.6                     |
| $R^*_{\infty d}, E_i$ | 0.654 (5.28) | 5.858 (47.25) | 7.222 (58.25) | 13.1 (106) <sup>a</sup> | 25.7 (207) <sup>b</sup> |

<sup>a</sup> [54], <sup>b</sup> [12]

**Table 5.11.** Calculated energies (meV) of the first donor transitions in GaN for different chemical donors [42]

|                             | <i>c</i> -GaN |      |      | <i>w</i> -GaN |      |      |
|-----------------------------|---------------|------|------|---------------|------|------|
|                             | Si            | O    | C    | Si            | O    | C    |
| $1s (E_i)$                  | 29.5          | 30.4 | 32.5 | 30.4          | 31.4 | 32.7 |
| $1s \rightarrow 2p_{\pm 1}$ | 21.8          | 22.7 | 24.4 | 22.3          | 23.3 | 25.1 |
| $1s \rightarrow 2p_0$       |               |      |      | 22.8          | 23.7 | 25.6 |
| $1s \rightarrow 3p_0$       | 26.1          | 26.9 | 29.0 | 27.0          | 28.0 | 30.1 |

The splitting between the  $1s \rightarrow 2p_{\pm 1}$  and  $1s \rightarrow 2p_0$  transitions is due to the difference between the values of  $m_{n//}$  and  $m_{n\perp}$  used for the calculation ( $0.19m_e$  and  $0.22m_e$ , respectively), leading to a value of  $\gamma > 1$ . This condition results in an energy of the  $2p_0$  level, which is smaller than that of the  $2p_{\pm 1}$  level.

As will be seen later, the experimental values of the lines of the QHD spectra show small differences with the calculated values of Table 5.10 due to small central-cell corrections for different donors and non-parabolicity effects. This latter effect leads to small changes in the values of  $m_n$  with increasing impurity concentrations. A consequence of these small binding energies is a large spread of the donor electronic density, which can be visualized by the effective Bohr radius of the donor electron  $a^*_{0d}$ . In the  $n$ th excited state,  $a^*_{0dn} = n^2 a^*_{0d}$ . For GaAs,  $a_{0d2}^*$  is  $\sim 40$  nm, but it rises to  $\sim 0.3 \mu\text{m}$  for InSb, and in this semiconductor, no donor spectrum can be observed without the help of an additional magnetic field because of the overlap of the donor envelope wave-functions. For QHD electrons (as well as for shallow acceptor holes) in a semiconductor, the most significant parameter is the effective magnetic

field parameter<sup>4</sup>.  $\gamma_B$ , which is defined as  $\hbar\omega_c/2R_\infty^*$ , where  $\omega_c$  is the cyclotron pulsation  $eB/m_a^*$  and  $R_\infty^*$  the appropriate effective Rydberg ( $\gamma_B$  is also defined as  $B/B_0$  with  $B_0 = R_\infty^* m_a^*/m_e\mu_B$ , where  $m_a^*$  is the effective mass expressed in mass unit). Typically, for values of  $\gamma_B < 1$ , the QHD spectra consist in transitions from  $1s$  to  $np_{m=-1}$ ,  $np_{m=0}$  and  $np_{m=+1}$  states. The energy of the  $2p_{m=-1}$  line does not change much with the magnetic field  $B$ , but the  $2p_{m=+1}$  line energy increases linearly with  $B$  (the  $2p_{m=+1} - 2p_{m=-1}$  energy splitting is  $\hbar\omega_c$ ) and the split  $3p$  components also show a strong magnetic field dependence, as can be judged from Fig. 5.1.

For  $\gamma_B \gg 1$ , the modelling of the interaction of the QHDs with a magnetic field, must be treated in the high-field case [64], but more general treatments have been given by [20, 55]. The donor energy levels are eigenvalues of an EM Hamiltonian including the magnetic field terms and in the high-field limit, they are labelled by three quantum numbers ( $N, M, \lambda$ ).  $N$  corresponds to the Landau level considered,  $M$  ( $N, N-1, N-2, \dots -\infty$ ) is the magnetic quantum number and  $\lambda$  (0, 1, 2, etc.) is the number of nodes of the eigenstates

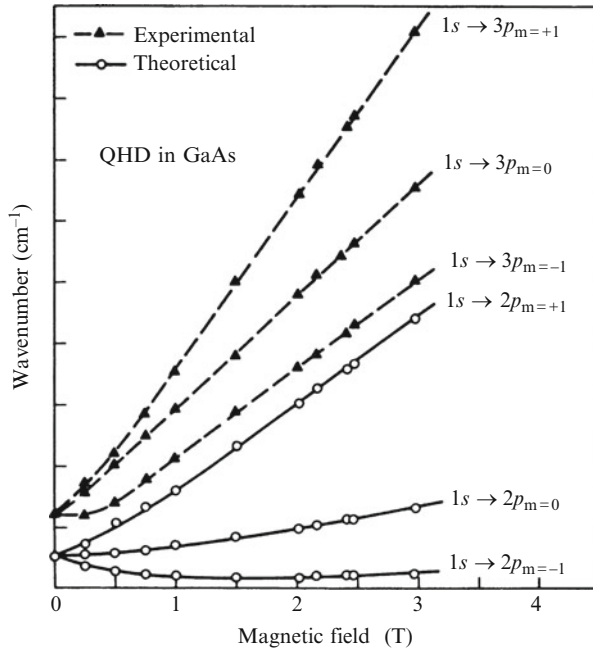


**Fig. 5.1.** Splitting of the  $1s \rightarrow 2p$  and  $1s \rightarrow 3p$  QHD transitions in GaAs as a function of magnetic field. The solid curves are from the variational calculations while the data points are derived from experiment (after [57]). Copyright 1977, with permission from Elsevier

<sup>4</sup> This parameter is usually denoted by  $\gamma$ , but to avoid a confusion with the ratio of the transverse and longitudinal effective masses, it is denoted here by  $\gamma_B$ .

in the direction of the magnetic field; the parity  $P$  of such a state is  $(-1)^{M+\lambda}$ . Let us first consider  $N = 0$  case in the high-field limit. For each value of  $M$  ( $0, -1, -2$ , etc.), there is an infinite number of bound states corresponding to the different values of  $\lambda$  and for large values of  $\gamma_B$ , the energy of the state with respect to  $N = 0$  Landau level decreases with increasing  $\lambda$ . Each of these bound states extrapolates to low-field  $(n, \ell, m)$  states, as shown below (the states are denoted here by  $(N M \lambda)$ ), but the physical context should prevent a confusion with the  $(h k l)$  planes defined by Miller indices  $h, k$  and  $l$  in cubic crystals).

|                        |                                     |                          |
|------------------------|-------------------------------------|--------------------------|
| $1s \rightarrow (000)$ | $2p_{m=-1} \rightarrow (0\bar{1}0)$ | $2p_0 \rightarrow (001)$ |
| $2s \rightarrow (002)$ | $3p_{m=-1} \rightarrow (0\bar{1}2)$ | $3p_0 \rightarrow (003)$ |
| $3s \rightarrow (004)$ | $3d_{m=-1} \rightarrow (0\bar{1}1)$ | $3d_0 \rightarrow (006)$ |

For  $N > 0$ , only those states with  $M = N$  extrapolate to hydrogen-like states at low field. All the states for which  $M < N$  are stable only for infinite magnetic fields and for intermediate fields, their lifetime is determined by autoionization into the  $N = 0$  continuum state, and they are considered as metastable states.

The strongest Zeeman transition with  $\mathbf{E} \perp \mathbf{B}$  is the one corresponding to the  $(0, \bar{1}, 0)$  state. One notes that the level corresponding to  $2p_{m=+1}$  is associated with the second Landau level, implying that the ionization energy of a QHD in the presence of a magnetic field becomes blurred because the split components can be associated with Landau levels with  $l > 1$ .

### 5.3 Acceptor Centres

The levels structure of the EM acceptor centres is determined by the characteristics of the  $VB$  of their host crystal near from its absolute extremum. As mentioned before, this extremum is located at  $\mathbf{k} = 0$  in most semiconductors. The contribution of the atomic  $p$  states of the constituent semiconductor atoms is predominant in the  $VB$  (for the compound crystals, it is related to the most electronegative atom). When spin-orbit (s-o) coupling is included, the pseudo-angular momentum  $\mathbf{J}$  associated with the upper  $VB$  is  $\mathbf{L} + \mathbf{S}$  where  $|\mathbf{L}| = 1$  corresponds to the  $p$  electrons of the host crystal. For this reason and since they correspond to the pseudo-angular momenta  $J = 3/2$  and  $1/2$ , in the description of the acceptor states in diamond-type semiconductors, the  $\Gamma_8^+$  and  $\Gamma_7^+$   $VB$ s are often labelled the  $p_{3/2}$  and  $p_{1/2}$  bands, respectively.

In the general case, Luttinger's Hamiltonian for a positive hole bound to a negative acceptor ion is derived from Hamiltonian (3.26) by adding the Coulomb potential and the s-o coupling term. It is necessary to consider s-o coupling when the magnitude of the s-o splitting  $\Delta_{so}$  is of the order of or smaller than the energies of the excited state. This is the case for Si, 3C-SiC,  $C_{diam}$ , and the sphalerite-type crystals with a light anion like cubic GaN. This yields a  $6 \times 6$  matrix operator for the Hamiltonian, as the parameters of both

the  $\Gamma_8^+$  or  $\Gamma_8$  and  $\Gamma_7^+$  or  $\Gamma_7$  VBs need to be considered. For Ge, where the s-o coupling is strong, only the upper  $\Gamma_8^+$  VB needs to be considered in the calculations, leaving still a  $4 \times 4$  matrix operator. Calculations of the first acceptor levels in germanium and in silicon considering the full cubic symmetry of the problem were first performed in [53]; more levels were calculated in germanium in [40] and in silicon in [41]. Luttinger's Hamiltonian (3.26) contains only quadratic terms  $p_i p_j$  and  $J_i J_j$  which can be put in a tensor form by introducing the second-rank tensor operators

$$P_{ij} = 3p_i p_j - \delta_{ij} p^2 \quad \text{and} \quad J_{ij} = \frac{3}{2} (J_i J_j + J_j J_i) - \delta_{ij} J^2 \quad (5.15)$$

where the  $\delta_{ij}$  are the Kronecker symbols, which are symmetric and have a zero trace ( $P_{ij}\delta_{ij}$  and  $J_{ij}\delta_{ij}$  are both zero). In the general case, by taking for energy and length units an effective Rydberg  $R_{\infty}^* = R_{\infty}/\gamma_1 \epsilon_s^2$  and an effective Bohr radius  $a_0 \gamma_1 \epsilon_s$ , where  $\gamma_1$  is one of the Luttinger VB parameters, the acceptor EM Hamiltonian including the s-o term can be written as:

$$H = \frac{1}{\hbar^2} \left( p^2 - \frac{1}{3} \left( \mu \left( P^{(2)} I^{(2)} \right) - \delta \left\{ \left[ P^{(2)} \times I^{(2)} \right]_4^{(4)} + \frac{\sqrt{70}}{5} \left[ P^{(2)} \times I^{(2)} \right]_0^{(4)} + \left[ P^{(2)} \times I^{(2)} \right]_{-4}^{(4)} \right\} \right) \right) + \frac{2}{3} \left( \frac{1}{2} - \mathbf{IS} \right) \Delta_{\text{so}} - \frac{2}{r} \quad (5.16)$$

where  $P^{(2)}$  and  $I^{(2)}$  are the second-rank Cartesian tensor operators defined in (5.15), with  $I_{ik} = 3(I_i I_k + I_k I_i)/2 - \delta_{ik} I^2$ .  $I_x$ ,  $I_y$  and  $I_z$  are the matrix elements of an angular momentum operator  $\mathbf{I}$  corresponding to  $\ell = 1$  (the definition of the tensor product terms in the Hamiltonian (5.16) are given in Appendix E). This Hamiltonian was given in [5], and it included the screening of the dielectric constant by a dielectric function not considered in (5.16). The VB coupling parameters  $\mu$  and  $\delta$  are expressed as a function of the Luttinger parameters used in Hamiltonian (3.26) as  $\mu = (6\gamma_3 + 4\gamma_2)/5\gamma_1$  and  $\delta = (\gamma_3 - \gamma_2)/\gamma_1$ . It was shown in [3] that this could be further simplified by separating the original Hamiltonian into a spherical part  $H_{\text{sph}}$  and a cubic part  $H_{\text{cub}}$ , whose expressions, for vanishing s-o interaction, are:

$$H_{\text{sph}} = \frac{1}{\hbar^2} \left( p^2 - \frac{1}{3} \mu \left( P^{(2)} I^{(2)} \right) \right) - \frac{2}{r} \quad (5.17a)$$

$$H_{\text{cub}} = \frac{\delta}{3\hbar^2} \left\{ \left[ P^{(2)} \times I^{(2)} \right]_{-4}^{(4)} + \frac{\sqrt{70}}{5} \left[ P^{(2)} \times I^{(2)} \right]_0^{(4)} + \left[ P^{(2)} \times I^{(2)} \right]_4^{(4)} \right\} \quad (5.17b)$$

The energy dispersion of the VB in terms of parameters  $\mu$  and  $\delta$  can then be written as [4]:

$$E_{\pm} = -\frac{\hbar^2 \gamma_1}{2m_e} \left\{ k^2 \pm \left[ \left( \left( \mu - \frac{6}{5} \delta \right)^2 k^4 + \frac{12}{5} \delta (5\mu - \delta) (k_x^2 k_y^2 + \text{c.p.}) \right)^{\frac{1}{2}} \right] \right\}$$

In the spherical approximation where  $\delta$  is neglected, it reduces to:

$$E_{\pm} = -\frac{\hbar^2 \gamma_1}{2m_e} (1 \pm \mu) k^2 \quad (5.18)$$

In [3], it has been considered that for semiconductors where the ratio  $\delta/\mu$  is small, the cubic term could be first neglected and later treated as a perturbation in the EM Hamiltonian. This condition is met for some semiconductors like Ge, but not for Si. Calculations have been performed in [3] as a function of the value of  $\mu$  in two limiting cases: no (or weak) s-o coupling and infinite s-o coupling. For the latter case, where the VB is split into  $J = 3/2$  and  $J = 1/2$  VBs,  $H_{\text{sph}}$  for the  $J = 3/2$  band is:

$$H_{\text{sph}} \frac{1}{\hbar^2} \left[ p^2 - \frac{1}{9} \mu \left( P^{(2)} \cdot J^{(2)} \right) \right] - \frac{2}{r} \quad (5.19)$$

The total pseudo-angular momentum  $\mathbf{F}$  for a hydrogenic atomic state with angular momentum  $\mathbf{L}$  is  $\mathbf{L} + \mathbf{J}$ . Thus, by analogy with the atomic notation, the  $nL_J$  states corresponding to  $|\mathbf{L}| = 0$  and 1 are denoted by  $nS_{3/2}$ ,  $nP_{1/2}$ ,  $nP_{3/2}$  and  $nP_{5/2}$  while those associated with the spin-orbit split  $J = 1/2$  VB are denoted by  $nS_{1/2}$ ,  $nP_{1/2}$  and  $nP_{3/2}$ . When the s-o splitting  $\Delta_{\text{so}}$  of the VBs is comparable to or larger than the ionization energies of the acceptors, the shallow acceptor states associated with the split-off band are resonant with the semiconductor VB (see Fig. 2.5) with the possible exception of the  $1S_{1/2}$  state. It can be shown that within the spherical approximation, the s-o coupling term in (5.16) couples states with the same value of  $F$  and  $\Delta L = 0, \pm 2$ . This means that  $nS_{3/2}$  states will couple with  $n'D_{3/2}$  states, and  $nP_{3/2}$  and  $nP_{5/2}$  states with  $n'F_{3/2}$  and  $n'F_{5/2}$  states. It must be noted that for these states with non-integral angular momentum, Kramers theorem [22] holds and their degeneracy is not removed, even under a perturbation symmetrical with respect to time reversal, as a uniaxial stress or an electric field. Such a doubly degenerate state is referred to as a Kramers doublet.

For vanishing s-o interaction, the appropriate spherical Hamiltonian is given by expression (5.17a). States where  $\mathbf{I} = \mathbf{L} + \mathbf{L}$  where  $L = 1$  is the pseudo-momentum associated with the VB when spin is neglected. Subsequently, when considering  $\mathbf{L} = 0$  and 1, the corresponding states are  $nS_1$  ( $nS$ ),  $nP_0$  and  $nP_1$  states.

The energies of the first acceptor states have been calculated as a function of the VB parameter  $\mu$  in the weak and strong s-o coupling limits ( $\Delta_{\text{so}} = 0$  and  $\Delta_{\text{so}} = \infty$ ) in the spherical approximation described by Hamiltonian (5.19). These energies are given in Tables 5.12 and 5.13.

For both strong and weak s-o couplings, the calculated energies diverge for a few levels when  $\mu = 1$ , this is consistent with the dispersion relation (5.18) which shows that for  $\mu = 1$ , the  $E_-$  heavy-hole VB becomes flat and gives rise to an infinite binding energy for a Coulomb potential. Not all levels

**Table 5.12.** First  $nL_J$  acceptor energy levels in semiconductors in units of the effective Rydberg  $R^*_{\infty a} = R_{\infty}/\gamma_1 \varepsilon_s^2$  as a function of the  $VB$  parameter  $\mu$  in the strong s-o coupling limit in the spherical approximation.  $R^*_{\infty a}$  is 24.46 and 4.34 meV for silicon and germanium, respectively [3]

| $\mu$ | $1S_{3/2}$ | $2S_{3/2}$ | $2P_{1/2}$ | $2P_{3/2}$ | $2P_{5/2}$ |
|-------|------------|------------|------------|------------|------------|
| 0.00  | 1.000      | 0.250      | 0.250      | 0.250      | 0.250      |
| 0.05  | 1.002      | 0.251      | 0.238      | 0.261      | 0.248      |
| 0.10  | 1.009      | 0.254      | 0.227      | 0.273      | 0.248      |
| 0.15  | 1.021      | 0.258      | 0.217      | 0.287      | 0.249      |
| 0.20  | 1.037      | 0.264      | 0.208      | 0.302      | 0.251      |
| 0.25  | 1.060      | 0.273      | 0.200      | 0.320      | 0.256      |
| 0.30  | 1.089      | 0.284      | 0.192      | 0.341      | 0.262      |
| 0.35  | 1.125      | 0.297      | 0.185      | 0.365      | 0.270      |
| 0.40  | 1.171      | 0.313      | 0.179      | 0.394      | 0.281      |
| 0.45  | 1.228      | 0.333      | 0.172      | 0.428      | 0.295      |
| 0.50  | 1.299      | 0.358      | 0.167      | 0.468      | 0.322      |
| 0.55  | 1.388      | 0.388      | 0.161      | 0.518      | 0.336      |
| 0.60  | 1.503      | 0.426      | 0.156      | 0.580      | 0.366      |
| 0.65  | 1.653      | 0.476      | 0.152      | 0.660      | 0.406      |
| 0.70  | 1.857      | 0.542      | 0.147      | 0.767      | 0.461      |
| 0.75  | 2.145      | 0.635      | 0.143      | 0.917      | 0.539      |
| 0.80  | 2.580      | 0.773      | 0.139      | 1.142      | 0.657      |
| 0.85  | 3.309      | 1.003      | 0.135      | 1.518      | 0.857      |
| 0.90  | 4.768      | 1.460      | 0.132      | 2.268      | 1.259      |
| 0.95  | 9.145      | 2.820      | 0.128      | 4.521      | 2.470      |
| 1.00  | $\infty$   | $\infty$   | 0.125      | $\infty$   | $\infty$   |

have diverging energies for  $\mu = 1$ , however, and this is the case for the  $nP_{1/2}$  and  $nP_0$  levels, associated with the  $E_+$  light-hole  $VB$ , which stays parabolic for  $\mu = 1$ .

A detailed analysis of the effect of the cubic part of the acceptor Hamiltonian on the binding energies was studied in [4] in the strong s-o coupling limit. This cubic part can be written in terms of vector products of the spherical tensor operators  $P^{(2)}$  and  $J^{(2)}$  already used for the spherical part of the Hamiltonian (the relevant properties of these tensors are given in Appendix E) and is:

$$H_{\text{cub}} = \frac{1}{9\hbar^2} \delta \left\{ \left[ P^{(2)} \times J^{(2)} \right]_4^{(4)} + \frac{\sqrt{70}}{5} \left[ P^{(2)} \times J^{(2)} \right]_0^{(4)} + \left[ P^{(2)} \times J^{(2)} \right]_{-4}^{(4)} \right\}$$

The simplest way to treat it qualitatively is to consider the way the hydrogenic wave functions transform when reducing the symmetry from  $R^+(3)$  (the 3D rotation group) to the  $T_d$  symmetry point group of the acceptor in a cubic crystal.



**Table 5.13.** First acceptor energy levels in semiconductors (same unit as in Table 5.12) as a function of the  $VB$  parameter  $\mu$  in the weak s-o coupling limit in the spherical approximation [3]

| $\mu$ | $1S_1$   | $2P_0$ | $2P_1$   | $2P_2$   |
|-------|----------|--------|----------|----------|
| 0.00  | 1.000    | 0.250  | 0.250    | 0.250    |
| 0.05  | 1.004    | 0.227  | 0.263    | 0.249    |
| 0.10  | 1.017    | 0.208  | 0.278    | 0.251    |
| 0.15  | 1.037    | 0.192  | 0.294    | 0.255    |
| 0.20  | 1.064    | 0.179  | 0.313    | 0.261    |
| 0.25  | 1.100    | 0.167  | 0.333    | 0.269    |
| 0.30  | 1.145    | 0.156  | 0.357    | 0.281    |
| 0.35  | 1.201    | 0.147  | 0.384    | 0.295    |
| 0.40  | 1.268    | 0.139  | 0.417    | 0.312    |
| 0.45  | 1.351    | 0.132  | 0.455    | 0.333    |
| 0.50  | 1.453    | 0.125  | 0.500    | 0.360    |
| 0.55  | 1.580    | 0.119  | 0.556    | 0.393    |
| 0.60  | 1.742    | 0.114  | 0.625    | 0.435    |
| 0.65  | 1.952    | 0.109  | 0.714    | 0.490    |
| 0.70  | 2.234    | 0.104  | 0.833    | 0.565    |
| 0.75  | 2.631    | 0.100  | 1.000    | 0.669    |
| 0.80  | 3.228    | 0.096  | 1.250    | 0.827    |
| 0.85  | 4.227    | 0.093  | 1.667    | 1.091    |
| 0.90  | 6.224    | 0.089  | 2.500    | 1.619    |
| 0.95  | 12.213   | 0.086  | 5.000    | 3.207    |
| 1.00  | $\infty$ | 0.083  | $\infty$ | $\infty$ |

The hydrogenic wave function for a  $S$  state transforms as  $IR \Gamma_1$  of  $T_d$  (see Table B.4 of Appendix B) while the one for a  $P$  state transforms as  $\Gamma_4$ . In the limit of infinite s-o coupling, the total wave function of a  $S_{3/2}$  acceptor state transforms as  $\Gamma_8$ . The wave functions of the acceptor  $P$  states associated with the  $\Gamma_8^+$   $VB$  transform as the direct product  $\Gamma_4 \times \Gamma_8$ , that can be decomposed into  $\Gamma_6 + \Gamma_7 + 2\Gamma_8$  by using Table B.4. It can be verified that the  $P_{1/2}$ ,  $P_{3/2}$  and  $P_{5/2}$  transform as  $\Gamma_6$ ,  $\Gamma_8$ , and  $\Gamma_7 + \Gamma_8$ , respectively. The cubic terms, thus, produce a splitting of the  $P_{5/2}$  states into  $P_{5/2}(\Gamma_7)$  and  $P_{5/2}(\Gamma_8)$  states. More refined calculations of the first acceptor levels in silicon and germanium considering the split of  $\Gamma_7^+$   $VB$  and a better description of the hole screening through the use of a dielectric function in the Coulomb potential term were performed in [5]. These calculations provided for the first time calculated values of the acceptor energy levels which allowed a clear identification of the first acceptor lines in these semiconductors.

The relative significance of the cubic contribution with respect to the spherical term in the  $VB$  structure of different semiconductors can be understood from Table 5.14.

The notations of the states usually follow the ones for the corresponding  $IRs$  of the  $T_d$  double group and the parity is indicated by superscript  $+$  or  $-$ .

**Table 5.14.** Values of the parameters  $\delta$  and  $\mu$  determining the importance of the cubic contribution over the spherical term for different cubic semiconductors deduced from Tables 3.4 and 3.6

|          | C <sub>diam</sub> | Si    | Ge    | SiC   | GaP <sup>a</sup> | GaAs  | InP   | InSb  | ZnSe  | ZnTe <sup>b</sup> | CdTe <sup>b</sup> |
|----------|-------------------|-------|-------|-------|------------------|-------|-------|-------|-------|-------------------|-------------------|
| $\mu$    | 0.372             | 0.477 | 0.768 | 0.342 | 0.48             | 0.767 | 0.792 | 0.935 | 0.795 | 0.60              | 0.72              |
| $\delta$ | 0.269             | 0.251 | 0.109 | 0.175 | 0.18             | 0.114 | 0.108 | 0.036 | 0.114 | 0.12              | 0.09              |

<sup>a</sup> [59], <sup>b</sup> [52]

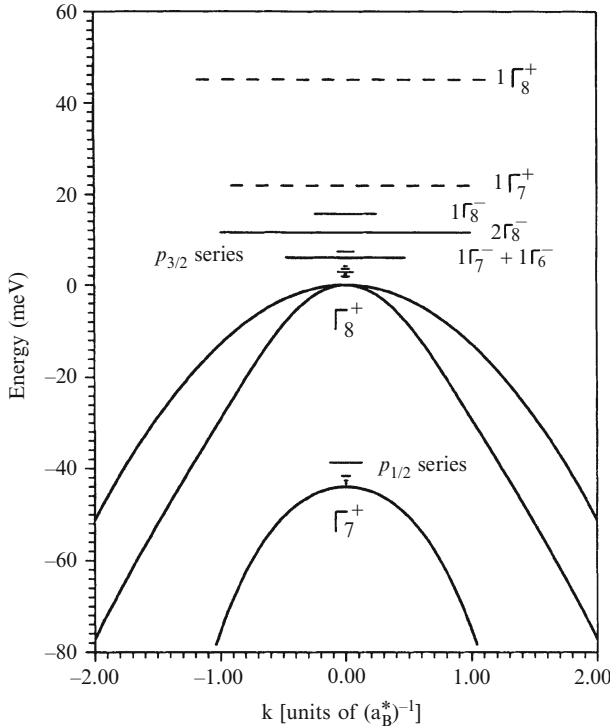


**Fig. 5.2.** Acceptor levels near from the top of the VB of a crystal with diamond structure (the energy scale corresponds to B in silicon). The  $\Gamma_7^+$  VB is separated from  $\Gamma_8^+$  by s-o splitting  $\Delta_{so}$ . The lengths of the solid segments of the odd-parity  $p_{1/2}$  and  $p_{3/2}$  states are proportional to the OSs of the optical transitions from the  $1\Gamma_8^+$  state (after [14]). Copyright 1992 by the American Physical Society

For the  $\Gamma_8^+$  VB, the  $1S_{3/2}$  ground state is denoted by  $1\Gamma_8^+$  and the  $nP$  states give  $n\Gamma_6^-$ ,  $n\Gamma_7^-$  and  $n\Gamma_8^-$  states. The same reasoning holds for the  $\Gamma_7^+$  spin-orbit split VB: the corresponding even-parity  $1S_{1/2}$  acceptor state is denoted by  $1\Gamma_7^+$ ; for the  $nD$  states ( $n > 2$ ), there are two  $n\Gamma_8^+$  and one  $n\Gamma_6^+$  levels. For silicon and diamond, where  $\Delta_{so}$  is comparable to or smaller than the acceptor binding energies,  $1\Gamma_7^+$  lies in the band gap (see Fig. 5.2),

but for germanium, where  $\Delta_{\text{so}}$  is about 30 times larger than the group-III acceptor binding energies,  $1\Gamma_7^+$  is resonant with the semiconductor  $VB$ .

The energy separation between  $1\Gamma_8^+$  and  $1\Gamma_7^+$  acceptor levels is called the acceptor spin-orbit splitting  $\Delta_{\text{so}}^A$  and it depends on the chemical nature of the acceptor and the host crystal. The  $nP_{1/2}$  and  $nP_{3/2}$  states associated with the  $\Gamma_7^+$   $VB$  give  $\Gamma_6^-$  and  $\Gamma_8^-$  states distinct from those of the  $\Gamma_8^+ VB$ , and are resonant with the  $VB$ . The acceptor transitions between the  $1\Gamma_8^+$  state and the odd-parity states associated with the  $p_{3/2} VB \Gamma_8^+$  are responsible for the so-called  $p_{3/2}$  spectrum. Logically, transitions between the  $1\Gamma_7^+$  state and the odd-parity resonant states associated with the  $p_{1/2} VB$  should also produce a distinct spectrum. No such transitions have been observed for Si, as the  $1\Gamma_7^+$  state, which lies in the band gap, is depopulated up to RT, but for diamond, due to the smaller value of  $\Delta_{\text{so}}^A$  in this material, weak transitions between  $1\Gamma_7^+$  and the odd-parity states associated with the  $\Gamma_7^+ VB$  have been observed near 80 K [27]. As no selection rule forbids them, transitions between the  $1\Gamma_8^+$  state and the  $p_{1/2}$  resonant acceptor states have indeed been observed in silicon, reported first in [66], and they are known as the  $p_{1/2}$  spectrum.

In order to improve the accuracy of the calculated acceptor levels in silicon and germanium, particularly for the even-parity ones, Lipari et al. [38] have used a screened point-charge impurity potential based on the wave-vector-dependent dielectric function calculated for Si, Ge, GaAs and ZnSe [65]. They make use of a phenomenological parameter  $\alpha$ , adjusted to fit the calculated  $\mathbf{q}$ -dependent dielectric function  $\varepsilon(\mathbf{q})$ , in this potential. The resulting potential in real space is:

$$V(r) = 2 [1 + (\varepsilon_s - 1) e^{-\alpha r}] r^{-1} \quad (5.20)$$

and it corresponds to  $r$ -dependent screened interaction between a hole and an isocoric acceptor ion ( $Al$  in silicon or  $Ga$  in germanium). For a non-isocoric acceptor, an additional short-range potential term  $Ar^{-1}e^{-\beta r}$  must be added to account for the central-cell corrections, with parameters  $A$  and  $\beta$  derived from the experimental ground state values [11, 14]. In the non-variational method of calculation of the acceptor levels used in [9], parameters of the EM ground state wave function obtained by a fit to the experimental energy of the impurity considered are used in the whole volume. This correction is called the zero-radius central cell approximation in the Russian literature. The results of different calculations of the first odd-parity EM bound acceptor states in silicon are given in Table 5.15. In the levels sequence, depending on the method used, there are sometimes inversions in the labels.

The notation  $\alpha(L)$  in [14] corresponds to  $\Gamma_{\alpha}^{\pm}(L)$ , where  $L$  is the angular momentum of the hydrogenic state and the  $+$  or  $-$  superscript corresponds to even- or odd-parity, respectively. The main difference between the unpublished results of Binggeli and Baldereschi and the other results is the energy ordering of  $1\Gamma_6^-$  and  $1\Gamma_7^-$ . It should be noted that a good quantitative agreement exists between the results obtained from variational method and those

**Table 5.15.** Correspondences between calculated energies (meV) of odd-parity  $p_{3/2}$  acceptor states in silicon with respect to the  $\Gamma_8^+ VB$ . The correspondence with the  $nL_J$  states is given for the first states. These levels are given in Table 1 of [37] with the only labelling of Binggeli and Baldereschi (1989), leading to some inversions in the energy ordering

| State <sup>a</sup>    | Energy <sup>a</sup> | State <sup>b</sup> | Energy <sup>b</sup> | State <sup>d</sup> | Energy <sup>d</sup> | State <sup>e</sup> | Energy <sup>e</sup> |
|-----------------------|---------------------|--------------------|---------------------|--------------------|---------------------|--------------------|---------------------|
| $1\Gamma_8^-2P_{3/2}$ | 15.5                | $1\Gamma_8^-$      | 15.63               | $1\Gamma_8$        | 15.79               | $1\Gamma_8^-$      | 15.78               |
| $2\Gamma_8^-2P_{5/2}$ | 11.4                | $2\Gamma_8^-$      | 11.54               | $2\Gamma_8$        | 11.48               | $2\Gamma_8^-$      | 11.69               |
| $3\Gamma_8^-3P_{3/2}$ | 7.3                 | $3\Gamma_8^-$      | 7.35                | $3\Gamma_8$        | 7.24                | $3\Gamma_8^-$      | 7.48                |
| $1\Gamma_7^-2P_{5/2}$ | 6.1                 | $1\Gamma_7^-$      | 6.08                | $1\Gamma_7$        | 6.23                | $1\Gamma_6^-$      | 6.13                |
| $1\Gamma_6^-2P_{1/2}$ | 5.8                 | $1\Gamma_6^-$      | 5.98                | $1\Gamma_6$        | 6.18                | $1\Gamma_7^-$      | 6.09                |
| $4\Gamma_8^-3P_{5/2}$ | 5.8                 | $4\Gamma_8^-$      | 5.87                | $4\Gamma_8$        | 5.95                | $4\Gamma_8^-$      | 6.00                |
| $5\Gamma_8^-4P_{3/2}$ | 4.1                 | $5\Gamma_8^-$      | 4.17                | $5\Gamma_8$        | 4.24                | $5\Gamma_8^-$      | 4.25                |
| $2\Gamma_6^-3P_{1/2}$ | 3.6                 | $2\Gamma_6^-$      | 3.70                | $6\Gamma_8$        | 3.84                | $2\Gamma_6^-$      | 3.82                |
| $6\Gamma_8^-4P_{5/2}$ | 3.5                 | $6\Gamma_8^-$      | 3.63                | $2\Gamma_6$        | 3.81                | $6\Gamma_8^-$      | 3.69                |
|                       |                     | $2\Gamma_7^-$      | 3.50                | $2\Gamma_7$        | 3.62                | $2\Gamma_7^-$      | 3.53                |
|                       |                     | $7\Gamma_8^-$      | 3.24                | $7\Gamma_8$        | 3.33                | $7\Gamma_8^-$      | 3.27                |
|                       |                     | $3\Gamma_6^-$      | 2.88                | $3\Gamma_6$        | 2.97                | $3\Gamma_6^-$      | 2.95                |
|                       |                     | $3\Gamma_7^-$      | 2.86                | $4\Gamma_7$        | 2.88                | $3\Gamma_7^-$      | 2.87                |
|                       |                     | $8\Gamma_8^-$      | 2.67                | $9\Gamma_8$        | 2.70                | $8\Gamma_8^-$      | 2.71                |
|                       |                     |                    |                     | $5\Gamma_7$        | 2.50                | $9\Gamma_8^-$      | 2.47                |
|                       |                     | $9\Gamma_8^-$      | 2.43                | $11\Gamma_8$       | 2.44                | $4\Gamma_6^-$      | 2.45                |
|                       |                     | $4\Gamma_6^-$      | 2.43                | $5\Gamma_6$        | 2.41                |                    |                     |
|                       |                     | $4\Gamma_7^-$      | 2.35                | $12\Gamma_8$       | 2.36                | $4\Gamma_7^-$      | 2.37                |
|                       |                     | $10\Gamma_8^-$     | 2.29                |                    |                     | $10\Gamma_8^-$     | 2.31                |
|                       |                     | $11\Gamma_8^-$     | 2.12                | $13\Gamma_8$       | 2.17                | $11\Gamma_8^-$     | 2.15                |
|                       |                     | $5\Gamma_6^-$      | 1.96                | $6\Gamma_7$        | 2.04                | $5\Gamma_6^-$      | 2.02                |
|                       |                     | $12\Gamma_8^-$     | 1.91                | $7\Gamma_6$        | 1.93                | $12\Gamma_8^-$     | 1.92                |
|                       |                     |                    |                     | $7\Gamma_7$        | 1.92                |                    |                     |
|                       |                     | $5\Gamma_7^-$      | 1.87                | $15\Gamma_8$       | 1.88                | $5\Gamma_7^-$      | 1.88                |
|                       |                     | $13\Gamma_8^-$     | 1.85                |                    |                     | $13\Gamma_8^-$     | 1.88                |
|                       |                     | $6\Gamma_6^-$      | 1.76                |                    |                     | $6\Gamma_6^-$      | 1.77                |
|                       |                     | $6\Gamma_7^-$      | 1.71 <sup>c</sup>   | $8\Gamma_7$        | 1.68                | $6\Gamma_7^-$      | 1.73                |
|                       |                     | $7\Gamma_7^-$      | 1.61 <sup>c</sup>   | $16\Gamma_8$       | 1.61                | $7\Gamma_7^-$      | 1.62                |
|                       |                     | $16\Gamma_8^-$     | 1.52 <sup>c</sup>   | $9\Gamma_7$        | 1.55                | $16\Gamma_8^-$     | 1.54                |
|                       |                     | $17\Gamma_8^-$     | 1.50 <sup>c</sup>   | $17\Gamma_8$       | 1.53                | $17\Gamma_8^-$     | 1.51                |
|                       |                     | $18\Gamma_8^-$     | 1.41 <sup>c</sup>   | $18\Gamma_8$       | 1.44                | $18\Gamma_8^-$     | 1.43                |
|                       |                     | $19\Gamma_8^-$     | 1.36 <sup>c</sup>   | $19\Gamma_8$       | 1.35                | $19\Gamma_8^-$     | 1.37                |

<sup>a</sup> [5], <sup>b</sup> [14]. <sup>c</sup> Buczko and Bassani (1989), unpublished results quoted in [37], <sup>d</sup> [9],

<sup>e</sup> Binggeli and Baldereschi (1989), unpublished results quoted in [37]

obtained from non-variational method [9]. This latter method produces label inversions with levels obtained by the variational method, and the appearance of the  $3\Gamma_7$ ,  $4\Gamma_8$ ,  $4\Gamma_6$ , and  $10\Gamma_8$  levels at energies of 3.07, 2.85, 2.77, and 2.61 meV, respectively, without any corresponding energy. For the shallowest

states, there are levels very close to each other and a correlation cannot be guaranteed. As a rule, the difference between the acceptor levels calculated by different authors is larger than those between the donor levels, and this can illustrate the differences in the approximations made and the inherent difficulty of such calculations.

The odd-parity acceptor states in germanium have been calculated variationally [14, 16]. As for silicon, the acceptor states in germanium have also been calculated by a non-variational method [36]. In this latter study, a screened Coulomb potential is used, but no correction is made for the acceptor-dependent central cell potential. The results of these calculations are given in Table 5.16.

Here again, the results obtained by variational and non-variational methods look very similar, except for the  $\Gamma_6$  states. The correspondence with the  $nL_J$  states shows that symmetry is not the only point and it will be shown in Chap. 8 that under uniaxial stress, states with the same symmetry can behave differently. The experimental ionization energies of all the substitutional group-III acceptors given in Tables 7.2 and 7.9 for silicon and germanium, respectively, are larger than the values of 31.56 and 9.73 meV obtained in the EMA by Baldereschi and Lipari [4] and it shows the importance of the central-cell contributions in the energy of the  $1\Gamma_8^+$  ground-state of the acceptor for silicon.

**Table 5.16.** Comparison of energies (meV) of the first odd-parity acceptor states in germanium with respect to the  $\Gamma_8^+$  VB calculated by different authors. The correspondence with the  $nL_J$  states is given for the first states. The values of the last column are obtained by a non-variational method

| State                  | Energy <sup>a</sup> | Energy <sup>b</sup> | Energy <sup>c</sup> |
|------------------------|---------------------|---------------------|---------------------|
| $1\Gamma_8^- 2P_{3/2}$ | 4.581               | 4.58                | 4.550               |
| $2\Gamma_8^- 2P_{5/2}$ | 2.875               | 2.88                | 2.867               |
| $1\Gamma_7^- 2P_{5/2}$ | 2.125               | 2.13                | 2.144               |
| $3\Gamma_8^- 3P_{3/2}$ | 2.103               | 2.10                | 2.091               |
| $4\Gamma_8^- 3P_{5/2}$ | 1.477               | 1.48                | 1.479               |
| $5\Gamma_8^- 4P_{3/2}$ | 1.210               | 1.22                | 1.213               |
| $1\Gamma_6^- 2P_{1/2}$ | 1.142               | 1.14                | -                   |
| $2\Gamma_7^- 3P_{5/2}$ | 1.140               | 1.15                | 1.155               |
| $6\Gamma_8^- 5P_{3/2}$ | 1.128               | 1.13                | 1.108               |
| $3\Gamma_7^- 4P_{5/2}$ | 1.012               | 1.01                | 1.023               |
| $7\Gamma_8^-$          | 0.920               | 0.93                | 0.930               |
| $8\Gamma_8^-$          | 0.777               | 0.80                | 0.798               |
| $9\Gamma_8^-$          |                     | 0.77                | 0.771               |
| $2\Gamma_8^-$          | 0.756               | 0.760               | 0.766*              |

\* Given as  $1\Gamma_6^-$ , <sup>a</sup> [16], <sup>b</sup> [14], <sup>c</sup> [36]

**Table 5.17.** Calculated energies (meV) of the first even-parity states of isocoric and non-isocoric acceptors in silicon and germanium with respect to the  $\Gamma_8^+VB$ , where the  $\Gamma_\alpha^+(\ell)$  states are denoted by  $\alpha(\ell)$  by [14]

| Silicon |               |       |         | Germanium |               |       |              |                   |
|---------|---------------|-------|---------|-----------|---------------|-------|--------------|-------------------|
| State   |               | Al    | B       | State     | Ga            | Al    | Point centre |                   |
| 8(0)    | $1\Gamma_8^+$ | 79.74 | (45.02) | 8(0)      | $1\Gamma_8^+$ | 11.35 | (11.15)      | 10.34             |
| 7(0)    | $1\Gamma_7^+$ | 56.72 | 21.94   | 8(0)      | $2\Gamma_8^+$ | 3.29  | 3.26         | 3.14              |
| 8(0)    | $2\Gamma_8^+$ | 17.22 | 13.34   | 8(2)      | $3\Gamma_8^+$ | 2.15  | 2.15         | 2.16              |
| 8(0)    |               | 7.43  | 6.75    | 6(2)      | $1\Gamma_6^+$ | 1.73  | 1.73         |                   |
| 8(2)    | $3\Gamma_8^+$ | 6.73  | 6.35    | 8(0)      | $4\Gamma_8^+$ | 1.69  | 1.69         | 1.64              |
| 6(2)    |               | 5.34  | 5.34    | 7(4)      | $1\Gamma_7^+$ | 1.33  | 1.33         |                   |
| 7(2)    |               | 4.99  | 4.60    | 8(2)      | $5\Gamma_8^+$ | 1.27  | 1.27         | 1.27              |
| 8(0)    |               | 4.18  | 3.97    | 8(2)      | $6\Gamma_8^+$ | 1.22  | 1.22         | 1.22              |
| 8(2)    | $4\Gamma_8^+$ | 3.96  | 3.75    | 6(2)      | $2\Gamma_6^+$ | 1.11  | 1.11         | 1.12 <sup>a</sup> |
| 8(2)    |               | 3.74  | 3.70    | 8(0)      | $7\Gamma_8^+$ | 1.04  | 1.0          | 1.01              |

For B in silicon and Al in germanium, the parameters  $A$  and  $\beta$  (see text) of the short-range potential are obtained from the experimental ground state energies. The last column gives the non-variational values of [36] for a point-centre acceptor

<sup>a</sup> Given as  $1\Gamma_7^+$  in [36]

The energies of the first even-parity levels have been calculated variationally for the isocoric acceptors in silicon and in germanium using potential (5.20) with  $\alpha = 0.93$  a.u. for both semiconductors, and for non-isocoric B in silicon ( $A = -23.7$  and  $\beta = 1$  a.u.) and Al in germanium ( $A = -7.86$  and  $\beta = 1$  a.u.). They are given in Table 5.17. In [14], the states are represented by  $\alpha(\ell)$  corresponding to  $\Gamma_\alpha(\ell)$ , where  $\ell$  is the angular momentum of the hydrogenic state. The energies of some even-parity states of B in silicon have been determined in 2-hole PL experiments [63] and also calculated by [38]. These even-parity states have also been calculated by [36] using a non-variational method. The correspondence between the calculated states, denoted by  $n\Gamma_\alpha^+$ , and the  $\alpha(\ell)$  states is given in Table 5.17, where it is compared with the results of [36] considering a point centre acceptor (no central cell correction).

With the possible exception of the ground state, the energies of the acceptor states associated with the  $\Gamma_7^+$  s-o split  $VB$  in silicon are smaller than the s-o splitting  $\Delta_{so}$  and they are resonant with the  $VB$ . One consequence is a possible interference with continuum-lying bound  $VB$  states, mentioned by Buczko and Bassani [14]. These resonant states have been calculated for silicon and germanium by these authors and their energies given in Table 5.18 for the even-parity ones. They can be calculated in the spherical approximation to the first order, and the hydrogen-like quantum numbers  $n$  and  $\ell$  are indicated in this table. Similar to the band-gap states, these states are denoted by the  $IRs$  of  $T_d$  derived from the correspondence between the even  $IRs$  of the 3D rotation group associated with  $\mathbf{F} = \ell + \mathbf{J}$  where  $J = 1/2$  and those of  $T_d$  (see for instance, [35], p. 101).

**Table 5.18.** Calculated energies (meV) of the first even-parity resonant bound states of isocoric and non-isocoric acceptors in silicon and germanium with respect to the  $\Gamma_7^+$  VB [14]

| n | $\ell$ | State        | Al in Si | B in Si  | $E_{n,\ell}$ |
|---|--------|--------------|----------|----------|--------------|
| 2 | 0      | $\Gamma_7^+$ | 4.09     | 4.39     |              |
| 3 | 2      | $\Gamma_8^+$ | 2.60     | 2.60     | 2.58         |
| " | 2      | $\Gamma_8^+$ | 2.56     | 2.56     |              |
| " | 2      | $\Gamma_6^+$ | 2.54     | 2.54     |              |
| " | 0      | $\Gamma_7^+$ | 2.03     | 2.03     |              |
| 4 | 2      | $\Gamma_8^+$ | 1.44     | 1.44     | 1.45         |
| " | 2      | $\Gamma_8^+$ | 1.41     | 1.41     |              |
| " | 2      | $\Gamma_6^+$ | 1.40     | 1.40     |              |
| " | 0      | $\Gamma_7^+$ | 1.23     | 1.20     |              |
| n | $\ell$ | State        | Ga in Ge | Al in Ge | $E_{n,\ell}$ |
| 1 | 0      | $\Gamma_7^+$ | 3.57     | 3.41     | 3.94         |
| 2 | 0      | $\Gamma_7^+$ | 0.994    | 0.987    | 1.02         |
| 3 | 2      | $\Gamma_8^+$ | 0.477    | 0.477    | 0.477        |
| " | 2      | $\Gamma_8^+$ | "        | "        |              |
| " | 2      | $\Gamma_6^+$ | "        | "        |              |
| " | 0      | $\Gamma_7^+$ | 0.451    | 0.450    | 0.460        |
| 4 | 2      | $\Gamma_8^+$ | 0.267    | 0.267    | 0.268        |
| " | 2      | $\Gamma_8^+$ | "        | "        |              |
| " | 2      | $\Gamma_6^+$ | "        | "        |              |
| " | 0      | $\Gamma_7^+$ | 0.253    | 0.253    | 0.261        |

In silicon, the  $n = 1$  state is in the band gap. The parameters  $A$  and  $\beta$  are the same as those used in Table 5.17. The values of the last column are calculated from (5.21)

For  $\mathbf{k}$ -vectors away from the centre of the  $BZ$ , the whole EM Hamiltonian combines with the Bloch functions of the  $\Gamma_8^+$  and  $\Gamma_7^+$  VB states, and this breaks the parabolicity of the  $\Gamma_7^+$  VB. Normally, for a parabolic band, the energy levels are independent from  $\ell$  and given by  $E_n$  (a.u.) =  $1/n^2$ . When non-parabolicity is taken into account, it has been shown by [14] that the modification of the energy levels from band mixing leads to a perturbation term yielding:

$$E_{n,\ell} = \frac{1}{n^2} - 2 \frac{\mu^2}{\Delta_{so}} \left[ \frac{8}{(2\ell + 1)n^3} - \frac{3}{n^4} \right] \quad (5.21)$$

The energies obtained from (5.21) are compared in Table 5.18 with those calculated from the EM Hamiltonian. It shows that for silicon, the two values are very close for  $\ell > 0$ .

The energies of the odd-parity resonant states have also been calculated for silicon and germanium, and the values for silicon are given in Table 5.19 (the values for germanium can be found in the original paper [14]). In this table, anticipating the next section, are also given the calculated OSs for the

**Table 5.19.** Calculated energies (meV) of the odd-parity  $p_{1/2}$  resonant bound states of acceptors in silicon with respect to the  $\Gamma_7^+$  VB and calculated OSs for transitions from the  $1\Gamma_8^+$  ground state of the acceptor [14]

| n | $\ell$ | State                                    | Energy | OS ( $\times 10^{-4}$ ) |       |
|---|--------|------------------------------------------|--------|-------------------------|-------|
|   |        |                                          |        | A1                      | B     |
| 2 | 1      | $\Gamma_6^-$                             | 5.34   | 25                      | 87    |
| " | 1      | $\Gamma_8^-$                             | 5.26   | 3.5                     | 15    |
| 3 | 1      | $\Gamma_6^-$                             | 2.41   | 7.4                     | 25    |
| " | 1      | $\Gamma_8^-$                             | 2.35   | 1.1                     | 4.0   |
| 4 | 3      | $2\Gamma_8^- + 2\Gamma_7^- + \Gamma_6^-$ | 1.48   | 0.62                    | 0.87  |
| " | 1      | $\Gamma_6^-$                             | 1.38   | 3.0                     | 11    |
| " | 1      | $\Gamma_8^-$                             | 1.26   | 0.34                    | 1.8   |
| 5 | 3      | $2\Gamma_8^- + 2\Gamma_7^- + \Gamma_6^-$ | 0.94   | 0.18                    | 0.15  |
| " | 1      | $\Gamma_6^-$                             | 0.895  | 1.8                     | 5.3   |
| " | 1      | $\Gamma_8^-$                             | 0.890  | 0.33                    | 0.84  |
| 6 | 5      | $4\Gamma_8^- + 2\Gamma_6^- + \Gamma_7^-$ | 0.67   | 0.094                   | 0.029 |
| " | 3      | $2\Gamma_8^- + 2\Gamma_7^- + \Gamma_6^-$ | 0.66   | 0.024                   | 0.032 |
| " | 1      | $\Gamma_6^-$                             | 0.628  | 1.0                     | 3.1   |
| " | 1      | $\Gamma_8^-$                             | 0.628  | 0.19                    | 0.49  |

transitions from the  $1\Gamma_8^+$  ground state. For  $\ell = 3$  and 5, the *IRs* indicated for the states with  $T_d$  symmetry correspond to the *IRs*  $D_{5/2}^+$  and  $D_{7/2}^+$  ( $\ell = 3$ ) and  $D_{11/2}^+$  and  $D_{9/2}^+$  ( $\ell = 5$ ) of the 3D rotation group.

Non-variational calculations of the excited acceptor states in cubic compound semiconductors using the finite element method and Arnoldi algorithm have also been performed, with application to some II–VI and III–V compounds [51, 52]. The  $nS_{3/2}$  states ( $n = 1$  to 8) have been calculated in the spherical approximation for  $\mu$  varying between 0 and 0.95 in steps of 0.05 while the  $nP_{3/2}$  ( $\Gamma_8$ ),  $nP_{5/2}$  ( $\Gamma_8$ ) and  $nP_{5/2}$  ( $\Gamma_7$ ) states ( $n = 2$  to 5) have been calculated including the cubic term  $\delta$  ( $\delta = 0.05$  and 0.15) for the same domain of variation of  $\mu$ . The case of the single and double acceptors in GaAs has been specifically studied by Fiorentini [18]. A discussion of the results of these calculations will be presented in relation to the experimental data.

## 5.4 Oscillator Strengths

Most of the lines observed in the EM donor and acceptor spectra can be identified from their energies alone as they fit reasonably well with those calculated from EMT. Closer identification can still be obtained from their relative intensities and this is one of the reasons why it is worth while to try and predict these intensities. This can be done for at least the parity-allowed transitions, and we give there an outline of the procedure. Let us consider an



electric-dipole absorption transition between state  $a$  with energy  $E_a$  and state  $b$  with energy  $E_b$  ( $E_a < E_b$ ). The OS of this transition is defined as:

$$f_{a \rightarrow b} = \frac{2m^*}{\hbar^2} (E_b - E_a) |\mathbf{1} \mathbf{r}_{ab}|^2$$

where  $\mathbf{r}_{ab}$  is the dipole matrix element and  $\mathbf{1}$  the unit polarization vector of the radiation. This OS is a dimensionless quantity that can be considered as a transition probability from state  $a$  to state  $b$  and it is normalized to unity ( $\sum_b f_{a \rightarrow b} = 1$ ). Note that the final states include discrete as well as continuous states and the sum is taken over all the possible states. The set of all transitions from state  $a$  can be considered as a spectrum and one can define the energy dependence of this spectrum with a higher limit  $E_{\max}$  as:

$$\int_0^{E_{\max}} \sigma(E) dE$$

where  $\sigma(E)$  is the absorption cross-section from state  $a$  at energy  $E$ ; for impurity states in semiconductors,  $E_{\max}$  can be safely taken as the band-gap energy  $E_g$ . Alternatively, when the absorption cross-section  $\sigma_{ab}$  of a transition from state  $a$  to an excited state  $b$  can be evaluated, the OS  $f_{ab}$  can be defined as the ratio of  $\sigma_{ab}$  to the whole cross-section spectrum. In order to satisfy the normalization condition, for cubic semiconductors, the correct donor effective mass to be used is the one given by (3.39) and for the acceptors, it is  $m_e/\gamma_1$ , where  $\gamma_1$  is one of the Luttinger  $VB$  parameters.

#### 5.4.1 Donor Transitions

We consider first the OS of the donor electron transitions corresponding to a single valley. With the axis orientation used in Hamiltonian (5.5), the matrix elements for transitions from the  $1s$  state to odd-parity states with  $m = 0$  are non-zero when the electric vector (polarization vector) of the radiation is parallel to the  $z$  axis; similarly those for transitions from the  $1s$  state to odd-parity states with  $m = \pm 1$  are non-zero when the electric vector is perpendicular to the  $z$  axis. The one-valley OSs are denoted accordingly as  $f_{//}$  and  $f_{\perp}$ . When considering the multi-valley degeneracy, it can be shown that for an arbitrary choice of the polarization vector, the OS for transitions from the  $1s$  ( $A_1$ ) ground state to the odd-parity states with  $m = 0$  is  $f_0 = \frac{1}{3}f_{//}$  and those for transitions from the  $1s$  ( $A_1$ ) ground state to the odd-parity states with  $m = \pm 1$  is  $f_{\pm 1} = \frac{2}{3}f_{\perp}$ . The ratio  $f_0/f_{\pm 1}$  is equal to  $\frac{\gamma|<1s|r|np_0>|^2}{2|<1s|r|np_{\pm 1}>|^2}$  and for comparable values of the matrix elements, the OSs of the transitions towards the  $np_0$  states are expected to be weaker than those towards the  $np_{\pm 1}$  states. These OSs have been calculated for donors in silicon and germanium in the EMA using one-valley wave functions derived from Hamiltonian (5.5) and also with a point charge potential including variable screening adjusted to the experimental energies of the  $1s$  ( $A_1$ ) state for different donors [7, 16]).

**Table 5.20.** Calculated OSs of shallow donor transitions from the  $1s(A_1)$  state in silicon

| Final state <sup>a</sup> | Energy <sup>b</sup> | OS <sup>c</sup> |         | OS <sup>b</sup>    |                        |
|--------------------------|---------------------|-----------------|---------|--------------------|------------------------|
| $2p_0$                   | 11.491              | 58.6            | (106.7) | 57.9               | (107.4)                |
| $2p_{\pm 1}$             | 6.401               | 287.7           | (524.0) | 287                | (532.5)                |
| $3p_0$                   | 5.485               | 8.1             | (14.8)  | 7.81               | (14.5)                 |
| $4p_0$                   | 3.309               | 2.9             | (5.3)   | 2.75               | (5.10)                 |
| $3p_{\pm 1}$             | 3.120               | 54.9            | (100)   | 53.9               | (100)                  |
| $4f_0$                   | 2.339               | 0.1             | (0.2)   | 0.057              | (0.11)                 |
| $5p_0$                   | 2.235               | 1.4             | (2.6)   | 1.27               | (2.36)                 |
| $4p_{\pm 1}$             | 2.187               | 18.7            | (34.1)  | 18.7               | (34.7)                 |
| $4f_{\pm 1}$             | 1.894               | 6.0             | (10.9)  | 6.00               | (11.1)                 |
| $5f_0$                   | 1.631               | 0.8             | (1.5)   | 0.74               | (1.37)                 |
| $6p_0$                   | 1.510               | —               | —       | 0.014              | (0.026)                |
| $5p_{\pm 1}$             | 1.449               | 14.9            | (27.1)  | 14.9               | (27.6)                 |
| $5f_{\pm 1}$             | 1.259               | 0.6             | (1.1)   | 0.594              | (1.10)                 |
| $6f_0$                   | 1.243               | —               | —       | 0.48               | (0.89)                 |
| $6p_{\pm 1}$             | 1.071               | 6.9             | (12.6)  | 6.89               | (12.8)                 |
| $6f_{\pm 1}$             | 1.002               | 0.0             | (0.0)   | $4 \times 10^{-4}$ | $(7 \times 10^{-4})$   |
| $6h_{\pm 1}$             | 0.886               | 4.4             | (8.0)   | 3.64               | (6.75)                 |
| $7p_{\pm 1}$             | 0.823               | 1.8             | (3.3)   | 2.26               | (4.19)                 |
| $7f_{\pm 1}$             | 0.750               | —               | —       | 1.41               | (2.61)                 |
| $7h_{\pm 1}$             | 0.678               | —               | —       | 2.69               | (4.99)                 |
| $8p_{\pm 1}$             | 0.637               | —               | —       | $7 \times 10^{-4}$ | $(1.3 \times 10^{-3})$ |
| $8f_{\pm 1}$             | 0.596               | —               | —       | 2.39               | (4.43)                 |
| $8h_{\pm 1}$             | 0.566               | —               | —       | 0.95               | (1.76)                 |

<sup>a</sup> [17], <sup>b</sup> [7], <sup>c</sup> [16]

The energies of the final state (meV) are indicated. The OSs given by Clauws et al. [16] have been multiplied by 1000 for an easier comparison with those of [7], where this factor had already been included. The values in parentheses are normalized to 100 for the  $1s(A_1) \rightarrow 3p_{\pm}$  transition

The EMA OSs are given in Tables 5.20 (silicon) and 5.21 (germanium) for the screened potential of Hamiltonian (5.5). The agreement between the results based on non-variational calculations (a) and those based on variational calculations (b) is remarkable, except for the highly excited donor states in germanium.

One can note that contrary to the  $np$  transitions, the variation with  $n$  of the OSs to the  $nf$  levels is not monotonous and that the OS to  $5f_0$  is larger than that to  $4f_0$ . The calculated OS to  $6f_{\pm 1}$  is very small in silicon and the predictive value of the above calculation is attested by the absence in the donor spectra of this crystal of a line that could be attributed to a transition to this state.

**Table 5.21.** Calculated OSs of shallow donor transitions from the  $1s$  ground state in germanium

| Final state <sup>a</sup> | Energy <sup>b</sup> | OS <sup>c</sup> | OS <sup>b</sup>      |
|--------------------------|---------------------|-----------------|----------------------|
| $2p_0$                   | 4.750               | 18.8            | 18.8                 |
| $3p_0$                   | 2.573               | 2.0             | 1.91                 |
| $2p_{\pm 1}$             | 1.720               | 233.7           | 233                  |
| $4p_0$                   | 1.689               | 0.7             | 0.648                |
| $4f_0$                   | 1.217               | 0.3             | 0.316                |
| $3p_{\pm 1}$             | 1.037               | 40.4            | 40.6                 |
| $5p_0$                   | 0.928               | —               | 0.184                |
| $5f_0$                   | 0.800               | —               | $1.7 \times 10^{-3}$ |
| $4p_{\pm 1}$             | 0.750               | 22.1            | 21.8                 |
| $6p_0$                   | 0.735               | —               | 0.116                |
| $4f_{\pm 1}$             | 0.607               | 20.0            | 20.3                 |
| $5p_{\pm 1}$             | 0.573               | 2.6             | 2.26                 |
| $5f_{\pm 1}$             | 0.467               | 7.3             | 7.11                 |
| $6p_{\pm 1}$             | 0.399               | 6.4             | 7.44                 |
| $6f_{\pm 1}$             | 0.384               | 2.6             | 1.40                 |
| $6h_{\pm 1}$             | 0.328               | 8.0             | 5.71                 |
| $7p_{\pm 1}$             | 0.313               | 0.0             | 2.01                 |
| $7f_{\pm 1}$             | 0.290               | —               | 0.16                 |
| $7h_{\pm 1}$             | 0.282               | —               | 2.28                 |
| $8p_{\pm 1}$             | 0.250               | —               | 2.80                 |
| $8f_{\pm 1}$             | 0.244               | —               | 0.79                 |
| $8h_{\pm 1}$             | 0.217               | —               | 2.87                 |
| $8k_{\pm 1}$             | 0.207               | —               | 1.44                 |

<sup>a</sup> [17], <sup>b</sup> [7], <sup>c</sup> [16]

The energies of the final state (meV) are indicated. The OSs given in [16] have been multiplied by 1000 for an easier comparison with those of [7], where this factor had already been included

As expected, the OSs of the transitions to the  $np_0$  states are weaker than those to the  $np_{\pm 1}$  states and the effect is more pronounced for germanium ( $\gamma = 0.051$ ) than for silicon ( $\gamma = 0.208$ ). At a difference with silicon, the OSs of the  $nf$  levels in germanium decrease monotonously with  $n$ . The sums of the OSs listed in Tables 5.20 and 5.21 are 0.47 (silicon) and 0.37 (germanium), respectively. Neglecting the OSs of the discrete transitions of higher energy, the differences with unity of these sums should correspond to the contributions of the OSs of the photoionization spectrum, viz. 0.53 for silicon and 0.63 for germanium. The contribution of the continuous transitions to the total OS has been evaluated [7] and it is in good agreement with the above differences.

For the quasi-hydrogenic donors discussed in Sect. 5.2.3, the OS  $f_{ab}$  between the two discrete levels a and b are assumed to be the same as those for the hydrogen atom, and the absorption cross section is scaled by the factor  $(\varepsilon_s^{1/2} m_n)^{-1}$  (Stillman et al. [57]). The OSs for the more important transitions, normalized to unity, are (Bethe and Salpeter, [10]):

|                                  |                                          |
|----------------------------------|------------------------------------------|
| $f_{1s \rightarrow 2p} = 0.4162$ | $f_{1s \rightarrow 3p} = 0.0791$         |
| $f_{1s \rightarrow 4p} = 0.0290$ | $f_{1s \rightarrow 5p} = 0.0139$         |
| $f_{1s \rightarrow 6p} = 0.0078$ | $f_{1s \rightarrow 7p} = 0.0048$         |
| $f_{1s \rightarrow 8p} = 0.0032$ | $f_{1s \rightarrow \text{cont}} = 0.436$ |

### 5.4.2 Acceptor Transitions

The OSs for shallow acceptor transitions between ground state (0) with degeneracy  $g_0$  and final state ( $f$ ) in cubic semiconductor can be expressed as:

$$f_{0f} = \frac{2m_e}{\gamma_1 \hbar^2 g_0} (E_f - E_0) \sum_{i,j} | \langle \Phi_{0,i} | z | \Phi_{f,j} \rangle |^2$$

where the summation is taken over the degeneracies of the ground and final states. The expression for the envelope wave-functions  $\Phi_k$  is given in expression (9) of [11]. OSs for shallow acceptor transitions in silicon and germanium have been calculated by different groups ([14, 16, 30], [46], and references therein).

OSs of the first transitions of the  $p_{3/2}$  spectrum in silicon and germanium obtained using different calculations are shown in Tables 5.22 and 5.23.

Table 5.22 shows notable differences for EM acceptors in silicon between the OSs calculated from the variational and non-variational methods for the highly excited states, as well as differences in the attribution for these states. On the other hand, Table 5.23 shows a good consistency of the values of the OSs obtained from variational methods by two different groups. The sum of the calculated OSs of the discrete  $Al$  transitions in silicon is close to 7%. For the Ga transitions in germanium, this sum amounts to 19% for the 24 first transitions calculated by Buczko and Bassani [14]. Even when adding the contribution of the resonant spectrum, it shows that the contribution of the photoionization spectrum is determinant in the OS of the transitions from the ground state. It must be kept in mind, however, that the OSs depend on the ground state energy and that the higher this energy, the smaller the contribution of the discrete transitions. This will be shown in the detailed comparison with the experimental results in Chap. 7.

In group-IV semiconductors, donors like P and As and acceptors like  $Al$  are monoisotopic, but others show an isotopic distribution (see appendix D). Beyond EMT, calculations of the isotopic splitting of the ground state of

**Table 5.22.** Calculated OSs of the first  $p_{3/2}$  transitions from the  $1\Gamma_8^+$  ground state of isocoric Al in silicon compared with those of non-isocoric B

| Level <sup>a</sup> | Energy <sup>a</sup> | OS (Al) <sup>a</sup> | OS (B) <sup>a</sup> | Level <sup>b</sup> | Energy <sup>b</sup> | OS (Al) <sup>b</sup> | OS (B) <sup>b</sup> |
|--------------------|---------------------|----------------------|---------------------|--------------------|---------------------|----------------------|---------------------|
| $1\Gamma_8^- (1)$  | 15.63               | 55.6                 | 194                 | $1\Gamma_8$        | 15.79               | 67                   | 177                 |
| $2\Gamma_8^- (1)$  | 11.54               | 272                  | 769                 | $2\Gamma_8$        | 11.48               | 276                  | 640                 |
| $3\Gamma_8^- (1)$  | 7.35                | 21.2                 | 53.8                | $3\Gamma_8$        | 7.24                | 25                   | 54                  |
| $1\Gamma_7^- (1)$  | 6.08                | 92.3                 | 370                 | $1\Gamma_7$        | 6.23                | 84                   | 260                 |
| $1\Gamma_6^- (1)$  | 5.98                | 95.5                 | 359                 | $1\Gamma_6$        | 6.18                | 146                  | 376                 |
| $4\Gamma_8^- (1)$  | 5.86                | 32.1                 | 32.1                | $4\Gamma_8$        | 5.95                | 22                   | 23                  |
| $5\Gamma_8^- (1)$  | 4.17                | 8.26                 | 5.1                 | $5\Gamma_8$        | 4.24                | 9                    | 17                  |
| $2\Gamma_6^- (1)$  | 3.70                | 2.75                 | 1.19                | $6\Gamma_8$        | 3.84                | 0.4                  | 0.03                |
| $6\Gamma_8^- (1)$  | 3.63                | 4.24                 | 2.23                | $2\Gamma_6$        | 3.81                | 10                   | 12                  |
| $2\Gamma_7^- (1)$  | 3.50                | 10.2                 | 27.4                | $2\Gamma_7$        | 3.62                | 12                   | 31                  |
| $7\Gamma_8^- (1)$  | 3.24                | 3.81                 | 3.37                | $7\Gamma_8$        | 3.33                | 4                    | 3                   |
|                    |                     |                      |                     | $3\Gamma_7$        | 3.07                | 2                    | 6                   |
| $3\Gamma_6^- (3)$  | 2.88                | 9.75                 | 27.1                | $3\Gamma_6$        | 2.97                | 19                   | 36                  |
| $3\Gamma_7^- (3)$  | 2.86                | 14.0                 | 50.6                | $4\Gamma_7$        | 2.88                | 15                   | 42                  |
|                    |                     |                      |                     | $8\Gamma_8$        | 2.85                | 0.3                  | 0.06                |
|                    |                     |                      |                     | $4\Gamma_6$        | 2.77                | 0.6                  | 2                   |
| $8\Gamma_8^- (1)$  | 2.66                | 3.96                 | 6.43                | $9\Gamma_8$        | 2.70                | 3                    | 5                   |
|                    |                     |                      |                     | $10\Gamma_8$       | 2.61                | 0.8                  | 02.1                |
|                    |                     |                      |                     | $5\Gamma_7$        | 2.50                | 5.2                  | 12.3                |
| $9\Gamma_8^- (3)$  | 2.43                | 0.835                | 0.0225              | $11\Gamma_8$       | 2.44                | 2.4                  | 3.9                 |
| $4\Gamma_6^- (3)$  | 2.43                | 1.15                 | 7.62                | $5\Gamma_6$        | 2.41                | 0.4                  | 1.7                 |
| $4\Gamma_7^- (3)$  | 2.35                | 4.48                 | 10.9                | $12\Gamma_8$       | 2.36                | 0.03                 | 0.01                |
| $10\Gamma_8^- (3)$ | 2.29                | 0.368                | 0.611               | $13\Gamma_8$       | 2.17                | 1.2                  | 1.0                 |
| $11\Gamma_8^- (3)$ | 2.12                | 2.34                 | 2.48                | $6\Gamma_6$        | 2.07                | 3.6                  | 3.8                 |
| $5\Gamma_6^- (3)$  | 1.96                | 2.22                 | 2.95                | $6\Gamma_7$        | 2.04                | 3.7                  | 8.8                 |
| $12\Gamma_8^- (3)$ | 1.91                | 0.0542               | 0.488               | $14\Gamma_8$       | 1.95                | 0.7                  | 1.5                 |
| $5\Gamma_7^- (3)$  | 1.87                | 7.30                 | 27.1                | $7\Gamma_6$        | 1.93                | 0.5                  | 1.8                 |
| $13\Gamma_8^- (1)$ | 1.85                | 1.90                 | 3.38                | $7\Gamma_7$        | 1.92                | 1.6                  | 5.4                 |
| $6\Gamma_6^- (3)$  | 1.76                | 3.59                 | 17.5                | $15\Gamma_8$       | 1.88                | 0.4                  | 0.5                 |

The OSs of the transitions calculated in [14], where  $\alpha(\ell)$  corresponds to  $\Gamma_{\alpha}^-(\ell)$ , are compared with some of the ones in [46]. There are differences in the attributions for the highly excited states. The original OSs have been multiplied by  $10^4$ . The energies (final states) are in meV

<sup>a</sup> [14], <sup>b</sup> [46]

impurities have been made [23, 29]. This isotopic splitting is attributed to the interaction of the weakly bound electron or hole with zero-point vibrations at the impurity site. As the frequency is the smallest for the heaviest isotope, the calculations predict that the heavier the isotope, the higher the ionization energy.

**Table 5.23.** Comparison of the calculated OSs of the isocoric Ga transitions from the  $1\Gamma_8^+$  ground state of the  $p_{3/2}$  spectrum in germanium obtained from variational calculations

| Final state   | Energy <sup>a</sup> | OS <sup>a</sup> | OS <sup>b</sup> |
|---------------|---------------------|-----------------|-----------------|
| $1\Gamma_8^-$ | 4.58                | 22.6            | 23              |
| $2\Gamma_8^-$ | 2.88                | 941             | 952             |
| $1\Gamma_7^-$ | 2.13                | 529             | 531             |
| $3\Gamma_8^-$ | 2.10                | 74.8            | 76              |
| $4\Gamma_8^-$ | 1.48                | 55.8            | 59              |
| $5\Gamma_8^-$ | 1.22                | 18.6            | 20              |
| $2\Gamma_7^-$ | 1.15                | 39.2            | 36              |
| $1\Gamma_6^-$ | 1.14                | 18.7            | 19              |
| $6\Gamma_8^-$ | 1.13                | 19.5            | 19              |
| $3\Gamma_7^-$ | 1.01                | 35.9            | 37              |
| $7\Gamma_8^-$ | 0.93                | 23.4            | 28              |
| $8\Gamma_8^-$ | 0.80                | 8.38            | 7               |
| $9\Gamma_8^-$ | 0.77                | 1.5             | 5               |
| $2\Gamma_6^-$ | 0.76                | 5.82            |                 |

The energy (meV) indicated is that of the final state. The original OSs values have been multiplied by  $10^4$

<sup>a</sup> [14], <sup>b</sup> [16]

## References

1. A.A. Abramov, B.B. Ditkin, N.B. Konyukhova, B.S. Pariiskii, V.I. Ul'yanova, Zh. Vychisl. Mat. Mat. Fiz. **20**, 1155 [USSR Comput. Maths. Math. Phys. **20**, 63] (1980)
2. A. Baldereschi, Phys. Rev. B **1**, 4673 (1970)
3. A. Baldereschi, N. Lipari, Phys. Rev. B **8**, 2697 (1973)
4. A. Baldereschi, N. Lipari, Phys. Rev. B **9**, 1525 (1974)
5. A. Baldereschi, N. Lipari, (1976) in Fumi FG (ed) *Proc. 10th Int'l Conf. on the Physics of Semiconductors* (Tipografia Marves, Rome, 1976) pp. 595–598
6. M. Bara, M. Astier, B. Pajot, Can. J. Phys. **63**, 437 (1985)
7. I.L. Beinikhes, Sh.M. Kogan, Sov. Phys. JETP **66**, 164 (1987)
8. I.L. Beinikhes, Sh.M. Kogan, A.F. Polupanov, R. Taskinboev, Solid State Commun. **53**, 1083 (1985)
9. I.L. Beinikhes, Sh.M. Kogan, M.G. Novak, A.F. Polupanov, in *Shallow Impurities in Semiconductors IV*, ed. by G. Davies (Trans Tech, Switzerland, 1991) Mater. Sci. Forum 65–66:259–264
10. H.A. Bethe, E.E. Salpeter, *Quantum Mechanics of One and Two Electron Atoms*. (Academic, New York, 1957), p. 265
11. N. Binggeli, A. Baldereschi, Solid State Commun. **66**, 323 (1988)
12. P. Blanconnier, J.F. Hogrel, A.M. Jean-Louis, B. Sermage, J. Appl. Phys. **52**, 6895 (1981)
13. J. Broeckx, P. Clauws, J. Vennik, J. Phys. C **19**, 511 (1986)
14. R. Buczko, F. Bassani, Phys. Rev. B **45**, 5838 (1992)

15. E. Burstein, E.E. Bell, J.W. Davisson, M. Lax, J. Phys. Chem. **57**, 849 (1953)
16. P. Clauws, J. Broeckx, E. Rotsaert, J. Vennik, Phys. Rev. B **38**, 12377 (1988)
17. R.A. Faulkner, Phys. Rev. **184**, 713 (1969)
18. V. Fiorentini, Phys. Rev. B **51**, 10161 (1995)
19. J. Fontanella, R.L. Johnston, J.H. Colwell, C. Andeen, Appl. Opt. **16**, 2949 (1977)
20. H. Friedrich, M. Chu, Phys. Rev. A **28**, 1423 (1983)
21. E. Gheeraert, N. Casanova, S. Koizumi, T. Teraji, H. Kanda, Diam. Relat. Mater. **10**, 444 (2001)
22. V. Heine, *Group Theory in Quantum Mechanics* (Pergamon Press, Oxford, 1964)
23. V. Heine, C.H. Henry, Phys. Rev. B **11**, 3795 (1975)
24. I.G. Ivanov, B. Magnusson, E. Janzén, Phys. Rev. B **67**, 165212 (2003)
25. I.G. Ivanov, A. Stelmach, M. Kleverman, E. Janzén, Phys. Rev. B **73**, 045205 (2006)
26. E. Janzén, R. Stedman, G. Grossmann, H.G. Grimmeiss, Phys. Rev. B **29**, 1907 (1984)
27. H. Kim, R. Vogelgesang, A.K. Ramdas, S. Rodriguez, M. Grimsditch, T.R. Anthony, Phys. Rev. Lett. **79**, 1706 (1997)
28. C. Kittel, A.H. Mitchell, Phys. Rev. **96**, 1488 (1954)
29. Sh.M. Kogan, Sov. Phys. Semicond. **13**, 1131 (1980)
30. Sh.M. Kogan, A.F. Polupanov, Sov. Phys. JETP **53**, 201 (1981)
31. Sh.M. Kogan, R. Taskinboev, Sov. Phys. Semicond. **17**, 1007 (1983)
32. W. Kohn, Phys. Rev. **98**, 1856 (1955)
33. W. Kohn, in *Shallow Impurity States in Silicon and Germanium*, ed. by F. Seitz, D. Turnbull. Solid State Physics Advances in Research and Application, vol 5 (Academic Press, New York, 1957), pp. 257–320
34. W. Kohn, J.M. Luttinger, Phys. Rev. **98**, 915 (1955)
35. G.F. Koster, J.O. Dimmock, R.G. Wheeler, H. Statz, *Properties of the Thirty-Two Point Groups*. (MIT, Cambridge, MA, 1963)
36. Yu.A. Kurskii, Phys. Rev. B **48**, 5148 (1993)
37. R.A. Lewis, P. Fisher, N.A. McLean, Aust. J. Phys. **47**, 329 (1994)
38. N. Lipari, A. Baldereschi, M.L.W. Thewalt, Solid State Commun. **33**, 277 (1980)
39. E.V. Loewenstein, D.R. Smith, R.L. Morgan, Appl. Opt. **12**, 398 (1973)
40. K.S. Mendelson, H.S. James, J. Phys. Chem. Solids **25**, 729 (1964)
41. K.S. Mendelson, D.R. Schultz, Phys. Stat. Sol. **31**, 59 (1969)
42. F. Mireles, S.E. Ulloa, Appl. Phys. Lett. **74**, 248 (1999)
43. W.J. Moore, J.A. Freitas, P.J. Lin-Chung, Solid State Commun. **93**, 389 (1995)
44. H. Nara, J. Phys. Soc. Jpn **20**, 778 (1965)
45. H. Nara, J. Phys. Soc. Jpn **20**, 1097 (1965)
46. B. Pajot, I.L. Beinikhes, Sh.M. Kogan, M.G. Novak, A.F. Polupanov, C. Song, Semicond. Sci. Technol. **7**, 1162 (1992)
47. S.T. Pantelides, Rev. Mod. Phys. **50**, 797 (1978)
48. P.J. Price, Phys. Rev. **104**, 1223 (1956)
49. A.K. Ramdas, S. Rodriguez, Rep. Prog. Phys. **44**, 1297 (1981)
50. T. Ruf, M. Cardona, C.S.J. Pickles, T. Sussmann, Phys. Rev. B **62**, 16578 (2000)
51. M. Said, M.A. Kanehisa, M. Balkanski, Y. Saad, Phys. Rev. B **35**, 687 (1987)
52. M. Said, M.A. Kanehisa, Phys. Stat. Sol. B **157**, 311 (1990)
53. D. Schetcher, J. Phys. Chem. Solids **23**, 237 (1962)
54. P.E. Simmonds, R.A. Stradling, J.R. Birch, C.C. Bradley, Phys. Stat. Sol. B **64**, 195 (1974)

55. J. Simola, J. Virtamo, J. Phys. B **11**, 3309 (1978)
56. G.E. Stillman, S.S. Bose, M.H. Kim, B. Lee, T.S. Low, in *Characterization and Properties of Semiconductors*, ed. by S. Mahayan. Handbook of Semiconductors, vol 3A (North Holland, Amsterdam, 1994), pp. 783–994
57. G.E. Stillman, C.M. Wolfe, J.O. Dimmock, in *Far-infrared photoconductivity in high purity GaAs*, ed. by R.K. Willardson, A.C. Beer. Semiconductors and Semimetals, vol 12 (Academic, New York, 1977), pp. 169–290
58. A.M. Stoneham, *Theory of Defects in Solids*. (Oxford, Clarendon, 1975), p. 778
59. R.A. Street, W. Senske, Phys. Rev. Lett. **37**, 1292 (1976)
60. S. Syed, J.B. Heroux, Y.J. Wang, M.J. Manfra, R.J. Molnar, H.L. Stormer, Appl. Phys. Lett. **83**, 4553 (2003)
61. H.S. Tan, T.G. Castner, Phys. Rev. B **23**, 3983 (1981)
62. W.E. Teft, R.G. Bell, H.V. Romero, Phys. Rev. **177**, 1194 (1969)
63. M.L.W. Thewalt, Solid State Commun. **23**, 733 (1977)
64. R.F. Wallis, H.J. Bowlden, J. Phys. Chem. Solids **7**, 78 (1958)
65. J.P. Walter, M.L. Cohen, Phys. Rev. B **2**, 1821 (1970)
66. S. Zwerdling, K.J. Button, B. Lax, L.M. Roth, Phys. Rev. Lett. **4**, 173 (1960)



---

## Donor and Donor-Like EM Spectra

### 6.1 Introduction

In 1956, Picus et al. [213] reported the observation of absorption lines, related to group-V donors in silicon, at low temperature. This nearly coincided with the calculations of Kohn and Luttinger [136] which resulted in an electronic level scheme of the group-V donor states in silicon (see also [134, 135]). The absorption of group-V donors in germanium was first reported by Fan and Fisher [59]. Since then, the situation has somewhat evolved. Section 5.2 dealt with the theoretical aspect of the EM donor spectra and the present chapter describes the experimental situation. It must be pointed out that there has been in this domain, as in other domains of the semiconductor field, a clear correlation between technological interest and the amount of results on a family of materials. For instance, research on extrinsic photodetectors in the 1970–1980s has been a strong inducement for optical studies of impurities in silicon and germanium while the development of LED technologies based on III-V compounds like GaAs and GaP has stimulated the studies on these materials.

The known donor centres can be classified into single and double donors. There is not much information on potential triple donors like the substitutional group-VII elements in group-IV semiconductors, and their solubility seems to be very small. Substitutional single donors are elements of the column of the Periodic Table next to that of the atom they replace, and the double donors are elements of the second next column. In binary compounds, the donor or acceptor property of an atom depends on the atomic sublattice it is located on. Besides isolated atoms or atom pairs, more complex structures like the centres produced by thermal annealing in O-containing silicon and germanium also display donor properties and EM donor spectra. Donor-like EM spectra have also been observed in semiconductors containing TMs, together with classical internal transitions. The isoelectronic centres with an attractive potential for holes are mentioned in Sect. 1.3.4. These centres can bind the hole of an exciton pair relatively strongly. The Coulomb interaction between the hole and the electron of an exciton pair is small (typically a few

meV), but the combined potentials of the isoelectronic centre and of the hole experienced by the electron are much larger, so that the exciton bound to such an isoelectronic centre can be seen as a pseudo-donor characterized by an EM-like donor spectrum and a well-defined ionization energy.

A single donor can either be neutral and optically active or ionized and optically inactive (however, the earlier-mentioned negatively charged donors produced under band gap illumination are not discussed here). A double donor can be neutral, singly and doubly ionized. In the neutral state, it gives an absorption spectrum very similar to that of a single donor. In the singly-ionized state, the energy positions of its absorption lines are about twice the energies of the neutral state and the spacing between lines about four times that between corresponding lines of the neutral state. Most of the absorption lines are due to optical transitions with a change of parity between the ground and excited states (see Sect. 5.1.1). However, for substitutional donors with ionization energies much higher than the EM value, absorption due to parity-forbidden transitions that are symmetry-allowed is also observed. The lines observed in the donor spectra can generally be well identified using a self-consistent comparison with the EMT developed in Chap. 5 and they are labelled by the final state of the transition.

In the  $k$ -space, for semiconductors with degenerate  $CB$ s, the free electrons are evenly distributed among the different  $CB$  minimums. For most donor centers, this situation is also encountered by the electrons in the shallow excited states (we will see later that the symmetry of some donor complexes imposes restrictions to this situation). During its lifetime in one  $CB$  minimum, an excited donor electron can be scattered into another minimum by phonons with appropriate wave vectors (this is the equivalent of the inter-valley scattering for free electrons). For silicon, the multi-valley structure of the  $CB$  is shown in Fig. 8.1. Phonon-assisted inter-valley scattering can take place between valleys on perpendicular axes ( $f$ -process) like pairs (3, 2) or (3, 5) of Fig. 8.1, or on the same axis ( $g$ -process), like the (3, 4) pair. For symmetry reasons, a few phonons are considered by these processes; they are the LA and TO phonons with  $S_1$  symmetry for the  $f$ -process and the LO phonon with  $\Delta'_2$  symmetry for the  $g$ -process. Their energies, given by Asche and Sarbei [11], have been re-evaluated by Janzén et al. [119], and for silicon, they are 48.1, 59.1, and 63.9 meV for  $fLA(S_1)$ ,  $fTO(S_1)$ , and  $gLO(\Delta'_2)$ , respectively. At low temperature, this can be radiation-induced through electron-phonon interaction at energies resonant with the photoionization continuum. This process produces what is known as a Fano resonance [60] and it was first reported in the photoconductivity spectrum of n-type silicon [194], and explained without reference to a Fano resonance. It is commonly observed in the chalcogen spectra in silicon and germanium [84, 119].

In the following, an attempt to provide the most useful absorption data on centres with donor effective-mass-like properties in semiconductors is made. The group-IV crystals are considered first, and then the III-V and II-VI compounds.

In the last section of the chapter are considered two kinds of low-frequency absorption related to donors. The first one is due to the negatively charged donors, which are solid-state equivalents of negatively charged hydrogen in atomic physics, and the second one due to the hopping of an electron from a neutral donor to a positive donor ion in a heavily-doped compensated semiconductor.

Most of the measurements described here and in the following chapters are performed at LHeT because at this temperature the intensities of the lines are the largest, and their widths the smallest. Moreover, there is a small decrease of the transition energies with temperature and the measurements at LHeT provide a convenient energy reference. However, for definite purposes (for instance, to populate thermally higher energy levels), measurements have to be performed at higher temperatures. In the figures and tables, the donor lines are identified by their EM final state.

## 6.2 Group-V and Li Donors in Group-IV Crystals

### 6.2.1 Silicon

In silicon, all the substitutional group-V elements display a characteristic donor behaviour, except nitrogen whose most stable configuration in silicon is the electrically-inactive interstitial split pair (Fig. 2.6). The observation of the ESR spectrum (SL5) of isolated substitutional nitrogen in laser-annealed N-implanted silicon has been reported by Brower [31]. This centre shows a trigonal distortion along a  $\langle 111 \rangle$  axis and it is stable up to  $\sim 400^\circ\text{C}$ ; a value of  $E_c - 0.33\text{ eV}$  for the  $\text{N}^+/\text{N}^0$  level has been given by Murakami et al. [175], but no discrete electronic absorption associated with this centre has been reported.

There exists a huge amount of spectroscopic data on donors in silicon, reflecting its technological importance. Figure 6.1a shows the absorption spectrum at liquid-helium temperature (LHeT) of a natural silicon ( $^{\text{nat}}\text{Si}$ ) sample doped with phosphorus by NTD. The lines observed are due to the parity-allowed transitions from the  $1s$  ( $A_1$ ) ground state of the P donor. This spectrum extends over about  $12\text{ meV}$  ( $\sim 100\text{ cm}^{-1}$ ) below the ionization energy of P in silicon ( $45.6\text{ meV}$ ). This energy span represents the ionization energy of the deepest final state ( $2p_0$ ) for parity-allowed transitions. The  $2p_{\pm 1}$  line of this spectrum is truncated to be able to observe less intense lines, and in Fig. 6.1b is displayed a spectrum where the relative line intensity can be appreciated.

The absorption cross-section of  $2p_0(\text{P})$  estimated from the spectra of Fig. 6.1a, b are  $6 \times 10^{-14}$  and  $3.4 \times 10^{-14}\text{ cm}^2$ , respectively. This difference is partly due to the fact that the FWHMs of the corresponding lines are  $21$  and  $26\text{ }\mu\text{eV}$ . The published LHeT spectra of other donors in  $^{\text{nat}}\text{Si}$  are similar to those of P [115], and for a FWHM of  $24\text{ }\mu\text{eV}$ , the absorption cross-section of  $2p_0(\text{As})$  estimated from the spectrum of Fig. 6.3 of this reference is  $3.8 \times 10^{-14}\text{ cm}^2$ .

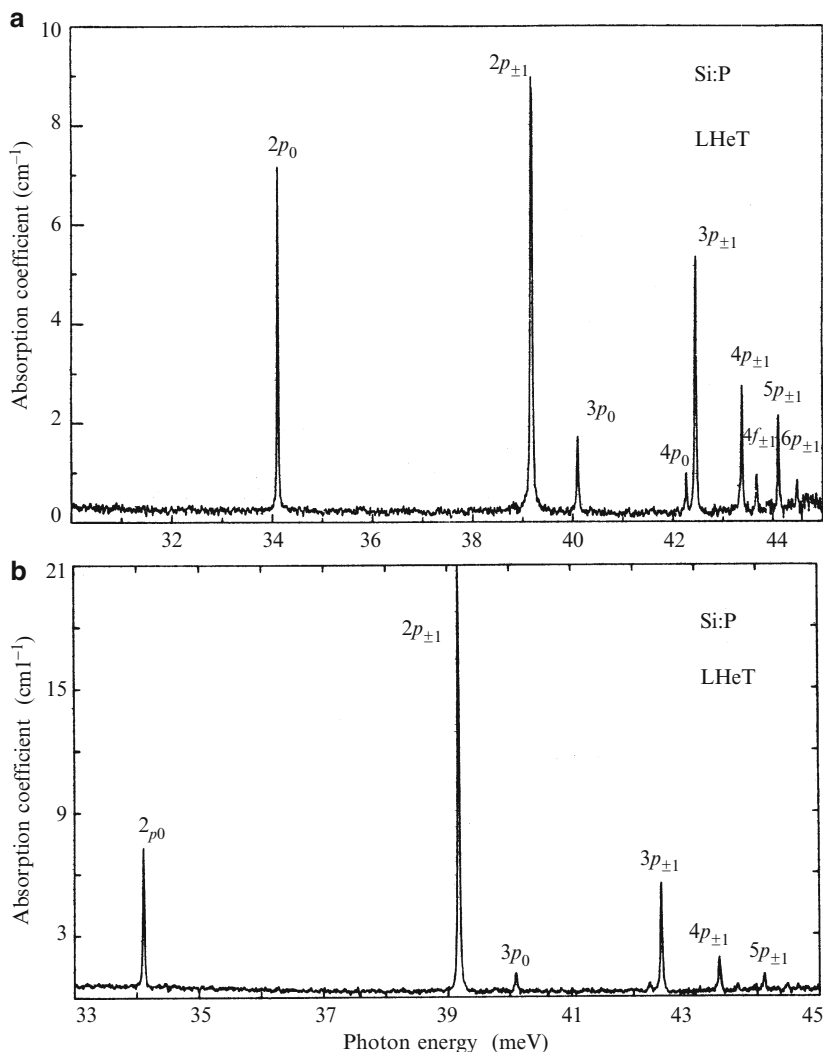


**Fig. 6.1.** (a) Overall absorption spectrum of P ( $\sim 1.2 \times 10^{14} \text{ cm}^{-3}$ ) in NTD <sup>nat</sup>Si between 250 and  $\sim 360 \text{ cm}^{-1}$  for an apodized resolution  $\delta\tilde{\nu}_s$  of  $11 \mu\text{eV}$  ( $\sim 0.09 \text{ cm}^{-1}$ ). The  $2p_{\pm 1}$  line is truncated because the transmission is close to zero with the sample used. (b) The same absorption between 266 and  $363 \text{ cm}^{-1}$  in a conventionally-doped <sup>nat</sup>Si thinner sample with  $[\text{P}] \sim 2 \times 10^{14} \text{ cm}^{-3}$ , where the relative intensity of the  $2p_{\pm 1}$  line can be estimated [115]. Copyright 1981 by the American Physical Society

LHeT and 1.6 K values of the FWHMs of donor lines in different FZ natural silicon (<sup>nat</sup>Si) and qmi <sup>28</sup>Si samples have been reported by different authors under high-resolution conditions. The results are summarized in Table 6.1.

**Table 6.1.** Measured FWHMs of donor lines in different FZ silicon samples. The spectral resolution is  $\delta\tilde{\nu}_s$ 

| T (K) | Dopant                                 | $\delta\tilde{\nu}_s$ | FWHM ( $\text{cm}^{-1}$ ( $\mu\text{eV}$ )) |                   |              |              |              |              |              |
|-------|----------------------------------------|-----------------------|---------------------------------------------|-------------------|--------------|--------------|--------------|--------------|--------------|
|       |                                        |                       | $2p_0$                                      | $2p_{\pm 1}$      | $3p_{\pm 1}$ | $4p_{\pm 1}$ | $5p_{\pm 1}$ | $6p_{\pm 1}$ | $7p_{\pm 1}$ |
| LHeT  | P in $^{\text{nat}}\text{Si}$          | 0.06 <sup>a</sup>     | 0.21                                        |                   | 0.27         | 0.20         |              |              |              |
|       | $2 \times 10^{14} \text{ cm}^{-3}$     | (7.4)                 | (26)                                        |                   | (33)         | (25)         |              |              |              |
| "     | P, NTD in $^{\text{nat}}\text{Si}$     | "                     | 0.17                                        | 0.22              | 0.24         |              |              |              |              |
|       | $1.2 \times 10^{14} \text{ cm}^{-3}$   |                       | (21)                                        | (27)              | (30)         |              |              |              |              |
| "     | P, NTD in $^{\text{nat}}\text{Si}$     | "                     | 0.20                                        |                   | 0.23         |              |              |              |              |
|       | $2 \times 10^{15} \text{ cm}^{-3}$     |                       | (25)                                        |                   | (28)         |              |              |              |              |
| "     | As in $^{\text{nat}}\text{Si}$         | "                     | 0.19                                        |                   | 0.23         |              |              |              |              |
|       | $7 \times 10^{14} \text{ cm}^{-3}$     |                       | (24)                                        |                   | (28)         |              |              |              |              |
| "     | Li in $^{\text{nat}}\text{Si}$         | "                     | 0.15                                        | 0.20              | 0.19         |              |              |              |              |
|       | $2 \times 10^{14} \text{ cm}^{-3}$     |                       | (18)                                        | (25)              | (23)         |              |              |              |              |
| "     | P in $^{\text{nat}}\text{Si}$          | 0.056 <sup>b</sup>    | 0.17                                        | 0.18              | 0.17*        |              | 0.17         | 0.17         |              |
|       | $5 \times 10^{13} \text{ cm}^{-3}$     | (6.9)                 | (21)                                        | (22)              | (21)         |              | (21)         | (21)         |              |
| "     | Sb in $^{\text{nat}}\text{Si}$         | "                     | 0.4                                         |                   | 0.48         |              |              |              |              |
|       | $n = 2 \times 10^{14} \text{ cm}^{-3}$ |                       | (~50)                                       |                   | (60)         |              |              |              |              |
| 1.6   | P* in $^{\text{nat}}\text{Si}$         | 0.012 <sup>c</sup>    | 0.082                                       | 0.123             | 0.105        | 0.089        | 0.072        | 0.07         | 0.057        |
|       | $3 \times 10^{12} \text{ cm}^{-3}$     | (1.5)                 | (10)                                        | (15)              | (13)         | (11)         | (8.9)        | (8.8)        | (7)          |
| 1.6   | P* in qmi $^{28}\text{Si}$             | "                     | 0.033                                       | 0.061             | 0.051        | 0.029        | 0.022        | 0.020        |              |
|       |                                        |                       | (4.0)                                       | (7.6)             | (6.3)        | (3.6)        | (2.7)        | (2.5)        |              |
| 1.6   | Li                                     | 0.014 <sup>d</sup>    |                                             | 0.13 <sup>†</sup> |              |              |              |              |              |
|       | in qmi $^{28}\text{Si}$                | (1.7)                 |                                             | (16)              |              |              |              |              |              |

\* Residual, <sup>†</sup> Doublet, <sup>a</sup> [115], <sup>b</sup> After [200], <sup>c</sup> [232], <sup>d</sup> [126]

PTI spectra of P in high-resistivity n-type  $^{\text{nat}}\text{Si}$ , obtained at 17.8 K with a resolution of  $0.03 \text{ cm}^{-1}$  ( $\sim 4 \mu\text{eV}$ ), have been reported to display lines with FWHMs of  $0.08 \text{ cm}^{-1}$  ( $\sim 10 \mu\text{eV}$ ) for the sharpest ones [225]. This implies that the true FWHMs of the P lines in FZ  $^{\text{nat}}\text{Si}$  depend moderately on temperature below 20 K, and also indicate that the FWHMs obtained in the high-resolution spectra in 1979–1981 were probably broadened by residual strains due to the mounting of the samples. A comparison of the FWHMs of residual P donor lines in a qmi  $^{28}\text{Si}$  sample enriched to 99.99% [232] shows a decrease of the FWHMs in this sample by a factor of  $\sim 2.5$ , compared to those in  $^{\text{nat}}\text{Si}$ . This is illustrated with  $2p_0(\text{P})$  in Fig. 6.2 (this figure also shows Li donor lines, which will be discussed later).

The relative peak amplitudes of the most intense P lines of Fig. 6.1a and OSs measured by Andreev et al. [9] are compared with the OSs calculated for P by Clauws et al. [46] in Table 6.2. The peak amplitudes are not the best reference as they do not include the line widths, given only for a few lines of the spectra, but the values are included in parentheses as products of the amplitudes by the line widths of Table 6.1.

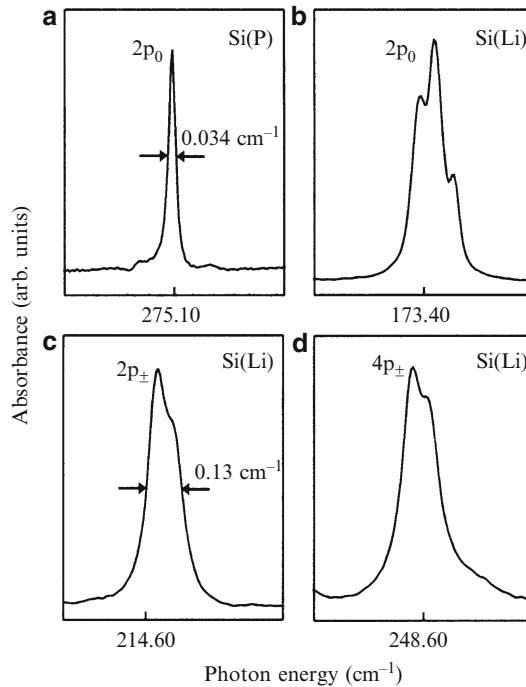


**Fig. 6.2.** Donor absorption lines observed with a resolution of  $0.014 \text{ cm}^{-1}$  ( $1.7 \mu\text{eV}$ ) in a qmi  $^{28}\text{Si}$  sample at 1.8 K. (a):  $2p_0$  (P) line, (b), (c) and (d):  $2p_0$  (Li),  $2p_{\pm 1}$  (Li) and  $4p_{\pm 1}$  (Li) lines, respectively. The spectral span for each line is  $0.8 \text{ cm}^{-1}$  ( $99 \mu\text{eV}$ ) [126]. Copyright 2003 by the American Physical Society

The uncertainties for the relative peak amplitudes of the  $2p_{\pm 1}$ (P) line are related to assumptions concerning its FWHM in spectrum 6.1b and possibly to saturation effects for the experimental OS. It has been pointed out in Sect. 5.4.1 that the calculated OS of the  $5f_0$  line was larger than that of  $4f_0$ , and this has been confirmed by experiment (see for instance, Fig. 2 of [16]).

In the absorption spectrum of Bi, the  $2p_0$  line at 59.4 meV is resonant with the  $\text{Si}f\text{TO}(S_1)$  phonon at 59.1 meV. This phonon produces an intervalley scattering of the bound electron in a given  $CB$  valley into perpendicular valleys, leading to a resonant broadening of  $2p_0(\text{Bi})$ , which can be shown in Fig. 6.3. This point is further discussed in Sect. 8.2.1.1.

Besides the group-V donors, another simple donor with tetrahedral symmetry is the interstitial Li ( $\text{Li}_i$ ), already mentioned in Sect. 1.3.2. Its ionization energy is relatively close to the one-valley EM donor energy in silicon, but ESR measurements revealed that the  $1s(\text{E})$  and  $1s(\text{T}_2)$  states of  $\text{Li}_i$  are degenerate and deeper than  $1s(\text{A}_1)$  by  $\sim 1.8 \text{ meV}$  [266]. The line spectrum of Li observed at LHeT originates from this  $1s(\text{E} + \text{T}_2)$  level, but a moderate temperature increase allows the observation of lines originating from  $1s(\text{A}_1)$

**Table 6.2.** Comparison of the relative intensities of the strongest P lines measured in  $^{nat}\text{Si}$  with the OSs calculated for P by [46]

| Line <sup>a</sup> | Position (meV) <sup>b</sup> | Peak amplitude <sup>c</sup>                     | OS (exper.) <sup>d</sup> | OS (calc.) |
|-------------------|-----------------------------|-------------------------------------------------|--------------------------|------------|
| $2p_0$            | 34.109                      | 134 (94) <sup>ca</sup> (96) <sup>cb</sup>       | 107                      | 104        |
| $2p_{\pm 1}$      | 39.175                      | $\sim 410^\dagger$ ( $\sim 343$ ) <sup>ca</sup> | 525                      | 442        |
| $3p_0$            | 40.104                      | 29                                              | 17                       | 21         |
| $4p_0$            | 42.269                      | 14                                              | 8                        | 9          |
| $3p_{\pm 1}$      | 42.458                      | 100 (100)                                       | 100                      | 100        |
| $4p_{\pm 1}$      | 43.389                      | 48                                              | 36                       | 36         |
| $4f_{\pm 1}$      | 43.684                      | 14                                              | 6                        | 12         |
| $5p_{\pm 1}$      | 44.119                      | 33                                              | 19                       | 29         |
| $5f_{\pm 1}$      | 44.312                      |                                                 | 2                        | 1.7        |
| $6p_{\pm 1}$      | 44.496                      | 10                                              | 9                        | 14         |

The relative intensities of the As lines are comparable. The values are normalized to those for the  $3p_{\pm 1}$  line. The values in parentheses are comparisons of the product of the amplitudes by the FWHMs of Table 6.1. Indices ca and cb correspond to Fig. 6.1a, b, respectively

<sup>a</sup> [61], <sup>b</sup> Rounded from Table 6.2, <sup>c</sup> From Fig. 6.1, <sup>d</sup> [9], resolution:  $8\mu\text{eV}$ ,

<sup>†</sup> Estimated from Fig. 6.1b

[115]. A high-resolution measurement of the Li spectrum introduced inadvertently in qmi  $^{28}\text{Si}$  at a concentration of  $\sim 1 \times 10^{14} \text{ cm}^{-3}$  shows (Fig. 6.2) an unresolved triplet structure of  $2p_0(\text{Li})$  and an unresolved doublet structure of  $2p_{\pm 1}(\text{Li})$  and  $4p_{\pm 1}(\text{Li})$ . The  $\sim 0.06 \text{ cm}^{-1}$  ( $7\mu\text{eV}$ ) splitting common to these three Li lines has been tentatively attributed to a very small splitting of  $1s(\text{E} + \text{T}_2)$  ground state level (Li isotope effect is ruled out because of the large difference between the  $^6\text{Li}$  and  $^7\text{Li}$  natural isotopic abundances). The additional splitting of  $2p_0(\text{Li})$  has been attributed to a valley-orbit splitting of the final  $2p_0$  state with  $\text{A}_1 + \text{E} + \text{T}_2$  representation [126]. Such a splitting is not observed for  $2p_0(\text{P})$  in Fig. 6.2, but a larger splitting is observed in the spectrum of the interstitial double donor Mg in silicon for  $2p_{\pm 1}$  [103].

In CZ silicon,  $\text{Li}_i$  can be trapped as a neighbour of electrically-inactive  $\text{O}_i$ , giving rise to  $(\text{Li},\text{O})$  donor complexes, and six such donors denoted A, B, C, D, E, and F were reported with ionization energies<sup>1</sup> of 39.7, 39.3, 38.7, 38.2, 36.6, and 35.4 meV, respectively [76]. At a difference with isolated Li, the deepest ground state of these  $(\text{Li},\text{O})$  donors is  $1s(\text{A}_1)$  [115]. From the results of Hall-effect measurements on Na-implanted silicon samples [276], the ionization energy of interstitial Na has been estimated to lie between 35 and 38 meV.

<sup>1</sup> These ionization energies are 0.5 meV higher than those in the original reference because the energy of the  $3p_{\pm 1}$  level used was 2.6 meV instead of the presently admitted value of 3.12 meV.

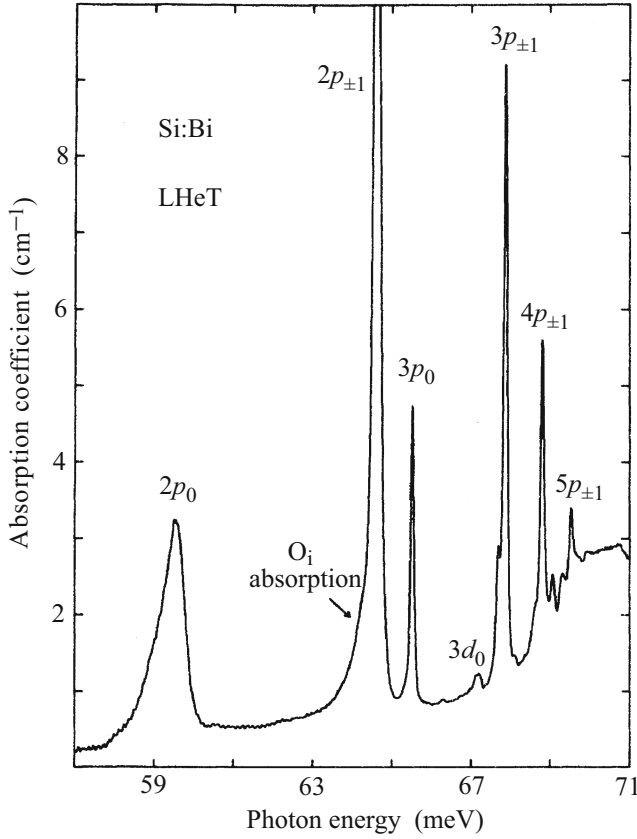


**Fig. 6.3.** Absorption spectrum of Bi donors in CZ silicon between 460 and  $\sim 573 \text{ cm}^{-1}$  ( $2p_{\pm 1}$  is truncated). Note the broadening and asymmetry of  $2p_0$  lines compared to the other lines, due to interaction with lattice phonons, and the parity-forbidden  $3d_0$  line.  $[\text{Bi}]$  is  $\sim 2 \times 10^{15} \text{ cm}^{-3}$  and the frequency of the interfering  $\text{O}_i$  vibrational mode is 64.1 meV or  $517 \text{ cm}^{-1}$  (after [35])

The measured positions of the first parity-allowed transitions of the group V, Li and (Li,O) donors in natural silicon are given in Table 6.3. The predicted OS of the  $4f_0$  line is only two thousandth of that of  $3p_{\pm 1}$  and the latter line has only been detected in P and Bi spectra. The  $5p_0$  and  $4p_{\pm 1}$  lines are  $\sim 50 \mu\text{eV}$  apart, and the  $4p_{\pm 1}$  line is more than ten times stronger than  $5p_0$ . These lines have, thus, been partially or wholly resolved only on some P spectra [200, 232, 275], but not for other donors. The optical ionization energies  $E_{i0}$  given in this table are obtained by adding to the experimental position of the  $3p_{\pm 1}$  line the calculated EM energy of the  $3p_{\pm 1}$  level (3.120 meV). The reason being that for a few centres related to oxygen thermal donors or to chalcogen, that are discussed later, the  $2p_{\pm 1}$  line is split, but not the  $3p_{\pm 1}$  line.



**Table 6.3.** Positions (meV) at LHeT of the first parity-allowed group-V, Li and Li-O donor lines in  $^{\text{nat}}\text{Si}$ 

| Line <sup>†</sup> | P <sup>a</sup>                           | As <sup>b</sup>                 | Sb <sup>b</sup>     | Bi <sup>b</sup>     | Li <sup>c</sup>    | (Li,O) <sup>c</sup> | EMT <sup>f</sup> |
|-------------------|------------------------------------------|---------------------------------|---------------------|---------------------|--------------------|---------------------|------------------|
| $2p_0$            | 34.1090 [11.469]<br>(275.108)            | 42.258<br>(340.83)*             | 31.237<br>(251.94)* | 59.54 <sup>d†</sup> | 21.483<br>(173.27) | 28.10 <sup>e</sup>  | 11.492           |
| $2p_{\pm 1}$      | 39.1748 [6.403]<br>(315.966)             | 47.359<br>(381.98)              | 36.370<br>(293.34)* | 64.598<br>(521.02)  | 26.601<br>(214.55) | 33.277<br>(268.40)  | 6.402            |
| $3p_0$            | 40.1039 [5.474]<br>(323.460)             | 48.274<br>(389.36)              | 37.270<br>(300.60)* | 65.50 <sup>d</sup>  | 27.53 <sup>e</sup> | 34.16 <sup>e</sup>  | 5.485            |
| $4p_0$            | $\pm$ 42.2688 [3.309]<br>(340.921)       | 50.459<br>(406.98)              | 39.44<br>(318.1)    | 67.68 <sup>d</sup>  | 29.70 <sup>e</sup> | 36.34 <sup>e</sup>  | 3.309            |
| $3p_{\pm 1}$      | 42.4583 [3.120]<br>(342.449)             | 50.638<br>(408.42)              | 39.643<br>(319.74)* | 67.863<br>(547.35)  | 29.879<br>(240.99) | 36.552<br>(294.81)  | 3.120            |
| $4f_0$            | 43.25 [2.33]<br>(348.8) <sup>b</sup>     |                                 |                     | 68.62 <sup>d</sup>  |                    |                     | 2.339            |
| $5p_0$            | 43.3386 [2.239]<br>(349.549)             |                                 |                     |                     | +                  | +                   | 2.235            |
| $4p_{\pm 1}$      | 43.3885 [2.189]<br>(349.952)             | 51.565<br>(415.90)              | 40.58<br>(327.3)*   | 68.777<br>(554.72)  | 30.808<br>(248.48) | 37.479<br>(302.29)  | 2.187            |
| $4f_{\pm 1}$      | 43.6842 [1.894]<br>(352.337)             | 51.85<br>(418.2)                | 40.84<br>(329.4)*   | 69.049<br>(556.92)  | 31.104<br>(250.87) | 37.767<br>(304.61)  | 1.894            |
| $5f_0$            | 43.9401 [1.638]<br>(354.401)             |                                 | 41.09<br>(331.4)*   | 69.31 <sup>d</sup>  | 31.38 <sup>e</sup> | 38.01 <sup>e</sup>  | 1.630            |
| $5p_{\pm 1}$      | 44.1187 [1.459]<br>(355.841)             | 52.297<br>(421.80)              | 41.29<br>(333.0)    | 69.507<br>(560.61)  | 31.537<br>(254.36) | 38.208<br>(308.17)  | 1.449            |
| $5f_{\pm 1}$      | 44.312 [1.266]<br>(357.40) <sup>b*</sup> | 52.487<br>(423.34) <sup>c</sup> |                     |                     | 31.73 <sup>e</sup> | 38.38 <sup>e</sup>  | 1.260            |
| $6p_{\pm 1}$      | 44.4964 [1.082]<br>(358.888)             | 52.671<br>(424.82) <sup>c</sup> | 41.67<br>(336.1)    | 69.917<br>(563.92)  | 31.914<br>(257.40) | 38.584<br>(311.20)  | 1.070            |
| $6h_{\pm 1}$      | 44.6797 [0.898]<br>(360.366)             |                                 |                     |                     |                    |                     | 0.886            |
| $E_{\text{io}}$   | 45.578<br>(367.604)                      | 53.758<br>(433.58)              | 42.763<br>(344.90)  | 70.983<br>(572.51)  | 33.999<br>(266.15) | 39.672<br>(319.97)  | 31.262           |

The values in  $\text{cm}^{-1}$  are indicated in parentheses when available. The (Li,O) donor is the one denoted A in [76]. The energy levels of the excited states of the P lines using the calculated  $3p_{\pm 1}$  reference are given in brackets, and the calculated energy levels in the last column

<sup>†</sup> Faulkner's attributions, <sup>±</sup> Reduced accuracy, \* Corrected, <sup>†</sup> Resonant phonon interaction, <sup>+</sup> Not detectable by PTIS, <sup>a</sup> [232], <sup>b</sup> [200], <sup>c</sup> [275] PTIS at 17 K, <sup>d</sup> [35], <sup>e</sup> [115], <sup>f</sup> [118]

Except for Li, the ground state of the transitions of Table 6.3 is  $1s(A_1)$ . The value for  $5f_{\pm 1}(\text{P})$  obtained by Yu et al. [275] by PTIS at 17 K is  $357.43 \text{ cm}^{-1}$  (44.316 meV), and there are small differences ( $\sim 0.03 \text{ cm}^{-1}$  or less) between the positions of the P lines of Table 6.3 and those reported in this reference. Transitions to levels above  $9h_{\pm 1}$  have also been identified by

absorption spectroscopy in the P spectrum in  $^{\text{nat}}\text{Si}$  [232]; their energies are given in Table 6.16 with corresponding ones observed in some S-related spectra. The measurements by Yu et al. [275] on  $^{\text{nat}}\text{Si}$  samples with low P content ( $4 \times 10^{12}$  at  $\text{cm}^{-3}$ , or even less) have also allowed to observe transitions up to  $9p_{\pm 1}$  because of the intrinsic sensitivity of PTIS for the highly excited levels.

It has been explained in Sect. 3.3.1 that when monoatomic semiconductors with several natural isotopes are grown with only one isotope (qmi crystals), the indirect band gap  $E_g$  of the qmi crystals increases with the mass of the isotope. For silicon, taking  $E_g(^{28}\text{Si})$  as a reference, the increases of  $E_g(^{29}\text{Si})$  and  $E_g(^{30}\text{Si})$  are  $8.72$  and  $15.98 \text{ cm}^{-1}$  ( $1.081$  and  $1.981 \text{ meV}$ ), respectively [246]. This increase reflects on the ionization energies of shallow impurities in these crystals. The effect is small, but because the line widths of the impurities in qmi crystals are small, small shifts can be detected under high-resolution conditions: At  $1.6 \text{ K}$ , the positions of  $3p_{\pm 1}(\text{P})$  measured at a resolution of  $0.012 \text{ cm}^{-1}$  ( $1.5 \mu\text{eV}$ ) in qmi  $^{28}\text{Si}$ ,  $^{29}\text{Si}$  and  $^{30}\text{Si}$  are  $342.429$ ,  $342.492$  and  $342.540 \text{ cm}^{-1}$  ( $42.4558$ ,  $42.4636$ , and  $42.4695 \text{ meV}$ ), respectively, compared to  $342.449 \text{ cm}^{-1}$  ( $42.4583 \text{ meV}$ ) in  $^{28.1}\text{Si}$  natural silicon [232]. The corresponding increases of  $E_{\text{io}}(\text{P})$  in  $^{30}\text{Si}$  with respect to  $^{28}\text{Si}$  is estimated to  $\sim 0.14 \text{ cm}^{-1}$  ( $\sim 17 \mu\text{eV}$ ). An extensive list of the positions of the P lines in qmi  $^{28}\text{Si}$ ,  $^{29}\text{Si}$  and  $^{30}\text{Si}$  compared to those in  $^{\text{nat}}\text{Si}$  is given by Steger et al. [232]. It shows that the silicon isotope effect concerns mainly the  $1s(A_1)$  ground state, and that no “substantial” effect is observed for the excited states, with the exception of the deepest  $2p_0$  odd-parity state: the shift of the  $6p_{\pm 1}$  line between qmi  $^{28}\text{Si}$  and  $^{30}\text{Si}$  samples is  $+0.126 \text{ cm}^{-1}$  ( $15.6 \mu\text{eV}$ ), but it is only  $+0.057 \text{ cm}^{-1}$  ( $7.1 \mu\text{eV}$ ) for  $2p_0$ .

The one-valley EMT developed in Sect. 5.2.1 gives results independent from the chemical nature of the donor. A near-independence is observed for the energies of the odd-parity states, and this should reflect on the spacing between lines corresponding to parity-allowed transitions of EM centres. This is relatively well observed for lines involving only  $|m| = 1$  excited states, but for differences involving a line with  $m = 0$  excited state related to the fully symmetric  $A_1$  IR, this is only true to the first order for the smaller values of the principal quantum number  $n$ . This can be shown in Table 6.4 where the experimental separations between line  $2p_{\pm 1}$  and other lines of Table 6.3 are compared with the calculated ones. This close correlation has been used for the identification of lines, together with the calculated OSs based on EMT.

It has been mentioned in Sect. 5.2.2 that the comparison of the experimental spacing of donor lines and the difference between corresponding excited levels could actually determine the volume change  $\Delta V$  produced in the lattice by a donor atom [237]. The donor-dependent difference between the donor-independent one-valley EMT results and the experimental data has been interpreted in the framework of the lattice-distortion model as the addition to the EMT value of a donor-dependent perturbation term. When considering the experimental separation  $S_{2p} = 2p_{\pm 1} - 2p_0$ , the order of magnitude of the

**Table 6.4.** Comparison of the experimental spacings (meV) between line  $2p_{\pm 1}$  and other donor lines in natural silicon with the calculated EMT spacing

| Spacing                   | P      | As     | Sb     | Bi                 | Li     | (Li,O) | EMT <sup>a</sup> | EMT <sup>b</sup> |
|---------------------------|--------|--------|--------|--------------------|--------|--------|------------------|------------------|
| $3p_{\pm 1} - 2p_0$       | 8.3492 | 8.380  | 8.406  | 8.32 <sup>†</sup>  | 8.396  | 8.45   | 8.372            | 8.371            |
| $2p_{\pm 1} - 2p_0$       | 5.0657 | 5.102  | 5.133  | 5.07 <sup>†</sup>  | 5.118  | 5.20   | 5.090            | 5.090            |
| $3p_0 - 2p_{\pm 1}$       | 0.9291 | 0.915  | 0.900  | 0.900              | 0.90   | 0.88   | 0.917            | 0.916            |
| $4p_0 - 2p_{\pm 1}$       | 3.0940 | 3.100  | 3.07   | 3.07               | 3.07   | 3.06   | 3.093            | 3.092            |
| $3p_{\pm 1} - 2p_{\pm 1}$ | 3.2835 | 3.278  | 3.273  | 3.265              | 3.278  | 3.274  | 3.282            | 3.281            |
| $4f_0 - 2p_{\pm 1}$       | 4.07   |        |        |                    | 4.01   |        | 4.063            | 4.062            |
| $5p_0 - 2p_{\pm 1}$       | 4.1638 | —      | —      | —                  | —      | —      | 4.167            | 4.166            |
| $4p_{\pm 1} - 2p_{\pm 1}$ | 4.2137 | 4.206  | 4.21   | 4.182              | 4.207  | 4.202  | 4.215            | 4.214            |
| $4f_{\pm 1} - 2p_{\pm 1}$ | 4.5094 | 4.49   | 4.47   | 4.451              | 4.503  | 4.489  | 4.508            | 4.507            |
| $5f_0 - 2p_{\pm 1}$       | 4.7653 |        | 4.71   | 4.70               | 4.76   | 4.73   | 4.772            | 4.770            |
| $5p_{\pm 1} - 2p_{\pm 1}$ | 4.9439 | 4.937  | 4.92   | 4.909              | 4.936  | 4.931  | 4.953            | 4.952            |
| $5f_{\pm 1} - 2p_{\pm 1}$ | 5.138  | 5.128  |        |                    |        | 5.11   | 5.142            | 5.142            |
| $6p_{\pm 1} - 2p_{\pm 1}$ | 5.3216 | 5.312  | 5.30   | 5.319              | 5.313  | 5.307  | 5.332            | 5.330            |
| $6h_{\pm 1} - 2p_{\pm 1}$ | 5.5049 |        |        |                    |        |        | 5.516            | 5.515            |
| $E_{2p_{\pm 1}}$          | 6.403  | 6.398  | 6.393  | 6.384              | 6.398  | 6.394  | 6.402            | 6.401            |
| $E_{2p_0}$                | 11.469 | 11.500 | 11.526 | 11.44 <sup>†</sup> | 11.516 | 11.57  | 11.492           | 11.491           |

When the line positions come from two sources, the spacing is measured from the same source. The  $3p_{\pm 1} - 2p_0$  spacing is included because it allows comparisons with donor centres where the  $2p_{\pm 1}$  line is split, as in the oxygen thermal donor spectra

<sup>†</sup> Resonant phonon broadening of  $2p_0$ , <sup>a</sup> [118], <sup>b</sup> [21]

relative volume change  $\Delta V/V_0$  brought about by the substitution of a donor atom D with a Si atom with volume  $V_0$  is [237]:

$$\Delta V/V_0 = 2.9(\text{meV}^{-1})(S_{2p}(\text{D}) - S_{2p}(\text{EMT}))(\text{meV}) \quad (6.1)$$

Using the values of Table 6.4, the relative volume changes for P, As and Sb derived from (6.1) are  $-0.07$ ,  $+0.004$  and  $+0.013$ , respectively and they are comparable to those ( $-0.08$ ,  $+0.04$  and  $+0.17$ , respectively) given by Pajot and Stoneham [205]. One must be aware that this relies heavily on the accuracy of the EMT calculations and for silicon, the values of  $S_{2p}$  obtained by variational and non-variational calculations are the same ( $5.090 \text{ meV}$ ), but this is not the case for germanium.

In Table 6.4, the variation of the  $3p_{\pm 1} - 2p_0$  spacing, which follows the same trend as the  $2p_{\pm 1} - 2p_0$  spacing for  $\text{Li}_i$  and  $(\text{Li},\text{O})$  with respect to the EM value, indicates a global perturbation of the electronic potential in the vicinity of the centre, and the changes in the values of these spacings are assumed to also provide a qualitative estimation of the perturbation for more complex centres.

Some parity-forbidden symmetry-allowed lines are also observed in the group-V donor spectra but they are usually weak. This is the case for the

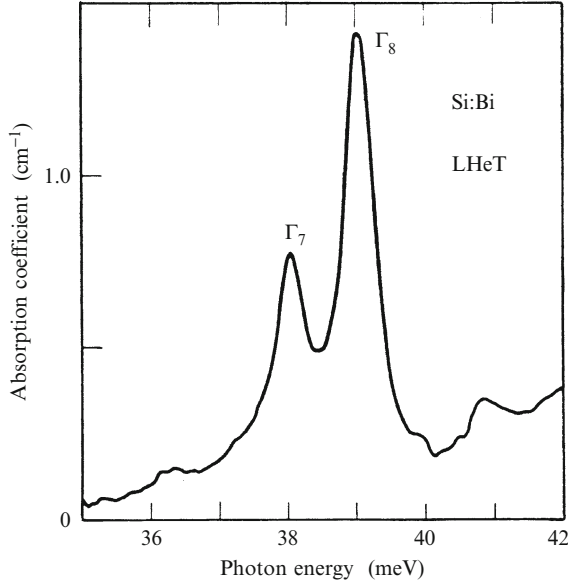


**Fig. 6.4.** Parity-forbidden absorption of the  $1s$  ( $A_1$ ) level to the  $1s$  ( $T_2$ ) state split by spin-orbit interaction at 38.08 and 39.08 meV ( $307.1$  and  $315.2$   $\text{cm}^{-1}$ ). The spectral range is  $282.3$ – $338.8$   $\text{cm}^{-1}$ .  $[\text{Bi}]$  is  $\sim 10^{16} \text{ cm}^{-3}$  (after [143])

$3d_0$  line, at 41.76, 50.0, and 67.18 meV ( $336.8$ ,  $620$ , and  $832.8$   $\text{cm}^{-1}$ ) in the P, As, and Bi spectra, respectively. Broad absorptions due to transitions to the  $1s$  states split by valley-orbit interaction have also been observed at 2 K in silicon samples doped with P and As at concentrations in the  $10^{18} \text{ cm}^{-3}$  range [253], and several parity-forbidden lines are observed for Bi. The deepest ones are due to transitions from the  $1s$  ( $A_1$ )  $\Gamma_6$  ground state to the spin-valley split  $1s$  ( $T_2$ )  $\Gamma_7$  and  $1s$  ( $T_2$ )  $\Gamma_8$  levels [143], shown in Fig. 6.4 ( $\Gamma_7$  and  $\Gamma_8$  are two-valued  $IR$ s of  $T_d$ ).

Considering the Bi concentrations, the peak absorption of this parity-forbidden doublet is about one order of magnitude weaker than the  $2p_0$  line of Fig. 6.3. Other  $n s$  ( $T_2$ ) lines together with the  $3d_0$  line have also been reported in the Bi spectrum [35]. For the other group V donors, the energies of the  $1s$  ( $T_2$ ) and  $1s$  ( $E$ ) levels have been obtained indirectly by raising the temperature of the samples to populate these levels by thermalization. Since  $E \rightarrow T_2$  and  $T_2 \rightarrow T_2$  transitions are symmetry-allowed, transitions from these levels are observed at lower energies [163]. For Si:Sb, this procedure also shows the spin-orbit splitting of the  $1s$  ( $T_2$ ) ground state (Fig. 6.5). Because of the lower mass of Sb compared to Bi, this splitting is reduced to 0.29 meV for Sb compared to 1.00 meV for Bi.

A positive shift of 0.09 meV ( $\sim 0.7$   $\text{cm}^{-1}$ ) of the energies of the  $1s$  ( $A_1$ )  $\rightarrow$   $2p_0$  (P) and  $1s$  ( $A_1$ )  $\rightarrow$   $2p_{\pm 1}$  (P) transitions between a nominal temperature

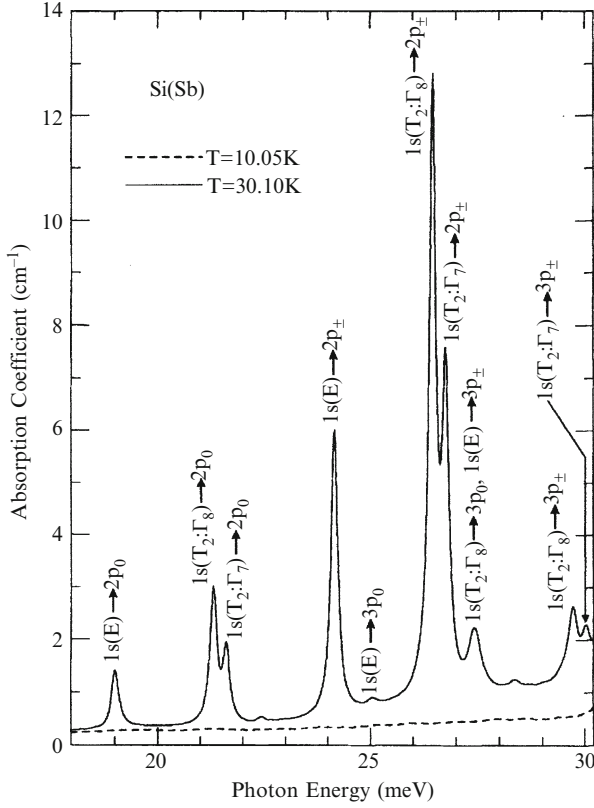


**Fig. 6.5.** Absorption spectrum from the  $1s$  excited states of Sb donors in silicon, showing the spin-valley splitting of the  $1s(T_2)$  state, observed by raising the temperature of the sample to  $\sim 30$  K. The lowest energy line of the  $1s(A_1)$  spectrum is at  $31.24$  meV ( $251.9$   $\text{cm}^{-1}$ ). The spectral range is  $145.2$ – $243.6$   $\text{cm}^{-1}$ . [Sb] is  $\sim 2.6 \times 10^{15} \text{ cm}^{-3}$  [163]. Copyright 1993 by the American Physical Society

of 4 and 54 K has been measured by White [268], and comparable results were obtained by Pajot [199]. This shift is due to the electron-phonon interaction, the main contribution coming from an increase of the  $1s(A_1)$  ground-state energy with temperature, higher than those for the excited states. For the  $1s(A_1) \rightarrow 2p_0$  transition, the shifts at 30 and 60 K deduced from the calculations of [43] are  $+0.030$  and  $+0.060$  meV, respectively. The shifts with temperature of transitions involving the  $1s(E)$  and  $1s(T_2)$  states can be deduced from a comparison between laser emission at LHeT [208, 209] and thermalized absorption at higher temperatures [3, 163]. A small negative shift of the energies of the  $1s(E) \rightarrow 2p_0(\text{As})$ ,  $1s(E) \rightarrow 2p_{\pm 1}(\text{As})$ , and  $1s(T_2) \rightarrow 2p_{\pm 1}(\text{As})$  transitions ( $-0.14$ ,  $-0.06$ , and  $-0.02$  meV, respectively) is found between LHeT and 60 K, and this trend is confirmed qualitatively by the measurements of the energies of the thermalized transitions from the

**Table 6.5.** Spectroscopically-determined energies (meV) with respect to the *CB* of the first even-parity states of group-V and Li donors in silicon at LHeT

| Level                           | P                   | As                  |                    | Sb                  | Bi                 | Li                 | (Li,O)             | EMT <sup>a</sup> |
|---------------------------------|---------------------|---------------------|--------------------|---------------------|--------------------|--------------------|--------------------|------------------|
| 1s (A <sub>1</sub> )            | 45.578              | 53.758              |                    | 42.763              | 70.99              | 31.24 <sup>b</sup> | 39.672             | 31.26            |
| 1s (T <sub>2</sub> ) $\Gamma_7$ | 33.88 <sup>c*</sup> | 32.69 <sup>c†</sup> | 32.70 <sup>k</sup> | 33.16 <sup>c‡</sup> | 32.89 <sup>d</sup> | 32.999             | 32.00 <sup>b</sup> | "                |
| 1s (T <sub>2</sub> ) $\Gamma_8$ | "                   | "                   |                    | 32.86 <sup>c‡</sup> | 32.83 <sup>l</sup> | 31.89 <sup>d</sup> | "                  | "                |
| 1s (E)                          | 32.55 <sup>c*</sup> | 31.26 <sup>c†</sup> | 31.36 <sup>k</sup> | 30.55 <sup>c‡</sup> | 29.9 <sup>c</sup>  | "                  | "                  | "                |
| 2s (A <sub>1</sub> )            | 10.61 <sup>e</sup>  | 11.28 <sup>e</sup>  |                    |                     |                    |                    |                    | 8.86             |
| 2s (T <sub>2</sub> )            | 9.07 <sup>f</sup>   | 9.11 <sup>g</sup>   |                    |                     | 8.78 <sup>h</sup>  |                    | 9.0 <sup>e</sup>   | "                |
| 3s (A <sub>1</sub> )            | 5.32 <sup>e</sup>   | 5.33 <sup>e</sup>   |                    |                     |                    |                    |                    | 4.78             |
| 3s (T <sub>2</sub> )            |                     |                     |                    |                     | 4.70 <sup>i</sup>  |                    | 5.0 <sup>e</sup>   | "                |
| 3d <sub>0</sub>                 | 3.82 <sup>j</sup>   | 3.8 <sup>m+</sup>   |                    |                     | 3.80 <sup>i</sup>  |                    |                    | 3.75             |
| 4s (A <sub>1</sub> )            | 3.14 <sup>e</sup>   |                     |                    |                     |                    |                    |                    |                  |
| 4s (T <sub>2</sub> )            |                     |                     |                    |                     | 2.89 <sup>i</sup>  |                    |                    | 2.91             |

The energies of the 1s (A<sub>1</sub>) states (1s (E + T<sub>2</sub>) state for Li) are the same as the values of  $E_{io}$  of Table 6.3. The energies obtained from laser emission are noted i.e. after the reference

\* At 45 K, † At 60 K, ‡ At 30 K at 89 K, + Identified as 4p<sub>0</sub> in this reference, <sup>a</sup> [30], <sup>b</sup> [115], <sup>c</sup> [163], <sup>d</sup> [143], <sup>e</sup> [221] PL, <sup>f</sup> [245] PL, <sup>g</sup> [105], <sup>h</sup> [141], <sup>i</sup> [35], <sup>j</sup> After [200], <sup>k</sup> [208] i.e., <sup>l</sup> [209] i.e., <sup>m</sup> [24]

1s (E) and 1s (T<sub>2</sub>) levels between 30 and 80 K for the P donor by Aggarwal and Ramdas [3]. These shifts are at the opposite of those observed for transitions from the 1s (A<sub>1</sub>) state, and they can also be explained qualitatively by the model of Cheung and Barrie [43].

Lines due to different *ns* states of P, As and Li have also been observed in silicon by two-electron PL spectroscopy [221, 245]. Laser emission of transitions involving the 1s (E) and 1s (T<sub>2</sub>) states as final states has also been observed in Si:As and Si:Sb at LHeT [208, 209]. A list of the experimentally-determined even-parity excited states of group-V, Li and (Li,O) donors in silicon is given in Table 6.5. Raman scattering between the 1s (A<sub>1</sub>) and 1s (E) levels has also been observed at LHeT for P, As and Sb [116, 270], providing a value of the energy of the 1s (E) level in good agreement with the thermalized absorption results.

In the 1s (A<sub>1</sub>) ground state, the probability of presence of the donor electron at the donor site is non-zero because of the analytical form of the wave functions (5.12) and of the values of the coefficients in Table 5.8. Therefore, when the donor atom has a nuclear spin *I*, it can interact with the donor electron spin in the 1s(A<sub>1</sub>) state. Though this interaction is small, it is responsible for the hyperfine interaction detected in ESR measurements [62]. A zero-field splitting of the ground state of the <sup>31</sup>P donor (*I* = 1/2) in silicon of 117.53 MHz (486 neV or 0.00392 cm<sup>-1</sup>) is measured by this method. The smallest FWHMs of the P lines measured in qmi <sup>28</sup>Si are ~2.5 μeV (Table 6.1) and the above splitting cannot be detected, but the situation is different in

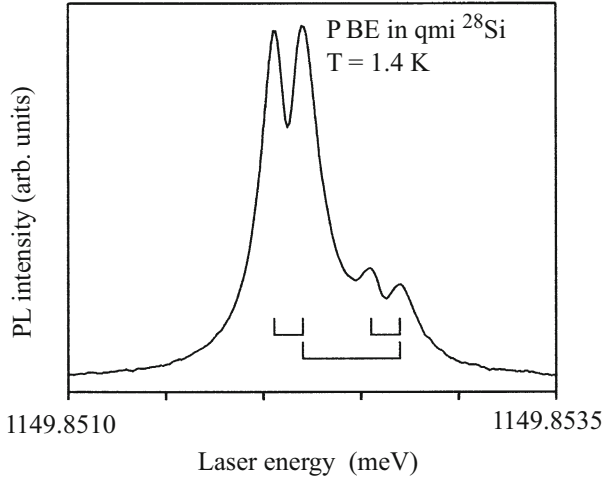


**Fig. 6.6.** PLE spectrum of the P BE due to the absorption of laser radiation tuned over the absorption range of the P BE no-phonon  $\alpha_1$  line near 1150 meV in a qmi silicon sample enriched at 99.991% with  $^{28}\text{Si}$ . The large bracket at the bottom corresponds to the 486 neV hyperfine splitting of the ground state of the P donor atom. For the two smaller brackets, see text [273]. Copyright 2006 by the American Physical Society

the near-IR. In this region, the absorption or PL of the P BE gives a ZPL at 1150.0 meV, known as the  $\alpha$  or  $\alpha_1$  line, due to a transition between the BE ground state and the  $1s(A_1)$  P state [101, 245]. In a silicon sample enriched to 99.991% with  $^{28}\text{Si}$ , a tunable laser providing a spectral resolution of 0.3 neV ( $2 \times 10^{-5} \text{ cm}^{-1}$ ) was tuned over the  $\alpha_1$  line. In order to get a better sensitivity, the PLE spectrum produced by the laser absorption was detected as the TO-phonon-assisted recombination radiation of the BE, about 58 meV below the ZPL or no-phonon line [248, 273]. The PL output as a function of the laser energy is displayed in Fig. 6.6.

This spectrum shows two relatively close components separated by a larger splitting. This splitting corresponds to the zero-field splitting of 117 MHz of the  $1s(A_1)$  ground state of the P donor due to the hyperfine interaction. The two smaller splittings are assumed to result from the coupling between the P electron spin with the spin of other neutral impurities randomly distributed around it [248, 273]. This measurement also shows the extreme sharpness of the P BE no-phonon transition in highly-enriched qmi silicon.

The above-described donor absorption spectra in the medium and far IR can be observed in  $^{\text{nat}}\text{Si}$  in a broad concentration range, from high-resistivity ( $\sim 10^4 \Omega \text{ cm}$ ) FZ samples to doped samples below the metal-insulator transition (MIT), introduced in Sect. 1.3.2 [173]. When the donor concentration increases, the FWHMs of the electronic lines starts increasing, due to the pro-

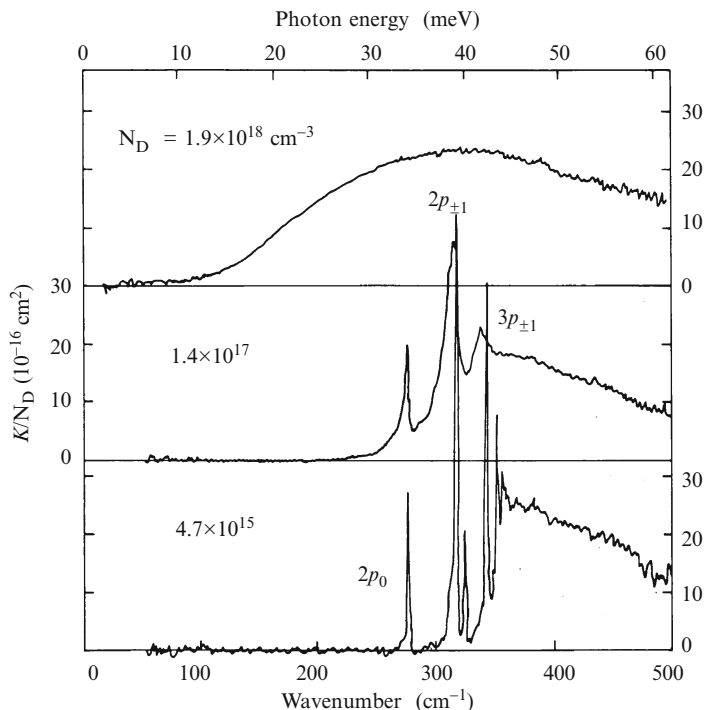


**Fig. 6.7.** Absorption cross-section spectrum of three silicon samples at  $\sim 2$  K (the concentration at the metal-insulator transition is  $\sim 3.5 \times 10^{18} \text{ cm}^{-3}$ ). Note the evolution from sharp isolated lines to asymmetrically broadened ones due to close pairs and finally to a smooth spectrum dominated by the absorption of random clusters (after [253]). Copyright 1981 by the American Physical Society

gressive overlap of the wave functions of the excited states. The variation of the donor absorption in silicon with increasing P concentrations toward the MIT has been investigated by several groups. In the 1980s, detailed investigations on the low-temperature absorption of Si:P in a broad concentration range, supported by a model based on donor pairs and clusters, were published by Thomas et al. [253]. Figure 6.7 shows the absorption near 2 K of three silicon samples with widely separated P concentrations.

The analysis of the contribution of donor pairs is based on the assumption of a random distribution of donors, with atoms closer to each other than the average  $nn$  distance  $r_c = N_D^{-1/3}$  (for a statistical Poisson distribution,  $\langle r_{nn} \rangle = 0.54r_c$ ). When two donor atoms are close enough, by analogy with the H atoms, the  $1s$  ground state energy is reduced because of the limited propensity to form a bond between the two atoms. In the pair description, the ground state is denoted  $D_{1s}D_{1s}$ . The first kind of excitation considered is a charge transfer giving rise to  $D^+D^-$ , sometimes referred to as a donor exciton. For P donors in silicon, the calculation of the energy of this excitation



as a function of the pair separation gives a minimum of 29.8 meV for a pair spacing of 6.5 nm [253].

The other excitations are more classical and they correspond, for the first ones, to  $D_{1s}D_{2p0}$  or  $D_{1s}D_{2p\pm1}$  pair states, where the electron of one of the neutral atoms of the pair makes a transition to a  $2p_0$  or  $2p_{\pm1}$  state, with an energy distribution corresponding to the pair separation. A representative spectrum, where the contribution of donor pairs to the electronic absorption can be appreciated, is shown in Fig. 6.8.

Absorption due to the donor pairs in germanium has also been reported by Kobayashi et al. [131].

Measurement of the intensity differences of the  $2p_{\pm1}$  line at LHeT in intrinsic FZ silicon samples and the same samples after NTD with different doses have been made by Pajot and Débarre [202]. The peak absorption coefficient  $K_{2p\pm1}$  of the  $2p_{\pm1}$  line was measured with a spectral resolution  $\delta\tilde{\nu}_s$  of  $0.45 \text{ cm}^{-1}$  ( $53 \mu\text{eV}$ ) and for the P concentrations introduced, the observed FWHM of  $2p_{\pm1}$  was equal to  $\delta\tilde{\nu}_s$ . For P concentrations up to  $1 \times 10^{15} \text{ cm}^{-3}$ , the valid relationship for  $\delta\tilde{\nu}_s \geq 0.45 \text{ cm}^{-1}$  is:

$$[P](\text{cm}^{-3}) = 2.13 \times 10^{13} \delta v_s(\text{cm}^{-1}) [K_{2p\pm1}(\text{cm}^{-1})]$$

and it agrees with the calibration factor of  $2.13 \times 10^{13} K_{2p\pm1}(\text{cm}^{-1})$  for the P concentration obtained by Kolbesen [138] for  $\delta\tilde{\nu}_s = 1 \text{ cm}^{-1}$ . Resolution-independent calibration factors based on the measurement of the integrated absorption of samples where the P concentration is deduced from RT resistivity measurements<sup>2</sup> have been given by Porrini et al. [215]. These factors, inverse of an integrated absorption cross-section, are 4.2, 1.2, and  $23 \times 10^{13} \text{ cm}^{-1}$  for the  $2p_0(\text{P})$ ,  $2p_{\pm1}(\text{P})$ , and  $3p_0(\text{P})$  lines, respectively (for  $2p_{\pm1}(\text{P})$ , a value of  $1.0 \times 10^{13} \text{ cm}^{-1}$  was given by Jones et al. [121]). For a sample of reasonable thickness (5–10 mm), a spectral resolution of  $0.1 \text{ cm}^{-1}$  and an adequate suppression of the interference fringes, a quantitative detection limit of about  $10^{11} \text{ cm}^{-3}$  can be achieved, well below [P] in the purest silicon samples (see Fig. 7.7). For qualitative detection of shallow donors in silicon, absorption spectroscopy does not compare with PTIS, whose detection limit is in the  $10^7 \text{ cm}^{-3}$  range, but requires temperatures above 10 K (see [225], and references therein).

For group-V donors in silicon, the photoionization cross-section at LHeT is maximum just above the ionization energy and, in units of  $10^{-15} \text{ cm}^2$ , it is given as 8.5, 2.5, 1.6, and 0.72 for Sb, P, As, and Bi, respectively ([21], and references therein).

<sup>2</sup> ASTM F 723, Standard practice for conversion between resistivity and dopant density for boron-doped, phosphorus-doped, and arsenic-doped silicon. The 1999 annual book of ASTM standards, American Society for Testing and Materials.

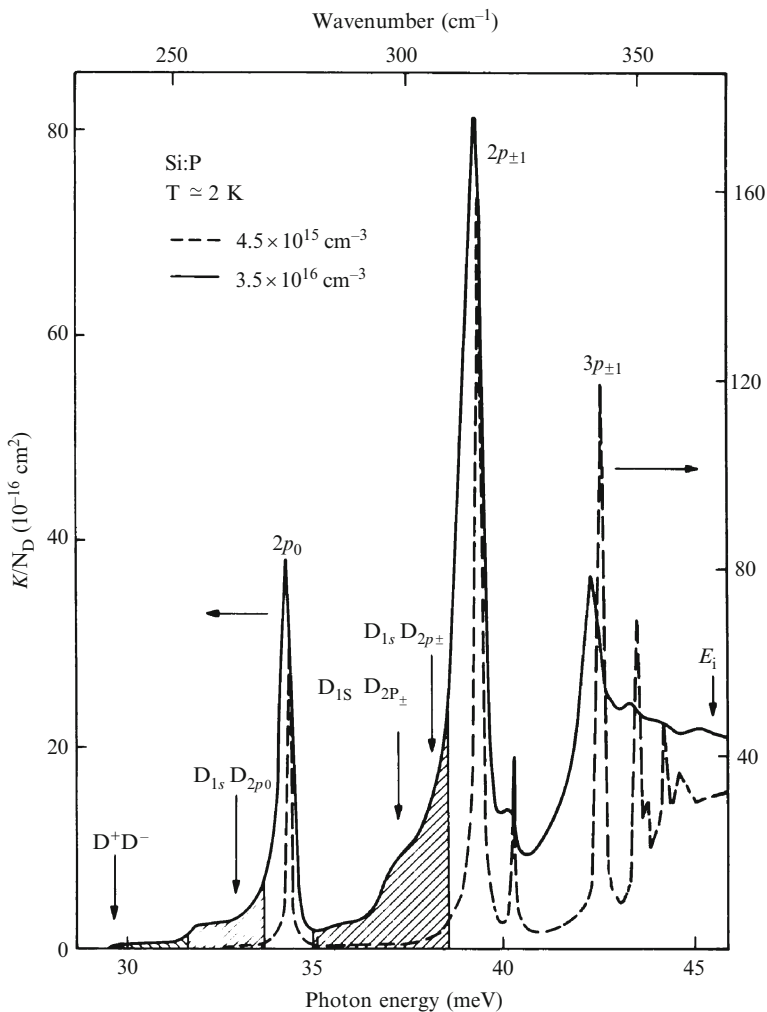


**Fig. 6.8.** Absorption cross-section of two Si:P samples showing absorption due to donor pairs (*shaded area*) for the more heavily-doped one. The vertical arrow indicates the theoretical energy minimum for the  $D^+D^-$  pair and  $E_i$  the ionization energy of isolated P (after [253]). Copyright 1981 by the American Physical Society

### 6.2.2 Germanium

The ionization energies of the EM group-V and Li donors in germanium are lower than those in silicon, and the discrete absorption spectra occur at photon energies below  $\sim 13$  meV. The published spectra in the vicinity of  $E_{i0}$  consist of parity-allowed transitions extending over about 5 meV ( $\sim 40$   $\text{cm}^{-1}$ ) below  $E_{i0}$ . For donors with cubic symmetry, the valley-orbit interaction splits the 1s state into a 1s ( $A_1$ ) singlet and a 1s ( $T_2$ ) triplet (see Sect. 5.2.2). The

ground state is  $1s(A_1)$  for group-V donors, but for  $Li_i$ , as in silicon, it is  $1s(T_2)$ . Spectrometers based on backward-wave tubes far IR sources have been used to directly detect the  $1s(A_1) \rightarrow 1s(T_2)$  absorption of P and As donors [36] and also the transitions from the first excited states (Gershenson and Gol'tsman [70]). For  $Li_i$ , the  $1s(T_2) - 1s(A_1)$  separation deduced from the splitting of the parity-allowed  $Li_i$  lines [49] is  $46 \mu\text{eV}$  ( $0.37 \text{ cm}^{-1}$ ). A larger value of the Li valley-orbit splitting ( $0.12 \text{ meV}$  or  $0.97 \text{ cm}^{-1}$ ) has also been deduced indirectly from an analysis of the electron-phonon scattering derived from thermal conductivity measurements of Li-doped germanium between 0.4 and 20 K [2], but the spectroscopic value is considered as more reliable. The valley-orbit splitting of the P, As and Bi donors has also been measured by Reuszer and Fisher [217] by thermalization of the  $1s(T_2)$  state in the same way as for silicon. As shown in Fig. 6.9, for Sb, thermalization of the  $1s(T_2)$  state is already present at LHeT because of the small value of the valley-orbit splitting for this donor. The third-order non-linear optical susceptibility of Ge:P and Ge:As samples has been measured by simultaneously illuminating the samples with frequencies  $\omega_1$  and  $\omega_2$  of two Q-switched  $\text{CO}_2$  lasers ( $\omega_1 > \omega_2$ ), and measuring the intensity of the radiation generated at frequency  $2\omega_2 - \omega_1$  due to the non-linear effect [269]. By tuning the frequencies  $\omega_1$  and  $\omega_2$ , a sharp

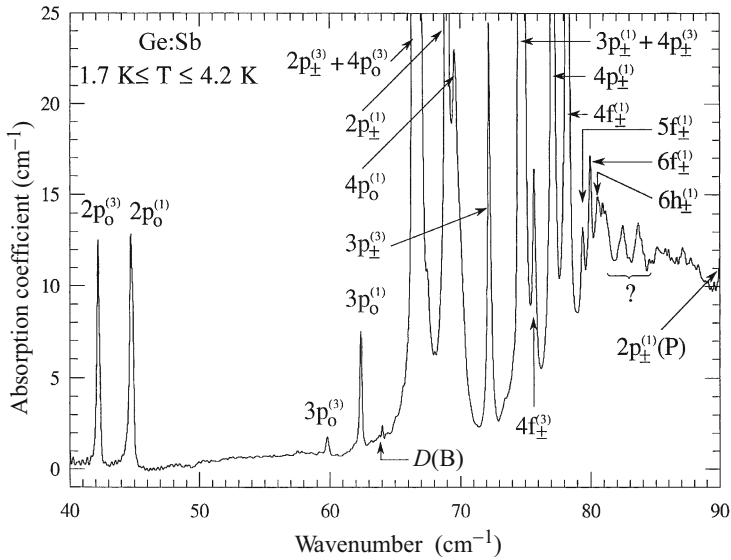


**Fig. 6.9.** Absorption spectrum between 5 and  $\sim 11.2 \text{ meV}$  of a Ge sample with  $[\text{Sb}] = 8 \times 10^{14} \text{ cm}^{-3}$  at a temperature between 1.7 and 4.2 K. The spectral resolution is  $0.14 \text{ cm}^{-1}$  ( $\sim 17 \mu\text{eV}$ ). The lines with indexes (1) and (3) originate from the  $1s(A_1)$  and  $1s(T_2)$  levels, respectively. Band gap radiation reaching the sample explains the sharpness of the lines and the observation of line D of the B acceptor. [15] Copyright 1997, with permission from World Scientific Publishing Co. Pte. Ltd, Singapore

**Table 6.6.** Valley-orbit splitting  $1s(A_1) - 1s(T_2)$  (meV (cm<sup>-1</sup> in parentheses)) of the isolated single donors in germanium

| P                          | As                         | Sb                        | Bi                       | Li <sub>i</sub>           |
|----------------------------|----------------------------|---------------------------|--------------------------|---------------------------|
| 2.812 (22.68) <sup>a</sup> | 4.118 (33.21) <sup>a</sup> | 0.316 (2.55) <sup>b</sup> | 2.85 (23.0) <sup>c</sup> | 0.046 (0.37) <sup>a</sup> |

<sup>a</sup> [49], <sup>b</sup> [15], <sup>c</sup> [217]

resonance of the generated radiation is observed when  $\omega_1 - \omega_2$  is equal to the valley-orbit splitting  $1s(A_1) - 1s(T_2)$  of the donor. The values obtained for P and As are 2.80 and 4.17 meV, respectively, and they compare reasonably well with the values of Table 6.6 obtained from absorption measurements. As already mentioned, the value of this valley-orbit splitting is often denoted  $4\Delta_c$  in germanium.

In germanium, the small energy differences between the excited levels requires high resolution, and only one high-resolution absorption study is known, for Ge:Sb (Fig. 6.9). PTIS is certainly the best-suited method to investigate the shallow donor spectra in germanium [49, 90, 224, 230], but it is difficult to detect the  $np_0$  lines with this method, and it does not give the relative intensities of the lines [49]. Values of  $np_0$  and  $nf_0$  transition energies with  $n \geq 4$  have been obtained for Sb from uniaxial stress absorption studies in the high-stress limit [14]. This limit is achieved when the identical splittings under stress of the  $np_0$  and  $np_{\pm 1}$  donor states are much larger than the valley-orbit splitting of the donor (see Sect. 8.2.1.1 and Fig. 8.7). It has been found that under this condition, for a force  $\mathbf{F} // \langle 111 \rangle$  and for the electric vector of the radiation  $\mathbf{E} // \mathbf{F}$ , the absorption spectrum at LHeT is dominated by lines denoted  $np_0(\infty)$  by Baker and Fisher, whose positions can be related simply to the zero stress positions.

An appreciation of the relative intensities of the donor lines in germanium from the absorption spectrum of Fig. 6.9 is difficult. In the absence of another detailed absorption spectrum of a shallow donor in germanium, an order of magnitude of the relative intensities can be obtained from the calculated OSs of Table 5.20: when the intensity of the  $2p_{\pm 1}$  line is taken as 100, the intensities  $>1$  expected for the other lines are approximately:  $2p_0$ : 10,  $3p_0$ : 1,  $3p_{\pm 1}$ : 20,  $4p_{\pm 1}$ : 10,  $4f_{\pm 1}$ : 10,  $5p_{\pm 1}$ : 1,  $5f_{\pm 1}$ : 3,  $6p_{\pm 1}$ : 3 (Faulkner's labels are used). The predicted strength of line  $5p_{\pm 1}$  is notably smaller than those of lines  $4f_{\pm 1}$  and  $5f_{\pm 1}$ , and this is corroborated by the absence of a line that could be attributed to  $5p_{\pm 1}$  in most of the experimental donor spectra in germanium. When this line is reported with Faulkner's label, the energy level of the excited state is generally found to be close to 0.46–0.47 meV, showing that it is actually  $5f_{\pm 1}$ . Values of the  $5p_{\pm 1}$  energy level of Sb and P in germanium (0.57 meV) have been deduced from the “hot”  $2s \rightarrow 5p_{\pm 1}$  PTIS transition [70], close to the calculated value (0.573 meV) for the  $5p_{\pm 1}$  level. A line at 9.24 cm<sup>-1</sup> (1.146 meV), above the  $2p_{\pm 1}$  line, has been reported in the PTIS spectrum of

P by Darken [49]. From the  $BC-2p_{\pm 1}$  separation of 1.729 meV in germanium, the energy of this line<sup>3</sup> is 0.583 meV, identifying it as  $5p_{\pm 1}(P)$ .

In the 1970s, the need to understand the role of impurities and defects in germanium nuclear radiation detectors led to the production of high-purity germanium crystals, and to their physico-chemical characterization. Because of its sensitivity, PTIS was a privileged tool and many results were obtained by this technique [90]. High-purity CZ germanium crystals were grown from silica crucibles under a hydrogen atmosphere, chosen because it was shown to produce crystals with the best characteristics for nuclear radiation detectors, and the residual impurities in these crystals were H and  $O_i$ . The measurement of the concentration of residual  $O_i$ , in the  $10^{12} - 10^{14} \text{ cm}^{-3}$  range in these crystals, by the lithium precipitation method [65] led to the study of the interaction of Li with  $O_i$ . Evidence for the formation of a (Li,O) complex, assumed to be the only one, was obtained by PTIS ([90], and references therein). This complex displays EM donor spectra with a complicated behaviour; four distinct spectra due to the splitting of the ground state are related to this complex [49, 90]. The spectrum corresponding to the deepest state is denoted here  $D_1(\text{Li,O})$  and its ionization energy is 10.48 meV. It was previously reported by Seccombe and Korn [224] and Skolnick et al. [230] as spectrum A and S, respectively. The positions of the lines of the  $D_1(\text{Li,O})$  spectrum are given in Table 6.7 with the values of [230]. The  $D_1(\text{Li,O})$  lines are sharp and insensitive to the uniaxial stress [89]. The results of ESR measurements of this  $D(\text{Li,O})$  donor at 23 GHz (95  $\mu\text{eV}$ ) with a high quality factor can be explained by single-valley donors oriented along a  $\langle 111 \rangle$  direction [90]. Initially, the conjunction of these two facts was explained by the existence of a dynamic tunnelling of the interstitial Li atom around the four equivalent  $\langle 111 \rangle$  orientations [89, 90], but a static model has also been proposed [91]. Three thermalized donor spectra of the (Li,O) complex have been reported [49, 90], and their lines are broad and stress-sensitive. They are noted here as  $D_2(\text{Li,O})$ ,  $D_3(\text{Li,O})$ , and  $D_4(\text{Li,O})$  and the positions of their  $2p_{\pm 1}$  lines are 8.313, 8.250, and 7.66 meV (67.05, 66.54, and 61.8  $\text{cm}^{-1}$ ) respectively, downshifted by 0.433, 0.496, and 1.09 meV from that of  $D_1(\text{Li,O})$ .

The ionization energy of  $\text{Li}_i$  (10.033 meV) is close to those of  $D_2(\text{Li,O})$  and  $D_3(\text{Li,O})$  (10.042 and 9.979 meV, respectively) and this explains why the  $\text{Li}_i$  spectrum can be measured in good condition only in germanium samples where  $[\text{Li}] \gg [\text{O}_i]$ .

We conclude the study of the Li-related complexes in germanium by mentioning two other centres labelled (Li,X) and (Li,Y). The (Li,X) spectrum is only observed in germanium crystals with  $[\text{Li}] \gg [\text{O}_i]$  grown from a silica crucible, and that of (Li,Y) in crystals grown from a graphite crucible. The  $2p_{\pm 1}(\text{Li,X})$  and  $2p_{\pm 1}(\text{Li,Y})$  positions are 70.72 and 62.90  $\text{cm}^{-1}$  (8.768 and 7.799 meV), respectively, giving  $E_{i0}(\text{Li,X})$  and  $E_{i0}(\text{Li,Y}) = 10.497$  and

<sup>3</sup> In this reference, it is identified as  $5F_{\pm 1}$  following the labels of Broecks et al. (1986).

**Table 6.7.** Positions (meV ( $\text{cm}^{-1}$  in parentheses when available)) at LHeT of the transitions of different EM shallow donors from their ground state in germanium

| Line <sup>†</sup>                    | P <sup>a</sup> | A <sub>s</sub> <sup>b</sup> | Sb <sup>d</sup> | Bi <sup>c</sup> | Li <sup>e*</sup>                        | D <sub>1</sub> (Li, O) <sup>f</sup> | D <sub>1</sub> (H, O) <sup>f</sup> | EMT <sup>g</sup>   |
|--------------------------------------|----------------|-----------------------------|-----------------|-----------------|-----------------------------------------|-------------------------------------|------------------------------------|--------------------|
| 2p <sub>0</sub>                      | 8.120(65.49)   | 9.44 <sup>c</sup>           | 5.548(44.75)    | 8.00            |                                         |                                     |                                    | 4.776              |
| 3p <sub>0</sub>                      | 10.302(83.09)  | 11.61 <sup>c</sup>          | 7.737(62.40)    | 10.20           |                                         |                                     |                                    | 2.586              |
| 2p <sub>±1</sub>                     | 11.157(89.99)  | 12.464(100.53)              | 8.587(69.26)    | 11.08           | 8.286                                   | 8.746(70.54)                        | 10.736(86.59)                      | 1.729              |
|                                      |                |                             |                 |                 | 8.304 <sup>a</sup> (66.98) <sup>a</sup> |                                     |                                    |                    |
| 4p <sub>0</sub>                      |                |                             | 8.628(69.59)    |                 |                                         |                                     |                                    | 1.696              |
| 3p <sub>±1</sub>                     | 11.843(95.52)  | 13.149(106.05)              | 9.268(74.75)    | 11.72           | 8.974                                   | 9.429(76.05)                        | 11.420(92.11)                      | 1.042              |
| 4p <sub>±1</sub> (4F <sub>±1</sub> ) | 12.128(97.82)  | 13.439(108.39)              | 9.563(77.13)    |                 | 9.259                                   | 9.717(78.37)                        | 11.708(94.43)                      | 0.753              |
| 4f <sub>±1</sub> (4P <sub>±1</sub> ) | 12.272(98.98)  | 13.585(109.57)              | 9.696(78.20)    |                 | 9.406                                   | 9.858(79.51)                        | 11.849(95.57)                      | 0.609              |
| 5p <sub>±1</sub> (5F <sub>±1</sub> ) | 12.303(99.23)  |                             |                 |                 |                                         |                                     |                                    | 0.573              |
| 5f <sub>±1</sub> (5P <sub>±1</sub> ) | 12.410(100.09) |                             | 9.874(79.64)    |                 | 9.546 <sup>†</sup>                      | 9.997(80.63)                        | 11.988(96.69)                      | 0.465              |
| 6p <sub>±1</sub> (6H <sub>±1</sub> ) | 12.478(100.64) | 13.761(110.99)              | 9.922(80.03)    |                 | 9.609 <sup>‡</sup>                      | 10.066(81.19)                       | 12.057(97.25)                      | 0.397              |
| 6f <sub>±1</sub> (6F <sub>±1</sub> ) | 12.547(101.20) | 13.832(111.56)              |                 |                 |                                         | 10.133(81.73)                       | 12.127(97.81)                      | 0.379              |
| 6h <sub>±1</sub> (6P <sub>±1</sub> ) | 12.562(101.32) |                             | 9.994(80.61)    |                 |                                         |                                     |                                    | 0.318              |
| 7p <sub>±1</sub> (7H <sub>±1</sub> ) | 12.598(101.61) |                             |                 |                 |                                         |                                     |                                    | 0.308              |
| E <sub>l<sub>0</sub></sub>           | 12.886         | 14.193                      | 10.316          | 12.81           | 10.033 <sup>a</sup> 10.02               | 10.475                              | 12.465                             | 9.835 <sup>b</sup> |

For the lines, the attributions in parentheses are those used by [49]. E<sub>l<sub>0</sub></sub> is obtained by adding 1.729 meV to the position of the 2p<sub>±1</sub> line. The EM energy levels of the final states are given in the last column.

\* Unresolved valley-orbit doublet, <sup>†</sup> Faulkner's attributions, <sup>a</sup> Darken [49], <sup>b</sup> After [8], <sup>c</sup> [217], <sup>d</sup> After [13], <sup>e</sup> [90], <sup>f</sup> After [230], <sup>g</sup> [46], <sup>h</sup> [133]

9.528 meV, respectively. For the observation of the spectra of these complexes, from the conditions mentioned above, it has been suggested that X is Si and Y is C [49]. It must be noted that the  $D_1(\text{Li},\text{O})$  and  $(\text{Li},\text{X})$  spectra are separated by only  $\sim 0.2 \text{ cm}^{-1}$  ( $25 \mu\text{eV}$ ).

When samples cut from high-purity germanium crystals are annealed at  $400 - 450^\circ\text{C}$ , and subsequently quenched to RT, two shallow acceptor centres, also called fast acceptors, are detected. After annealing slightly above RT, they are replaced by a moderately stable “fast” shallow donor, which vanishes under annealing at  $\sim 150^\circ\text{C}$  [87]. The production of this shallow donor requires the simultaneous presence in the crystals of hydrogen and  $\text{O}_i$ , and it was therefore proposed that hydrogen was involved in this donor as well as in the acceptors. This was confirmed by the observation of an IS of about  $-0.41 \text{ cm}^{-1}$  ( $-51 \mu\text{eV}$ ) of the lines of this donor in samples cut from crystals grown in a deuterium atmosphere [88]. This donor centre is denoted  $D(\text{H},\text{O})$  by Haller et al. [90] and the positions of the lines from its ground state spectrum  $D_1(\text{H},\text{O})$  are given in Table 6.7. A weak signature of  $D_1(\text{H},\text{O})$  can be seen, inverted, in the upper PTI spectrum of Fig. 4.4. This spectrum had been reported before without attribution by Seccombe and Korn [224], and by Skolnick et al. [230] as spectrum C.

As for  $D_1(\text{Li},\text{O})$ , the lines of the  $D_1(\text{H},\text{O})$  spectrum are sharp and insensitive to the uniaxial stress, but there is an upper limit of  $\sim 21 \text{ MPa}$  where the  $D_1(\text{H},\text{O})$  spectrum rapidly diminishes in intensity, disappears and is replaced for increasing stress by a new donor spectrum shifted toward lower energies by 2.65 meV. The lines of this new spectrum are also sharp and insensitive to stress up to the maximum stress, compatible with these PTIS experiments ( $\sim 150 \text{ MPa}$ ). To end this unconventional behaviour under stress, it must be added that the effect of the large uniaxial stress is partly reversible and that the  $D_1(\text{H},\text{O})$  spectrum can be made to reappear by raising the temperature to 9 K and above [122]. The sharpness of  $n p_{\pm 1}$  lines of the ground state spectrum of  $D(\text{H},\text{O})$  has been evaluated from low-field magneto-optical measurements ( $0.05 - 0.3 \text{ T}$ ) using low-frequency lasers (see Sect. 3.8) and for the  $2 p_{\pm 1}$  Zeeman components, a FWHM value of  $8 \mu\text{eV}$  ( $0.07 \text{ cm}^{-1}$ ) has been reported [186], and this is consistent with the absence of response of these electronic lines to stress.

At zero stress, a moderate temperature rise of samples containing the  $D(\text{H},\text{O})$  centres results in the observation of two thermalized spectra  $D_2(\text{H},\text{O})$  and  $D_3(\text{H},\text{O})$  with  $2 p_{\pm 1}$  lines at 8.224 and 7.76 meV, respectively [185]. If it is assumed that the final states of the lines of these spectra are the same as those of  $D_1(\text{H},\text{O})$ , one deduces  $D_1(\text{H},\text{O}) - D_2(\text{H},\text{O})$  and  $D_1(\text{H},\text{O}) - D_3(\text{H},\text{O})$  energy separations of 2.512 and 2.98 meV, respectively. Thus, the thermal population of the  $1s(D_2)$  and  $1s(D_3)$  states corresponding to these energy differences should result in intensity ratios between the  $D_2$  and  $D_3$  spectra on the one hand and the  $D_1$  spectrum on the other hand, smaller than those actually measured. A fit of the measured intensity ratios to the splitting deduced from the realistic Boltzmann factors gives only 1.57 and 1.94 meV for

the  $D_1(\text{H}, \text{O}) - D_2(\text{H}, \text{O})$  and  $D_1(\text{H}, \text{O}) - D_3(\text{H}, \text{O})$  energy separations. This can be explained by the splitting of the  $np_{\pm 1}$  levels by 0.98 meV, with transitions from the  $1s(D_1)$  state to the highest  $np_{\pm 1}$  component and from the  $1s(D_2)$  and  $1s(D_3)$  states to the lowest  $np_{\pm 1}$  component [185]. A model for the electronic structure of this centre accounting for its stress-induced reorientation for a stress along a  $\langle 111 \rangle$  direction was proposed by Broeckx et al. [29]. The tunnelling hydrogen model and some static models explaining some of the spectral features of the D(H,O) complex were compared by Ham [91], but the experimental tests suggested to favour one of them have apparently not been done.

The positions of the lines of the known EM donor spectra reported in germanium for different centres (except the so-called thermal double donors, discussed separately, and those where the position of only one line is known) are given in Table 6.7.

In the PTIS spectrum of P [49], lines have also been observed at 12.630, and 12.660 meV (101.87, and 102.11  $\text{cm}^{-1}$ ), with semi-experimental excited state energy values of 0.256 and 0.226 meV, respectively, which can be ascribed to  $8p_{\pm 1}$  and  $8h_{\pm 1}$  levels [20]. The positions of the  $4f_0$ ,  $5p_0$ ,  $6p_0$ , and  $6f_0$  lines of Sb extrapolated from absorption measurements in the high-stress limit [14] are 73.40, 75.72, 77.76, and 78.40  $\text{cm}^{-1}$  (9.100, 9.388, 9.641, and 9.720 meV), respectively. It is interesting to note that in this study, no value is reported at the position expected (76.75  $\text{cm}^{-1}$ ) for  $5f_0$ . This absence is correlated with a calculated OS for that line about two orders of magnitude smaller than those for the other lines of the series (see Table 5.21).

The comparison between the experimental and calculated line spacings is fundamental for the correct attribution of the lines observed (Table 6.8). One can, however, observe some scattering for the values of the highest energy As lines and for  $6f_{\pm 1}(\text{P})$ , though the reason for this is not clear.

The FWHMs of the  $2p_{\pm}(\text{As})$  line in  $^{\text{nat}}\text{Ge}$  has been measured at 3.2 K as a function of [Ga] to determine the contribution of the Stark broadening, and the value of the homogeneous line width for negligible compensation is 0.072  $\text{cm}^{-1}$  (9  $\mu\text{eV}$ ) [127]. The concentration dependence of the donor spectra in germanium has been investigated theoretically in the low-concentration region of impurity conduction (up to  $4 \times 10^{16} \text{ cm}^{-3}$ ) and compared with experimental As spectra ([110], and references therein).

What is known from the even-parity donor states in germanium above  $1s(\text{T}_2)$  has been obtained mainly from the absorption or PTIS measurements from excited states on the Sb donor between  $\sim 10$  and 12 K [72], and references therein). The  $2s \rightarrow 4p_{\pm 1}$ ,  $3s \rightarrow 4p_{\pm 1}$ , and  $3d_0 \rightarrow 4p_{\pm 1}$  transitions are, for instance, observed at 2.86, 1.40, and 0.74 meV (23.1, 11.3, and 6.0  $\text{cm}^{-1}$ ), respectively. The  $2s$ ,  $3s$ , and  $3d_0$  energies deduced from these results using Table 6.7 are 3.62, 2.16, and 1.50 meV, respectively, in reasonable agreement with the calculated EM values of Table 5.6.



**Table 6.8.** Comparison of the experimental spacings (meV) deduced from Table 6.7 between line  $2p_{\pm 1}$  and other lines of different donors in germanium with those between the corresponding calculated EM energy levels

| Spacing                   | P     | As    | Sb                 | Bi   | Li    | $D(\text{Li, O})$ | $D(\text{H, O})$ | EMT <sup>a</sup> | EMT <sup>b</sup> |
|---------------------------|-------|-------|--------------------|------|-------|-------------------|------------------|------------------|------------------|
| $2p_{\pm 1} - 2p_0$       | 3.037 | 3.00  | 3.039              | 3.08 |       |                   |                  | 3.047            | 3.030            |
| $3p_0 - 2p_{\pm 1}$       | 0.855 | 0.83  | 0.851              | 0.88 |       |                   |                  | 0.857            | 0.853            |
| $4p_0 - 2p_{\pm 1}$       |       |       | 0.041              |      |       |                   |                  | 0.033            | 0.031            |
| $4f_0 - 2p_{\pm 1}$       |       |       | 0.513 <sup>c</sup> |      |       |                   |                  | 0.509            | 0.503            |
| $3p_{\pm 1} - 2p_{\pm 1}$ | 0.686 | 0.684 | 0.681              | 0.64 | 0.688 | 0.683             | 0.684            | 0.687            | 0.683            |
| $5p_0 - 2p_{\pm 1}$       |       |       | 0.801 <sup>c</sup> |      |       |                   |                  | 0.80             | 0.792            |
| $4p_{\pm 1} - 2p_{\pm 1}$ | 0.971 | 0.975 | 0.976              |      | 0.973 | 0.971             | 0.968            | 0.976            | 0.970            |
| $6p_0 - 2p_{\pm 1}$       |       |       | 0.992 <sup>c</sup> |      |       |                   |                  | 1.00             | 0.985            |
| $4f_{\pm 1} - 2p_{\pm 1}$ | 1.115 | 1.121 | 1.108              |      | 1.120 | 1.112             | 1.113            | 1.120            | 1.113            |
| $5p_{\pm 1} - 2p_{\pm 1}$ | 1.146 |       |                    |      |       |                   |                  | 1.156            | 1.147            |
| $6f_0 - 2p_{\pm 1}$       |       |       | 1.133 <sup>c</sup> |      |       |                   |                  | 1.15             |                  |
| $5f_{\pm 1} - 2p_{\pm 1}$ | 1.253 |       | 1.287              |      | 1.260 | 1.251             | 1.249            | 1.264            | 1.253            |
| $6p_{\pm 1} - 2p_{\pm 1}$ | 1.321 | 1.297 | 1.335              |      | 1.323 | 1.321             | 1.319            | 1.332            | 1.321            |
| $6f_{\pm 1} - 2p_{\pm 1}$ | 1.390 | 1.367 |                    |      |       |                   |                  | 1.350            | 1.336            |
| $6h_{\pm 1} - 2p_{\pm 1}$ | 1.405 |       | 1.407              |      |       | 1.388             | 1.395            | 1.411            | 1.392            |

<sup>a</sup> [46], (1986), <sup>b</sup> [20], <sup>c</sup> [14], see above

**Table 6.9.** Calibration factors ( $\text{cm}^{-1}$ ) of the integrated absorption of the  $2p_{\pm 1}$  and  $3p_{\pm 1}$  lines for some donors in germanium (after [218])

|              | P                    | As                   | Sb                   |
|--------------|----------------------|----------------------|----------------------|
| Line         |                      |                      |                      |
| $2p_{\pm 1}$ | $8.3 \times 10^{12}$ | $1.0 \times 10^{13}$ | $4.6 \times 10^{12}$ |
| $3p_{\pm 1}$ | $4.8 \times 10^{13}$ | $5.3 \times 10^{13}$ | $3.7 \times 10^{13}$ |

Integrated absorption radii (the inverse of the integrated calibration factors mentioned for P in silicon) relating the integrated intensities of group-V donor lines at LHeT and the actual donor concentration were obtained by Rotsaert et al. [218]. The calibration factors are given in Table 6.9.

As in silicon, for group-V donors in germanium, the photoionization cross-section at LHeT is maximum just above the ionization energy, but it is larger: in units of  $10^{-14} \text{cm}^2$ , it is given as 1.8, 1.5, and 1.1 for Sb, P, and As, respectively ([21], and references therein).

### 6.2.3 Silicon Carbide

The only donor characterized spectroscopically in 3C-SiC is nitrogen on a C site ( $\text{N}_\text{C}$ ) [170]. The  $CB$  minimum of 3C-SiC is located at the X point of the surface of the BZ so that it is only threefold degenerate, compared to sixfold

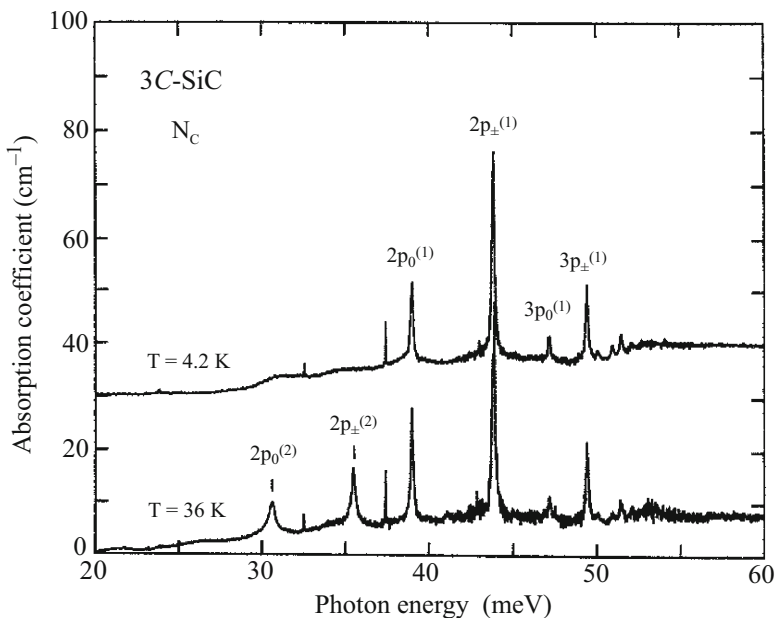


**Fig. 6.10.** Absorption spectrum of substitutional N in 3C-SiC at two temperatures. The transitions from the  $1s(A_1)$  and  $1s(E)$  levels of  $N_C$  are indexed (1) and (2), respectively. The three small sharp lines belong to the unidentified EMD spectrum (after [170]). Copyright 1995, with permission from Elsevier

for silicon. For the  $ns$  and  $np_0$  states, there are three linear combinations of one-valley wave functions corresponding to the non-degenerate  $A_1$  and doubly degenerate  $E$   $IRs$  of  $T_d$ . Figure 6.10 shows the absorption at two temperatures of a 3C-SiC sample containing  $N_C$ .

A valley-orbit splitting of the  $1s$  state of  $N_C$  is apparent from this figure as a temperature raise populates the  $1s(E)$  state (a normal ordering of the levels is assumed). The transitions from the  $1s(E)$  state are clearly broader than those from  $1s(A_1)$ . Small sharp lines can also be observed in the two spectra of Fig. 6.10, showing no thermalization effect. They are attributed to an unidentified effective-mass donor with no detectable valley-orbit splitting, denoted EMD in the original reference [170].

Table 5.3 gives a semi-empirical value of the effective Rydberg  $R_{\infty d}^*$  for EM donors in 3C-SiC. It is the ratio of the experimental  $3p_{\pm 1} - 2p_{\pm 1}$  spacing of the  $N_C$  spectrum obtained from Table 6.10 to the same spacing in atomic units, obtained by a linear interpolation of the calculated energy levels of Table 5.2 for  $\gamma^{1/3} = 0.7181$ . This value of  $R_{\infty d}^*$  (34.85 meV) is used to calculate the energies of the other donor levels by the same interpolation method. The first two rows of Table 6.10 gives the experimental positions of the lines attributed to  $N_C$  and to the EMD centre in 3C-SiC by Moore et al. [170]. The calculated

**Table 6.10.** Below the label Position: Positions (meV) of the lines of the  $N_C$  and EMD donor spectra in 3C-SiC at LHeT

| Line           | $2p_0$ | $2p_{\pm 1}$ | $3p_0$ | $3p_{\pm 1}$ | $4p_0$ | $4p_{\pm 1}$ | $4f_{\pm 1}$ | $5p_{\pm 1}$ | $6p_{\pm 1}$ | $E_{i_o}$ or $1s$ |
|----------------|--------|--------------|--------|--------------|--------|--------------|--------------|--------------|--------------|-------------------|
| Position       |        |              |        |              |        |              |              |              |              |                   |
| $N_C(1s(A_1))$ | 38.99  | 43.84        | 47.49  | 49.43        | 50.09  | 50.95        | 51.45        | 52.1         | 52.69        | 54.19             |
| $N_C(1s(E))$   | 30.63  | 35.1         |        | 41.1         |        | 42.61        | 43.17        |              |              | 45.83             |
| EMD            | 32.54  | 37.41        |        | 42.99        |        | 44.47        | 45.01        |              |              | 47.75             |
| Level energy   |        |              |        |              |        |              |              |              |              |                   |
| Calculated     | 15.21  | 10.35        | 6.99   | 4.76         | 4.09   | 3.25         | 2.75         | 2.11         | 1.52         | 47.15             |
| $N_C$          | 15.20  | 10.35        | 7.00   | [4.76]       | 4.10   | 3.24         | 2.74         | 2.1          | 1.50         |                   |
| EMD            | 15.21  | 10.34        |        | [4.76]       |        | 3.28         | 2.74         |              |              |                   |

Below the label Level energy: Calculated energies (meV) of the EM donor states in 3C-SiC and semi-empirical energy levels of the excited donor states of  $N_C$  and EMD (after [170])

energy of the  $3p_{\pm 1}$  level (4.76 meV) is added to the positions of the  $3p_{\pm 1}$  lines to give the ionization energies  $E_{i_o}$ . The third row gives the energies of the corresponding EM ground state and excited levels calculated by the above-mentioned method. The last two rows give the energy levels of the donor centres obtained by assuming the same calculated value of the  $3p_{\pm 1}$  level for the two centres.

The measured  $1s(A_1) - 1s(E)$  valley-orbit splitting of the  $N_C$  donor is 8.36 meV so that the  $1s(E)$  level energy is 45.83 meV, slightly less than the one-valley EM value, but such a situation is also encountered for the Sb and Bi  $1s(E)$  levels in silicon (Table 6.5). For EMD,  $E_{i_o}$  is close to that calculated in the EMA and no valley-orbit splitting is detected.

For the 4H-SiC polytype, a detailed study of the donor level classification and selection rules for an EM donor at the hexagonal ( $h$ ) site has been given by Ivanov et al. [114]. It has been applied to the N donor, for which 10 electronic lines between 38 and 56 meV have been reported by different groups, with an ionization energy  $E_h(N)$  of 61.4 meV ([114] and references therein). This value of  $E_h(N)$  contrasts with the value obtained for the ionization energy  $E_c(N)$  at the cubic site, which rises to 125.5 meV ([113]).

The absorption of N donors in 6H-SiC has been reported by Suttrop et al. [241], where a donor can locate on an hexagonal ( $h$ ) site and on two different cubic sites  $k_1$  and  $k_2$  (see Fig. B.5 of appendix B). The values of  $E_h$ ,  $E_{c1}$ , and  $E_{c2}$  deduced from these measurements are 81.0, 137.6, and 142.4 meV, respectively, with a valley-orbit splitting of 12.6 meV for the  $h$  donor centre.

Absorption spectra observed at LHeT in N-doped 4H- and 6H-SiC doped with P by NTD between  $\sim 33$  and 89 meV have been attributed to P and N electronic transitions [99], but no correlation with specific EM donor spectra has been attempted.

### 6.2.4 Diamond

In diamond,  $N_C$  is a deep donor, with an optical ionization energy of 2.2 eV and a thermal ionization energy of 1.7 eV due to the lattice relaxation between the neutral and ionized states. The only clearly identified shallow donor is P, introduced in synthetic diamonds by adding phosphine to the gases used in the CVD growth [137]. A first value of its ionization energy (630 meV) was obtained from cathodoluminescence measurements of the DAP spectra in different samples by Sternschulte et al. [234]. Electronic absorption of phosphorus in the 500–1000 meV region was later reported by Gheeraert et al. [73,74], consisting in a discrete spectrum between  $\sim 500$  and 600 meV, followed by a photoionization spectrum. Fano resonances involving inter-valley phonons superimposed on the photoionization spectrum have also been reported. The most intense structures involve a LO phonon with an energy in the 152–155 meV range [73,86] and these resonances have been used to determine the energies of some electronic excitations.

Three absorption lines of the P donor observed below the ionization limit are shown in Fig. 6.11.

The characteristics of the P lines and of the first energy levels of P in diamond are given in Table 6.11. The calculated EMT positions are derived

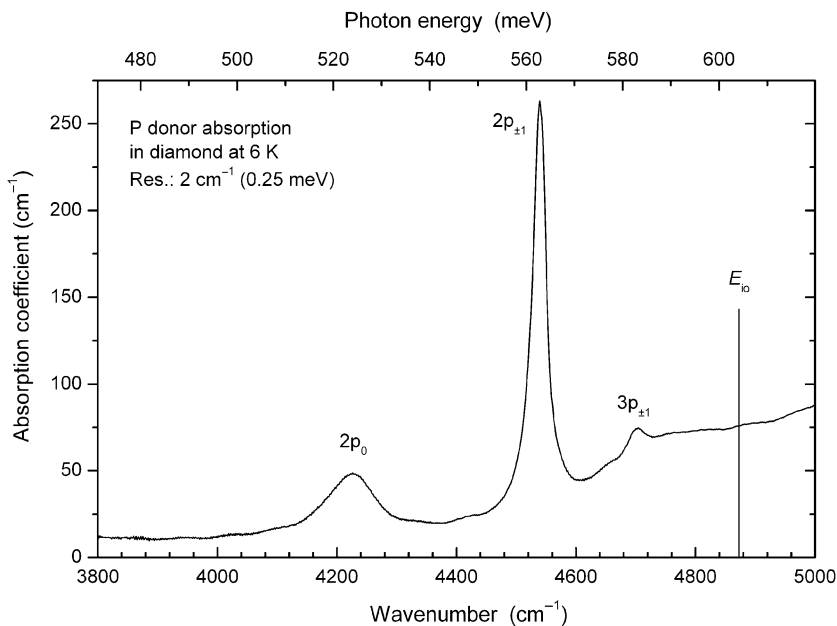


**Fig. 6.11.** Absorption spectrum of a 5  $\mu\text{m}$ -thick P-doped diamond sample at LHeT ( $[P]$  is estimated to be  $\sim 1 \times 10^{18} \text{ cm}^{-3}$ ). The demarcation of the P photoionization spectrum is not clearly defined. The bar indicates the optical ionization energy  $E_{io}$  [75]

**Table 6.11.** Spectroscopic characteristics (meV ( $\text{cm}^{-1}$  in parentheses)) of the P lines of the spectrum of Fig. 6.11

| Line            | EMT level | Position (exp.)                  | Level (exp.) | FWHM          | Peak absorption ( $\text{cm}^{-1}$ ) |
|-----------------|-----------|----------------------------------|--------------|---------------|--------------------------------------|
| $2p_0$          | 79.0      | 524.0 (4226)                     | 80.0         | 11.4 (92)     | 33                                   |
| $2s$            | 60.4      | 544 <sup>a</sup> ( $\sim 4390$ ) | 60           |               | (Fano resonance)                     |
| $2p_{\pm 1}$    | 41.2      | 562.8 (4539)                     | [41.2]       | 3.4 (27)      | 235                                  |
| $3p_{\pm 1}$    | 20.7      | 583.0 (4702)                     | 21.0         | $\sim 4$ (32) | $\sim 10$                            |
| $4p_{\pm 1}$    | 14.4      | 590 <sup>a</sup> ( $\sim 4760$ ) | 14           |               |                                      |
| $E_{\text{io}}$ | 205.8(1s) |                                  | 604.0        |               |                                      |

The positions of the levels are given with respect to the  $CB$ .  $E_{\text{io}}$  is obtained by adding 41.2 meV to the position of the  $2p_{\pm 1}$  line. The peak absorption has been determined after subtraction of the photoionization background. Features observed at 77 K by [86] have also been included with index a

self-consistently by linear interpolation from Tables 5.1 and 5.2 for  $\gamma^{1/3} = 0.56$  (this value of  $\gamma^{1/3}$  is obtained by first converting the experimental  $3p_{\pm 1} - 2p_{\pm 1}$  meV spacing into a value in atomic units by using  $R^*_{\infty d} = 125.8$  meV, and then finding by interpolation the corresponding value of  $\gamma^{1/3}$  in Table 5.2).

By assuming a similarity with P in silicon, the expected energy of the  $1s$  ( $T_2$ ) level should be comparable to the  $1s$  EMT energy and the  $1s$  ( $T_2$ ) line observed in the 400 meV ( $\sim 3200 \text{ cm}^{-1}$ ) range. The measured value of the  $2p_{\pm 1} - 2p_0$  spacing is 38.8 meV, compared to a calculated spacing of 37.8 meV. The binding energy of the 590 meV feature measured at 77 K by photocurrent spectroscopy by Haenen et al. [86] is 14 meV and it is attributed to the  $4p_{\pm 1}$  transition. Similarly, in the same work, a Fano resonance is reported to correspond to an energy of 544 meV, close to the difference ( $\sim 543$  meV) between  $E_{\text{io}}$  and the calculated  $2s$  energy level, and it could be due to the  $2s$  ( $E$ ) level.

The optical ionization energy  $E_{\text{io}}$  of Table 6.11 is in good agreement with the value of  $(610 \pm 10)$  meV obtained from electrical measurements [74].

The FWHM at LNT of the  $2p_{\pm 1}$  (P) line has been correlated with the RT electrical mobility of CVD diamond films [73] and values of 2.9 meV ( $23 \text{ cm}^{-1}$ ) have been reported for the samples with the highest mobilities ( $\sim 120 - 200 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ). This shows the importance of the role of compensation by impurities or defects in the line shapes of the P spectrum in diamond.

The electrically-detected ESR at RT and at 120 K of two P-related centers has been reported in a n-type diamond containing the P donor [78]. One of these centres showed a low spin density on the P site, suggesting a P-containing complex, while the other, observed inadvertently in these experiments, could be accounted for by an EM centre with a large spin density on the P site. The results of pulsed ESR measurements at 10 K of P-containing diamond and SiC have been reported by Isoya et al. [111]. The spectra obtained, clearly related to P, show that at a difference with the P donor in

silicon, the wave function of the ground state at the P site has predominantly a  $p$ -like character (small spin density). They also show that the symmetry of the P atom lowers from  $T_d$  in silicon and germanium to  $D_{2d}$  in diamond and 3C-SiC. In the valley-orbit-splitting scheme, the first result is an equivalent of a  $T_2$  ground state in  $T_d$  symmetry, with an energy not too different from that of an EM donor, a situation more or less comparable to that for  $Li_i$  in silicon [266]. If the ESR spectrum corresponds to an isolated P donor, this represents an EM ground state of  $\sim 0.6$  eV, rather different from the value of  $\sim 0.2$  eV deduced from the above IR measurements, and one wonders if this centre is the isolated donor or another P-related centre.

All the calculations of the site symmetry of substitutional P in diamond indicate a symmetry lower than  $T_d$ , as the atomic radius of P is about 40% larger than that of C. The most recent *ab-initio* calculations [197], and references therein) show that a  $D_{2d}$  symmetry is marginally more stable than a  $C_{3v}$  one. They also predict an outward distortion of the  $nn$  C atoms by  $\sim 10\%$ , while quantitatively, the  $D_{2d}$  symmetry remains relatively close to the  $T_d$  one.

## 6.3 Group-VI- and Mg Donors in Group-IV Crystals

### 6.3.1 Silicon

In this section, the electronic spectra associated to the group-VI elements S, Se, and Te in silicon are considered. These elements, often called chalcogens,<sup>4</sup> are represented here generically as Ch. From their electronic configuration, they are expected to be double donors when substitutional. Compared to the group-V donors, the isolated S and Se atoms are relatively deep donors in silicon, with 0/+ and +/+ levels located at  $\sim 0.3$  and  $0.6$  eV, respectively, below the  $CB$ . The group-IIA element Mg, which is a double interstitial donor  $Mg_i$  in silicon [67], is also included in this section. As noted before, in the EM donor picture where the group-V donors are compared with H, the group-VI donors and  $Mg_i$  could be qualitatively compared with He and the ionization energies are much larger than those of the group-V donors. Besides the isolated substitutional form, chalcogen atoms can also be found in close pairs, which are also double donors, and in other complex centres. Extensive studies on chalcogen donors in silicon have been performed at Wacker Heliotronic [262] in the 1980s and by the group at the University of Lund [83].

#### 6.3.1.1 The Neutral Charge State

In the neutral charge state, one expects that the interactions between the two electrons bound to the Ch double donors would give rise to a He-like energy spectrum. However, these double donors are characterized by two electrons with wave functions very different in their spatial extension, and the inner

<sup>4</sup> From the Greek *chalcos* “ore”, literally: ore generating (many sulphides are metallic ores).

electron provides an almost perfect screening of the extra ionic charge. As a consequence, the spectrum observed in the neutral charge state is very similar to those for the group-V H-like donors. In the singly-ionized state, however, these double donors must be compared to  $\text{He}^+$ , and their energy levels with respect to the H-like donors must be scaled by the ratio of the ionization energies of  $\text{He}^+$  and H, which is close to 4.00. Another difference between group-V and group-VI elements is that the latter are involved in several EM donor complexes, some being double donors and others single donors. First, the double donor centres are considered.

Besides the isolated Ch donors, other chalcogen-related double donors known in silicon are the Ch pairs, noted as  $\text{Ch}_2$ . The existence of S pairs has been inferred by Ludwig [156] from the ESR results and from the interpretation of piezospectroscopic measurements on Si:S by Krag et al. [144]. The reason for the  $\text{Ch}_2$  pairs being double donors can be explained by their proposed configuration: three electrons from each of the two  $nn$  substitutional Ch atoms are involved in the bonding with three  $nn$  atoms of the host crystal and two electrons of each atom involved in the Ch-Ch interaction, which could be considered the same as those in the  $\text{Ch}_2$  molecule ([198] and references therein). This leaves one unpaired electron on each Ch atom that accounts for the double donor characteristics of the pair. The propensity to form pairs depends on the closeness of the atomic radius of the Ch atom to that of silicon. Hence, the  $\text{S}_2$  pair is the dominant centre in S-doped silicon after natural cooling from the diffusion temperature, but isolated S concentration can be increased by quenching. This dominance is illustrated by the fact that in the first absorption measurements on sulphur donors [145], the ionization energies obtained in the S-doped silicon samples and attributed to the  $\text{S}^0$  and  $\text{S}^+$  were shown later to correspond to  $\text{S}_2^0$  and  $\text{S}_2^+$ . Inversely, the spectrum of the  $\text{Te}_2$  pair is about one order of magnitude less intense than that of isolated Te. The point group symmetry of the homonuclear  $\text{Ch}_2$  pairs is  $D_{3d}$ . With this symmetry, the states with  $|m| = 0$  correspond to the sum  $A_1^+ + A_1^- + E^+ + E^-$  of IRs of  $D_{3d}$  and those with  $|m| = 1$  to  $A_1^+ + A_1^- + A_2^+ + A_2^- + 2E^+ + 2E^-$ . The deepest state is  $1s(A_1^+)$  followed in this order by  $1s(E^+)$ ,  $1s(E^-)$ , and  $1s(A_1^-)$ . The symmetry-allowed transitions from the  $1s(A_1^+)$  ground state are towards states involving the  $A_1^-$  and  $E^-$  IRs [118]. In silicon samples doped with different chalcogen atoms (S/Se and Se/Te), spectra ascribed to mixed pairs have also been reported [262].

At a difference with the inverted ground state configuration of interstitial Li, the deep ground state of  $\text{Mg}^0$  is  $1s(A_1)$ . The  $\text{Mg}^0$  spectrum in silicon is shown in Fig. 6.12, together with an unidentified Mg-related complex denoted  $\text{X}_{\text{Mg}}$ . This complex has been ascribed to a (Mg,O) centre ([102], and references therein). The spectrum of Mg-diffused silicon also shows electronic lines on the low-energy side of the  $\text{Mg}^0$  spectrum, which have been attributed to another Mg-related centre with an ionization energy of  $\sim 93$  meV [152]. No transition toward the even-parity states has been observed for this donor [103].

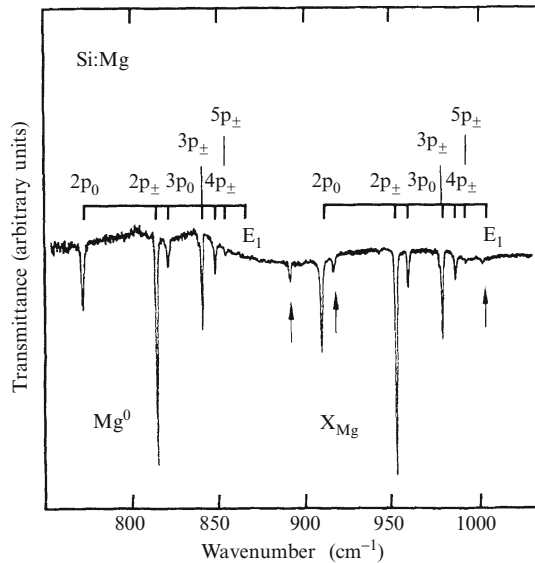


**Fig. 6.12.** Transmittance spectrum of the  $\text{Mg}^0$  EM donor in silicon at LHeT, followed at higher energy by another EM donor spectrum due to a Mg-related complex  $\text{X}_{\text{Mg}}$ , identified later as a (Mg,O) centre. The lines are denoted by their excited state. The arrows indicate unidentified lines and  $E_I$  the ionization energies. The energy range is 93–130 meV [249]. Copyright 1994 by the American Physical Society

The Ch-related donor spectra differ on that point as several parity-forbidden transitions are observed. They start with symmetry-allowed transitions from the  $1s$  ground state to the valley-orbit split  $1s$  excited states, and are supplemented with  $2s$  ( $T_2$ ) and  $3s$  ( $T_2$ ) lines and Fano resonances within the photoionization spectrum. This is shown in Fig. 6.13 for  $\text{Se}^0$ . Compared to group-V donors, this extends the energy span of the  $\text{Ch}^0$ -related spectra to the ionization energy of the  $1s$  ( $T_2$ ) level (35–40 meV in isolated chalcogens) and it can even increase to 40–48 meV when singlet-triplet spin-forbidden transitions are observed.

The  $1s$  state of isolated chalcogens, with  $T_d$  symmetry, displays the same kind of valley-orbit splitting as that of group-V donors. The  $1s$  ( $A_1$ )  $\rightarrow$   $1s$  ( $T_2$ ) transition is observed for all the chalcogen atoms and its intensity is comparable to that of the parity-allowed transitions, as seen in Fig. 6.13a while it was about one order of magnitude weaker for Bi. Considering the magnitude of the valley-orbit splitting, thermalization is clearly inappropriate in determining the energy of the  $1s$  ( $E$ ) state. Fortunately, there are no strict selection rules for the Fano resonances with the photoionization spectrum, and such resonances have been attributed to the  $1s$  ( $A_1$ )  $\rightarrow$   $1s$  ( $E$ ) transitions assisted with  $f$ TO and  $g$ LO phonons [119]. The  $1s$  ( $A_1^+$ )  $\rightarrow$   $1s$  ( $E^+$ ) transition of the  $\text{Ch}_2$  pairs is symmetry-forbidden, but the positions of the  $1s$  ( $E^+$ ) and  $2s$  ( $A_1^+$ )



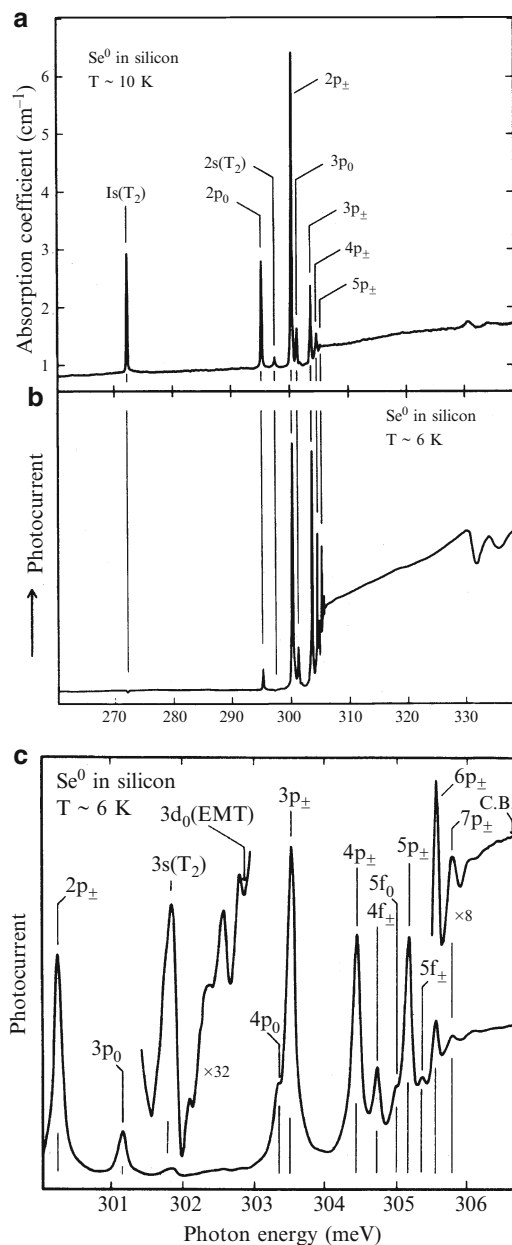


**Fig. 6.13.** Comparison between Se<sup>0</sup> spectra in silicon (a) absorption at a resolution of 1 cm<sup>-1</sup> or ~0.12 meV ([Se] ~ 3 × 10<sup>16</sup> cm<sup>-3</sup>), and (b) PTIS at a resolution of 0.25 cm<sup>-1</sup> or ~30 μeV ([Se] ~ 3 × 10<sup>15</sup> cm<sup>-3</sup>) between ~2100 and 2740 cm<sup>-1</sup>. The Fano resonances above 330 meV are clearly observed in the PTI spectrum. (c) Enlarged view of (b) showing more details of the spectrum. C.B. corresponds to the ionization energy of Se<sup>0</sup> [118]. Copyright 1984 by the American Physical Society

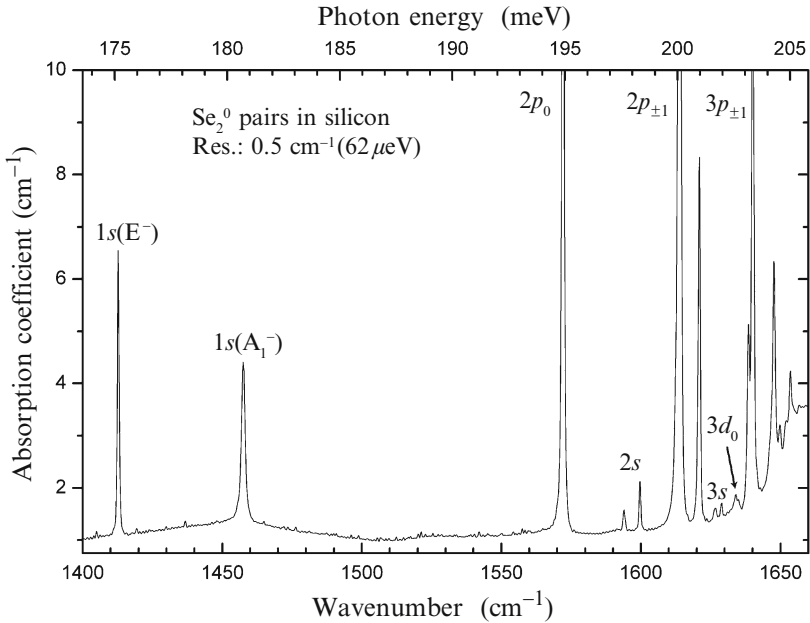


**Fig. 6.14.** Absorption spectrum at LHeT of the  $\text{Se}_2^0$  pairs in silicon showing the first  $ns(A_1^-)$  and  $ns(E^-)$  lines and the  $3d_0$  line

levels have also been determined from Fano resonances with the photoionization spectra while the first  $ns(E^-)$ , and  $ns(A_1^-)$  levels are determined more accurately from the symmetry-allowed transitions, as shown in Fig. 6.14. The ordering of the  $1s(E^-)$  and  $1s(A_1^-)$  levels has been deduced from absorption measurements under a uniaxial stress [144].

The total spin of the donor electrons of the neutral double donors can be 0 or 1. Repulsion energy is minimized in the ground state for a spin zero state and the singlet to triplet spin transition is in principle forbidden. However, besides the relatively strong  $1s(A_1) \rightarrow 1s(T_2)$  line, a weak line attributed to the  $1s(A_1) \rightarrow 1s(^3T_2)$  singlet-triplet transition has been observed in  $\text{Se}^0$  and  $\text{Te}^0$  spectra [22, 210]; Pajot unpublished). The positions and FWHMs of these lines are given in Table 6.12.

The singlet and triplet  $1s(T_2)$  transitions of  $\text{Se}^0$  are shown in Fig. 6.15, where the intensities of the allowed  $1s(T_2)$  and forbidden  $1s(^3T_2)$  transitions are in a ratio  $\sim 50/1$  when weighted by the FWHMs, not far from  $45/1$  measured by Peale et al. [210]. This ratio decreases when the lattice distortion induced by the foreign atom increases, and is  $\sim 10/1$  for  $\text{Te}^0$  [210].

In a  $^{\text{nat}}\text{Si}$  sample doped with  $^{34}\text{S}$ , a negative sulphur IS of  $-76 \mu\text{eV}$  ( $-0.61 \text{ cm}^{-1}$ ) with respect to  $^{32}\text{S}$  is observed for the  $1s(T_2)$  line of  $\text{S}^0$ , and this IS becomes  $-87 \mu\text{eV}$  ( $-0.70 \text{ cm}^{-1}$ ) for the  $2p_{\pm}(S_2^0)$  line in a sample doped with  $^{\text{nat}}\text{S}$  [233], in agreement with the isotopic shift model of [132]. Inversely,

**Table 6.12.** Energies and FWHMs (meV ( $\text{cm}^{-1}$  in parentheses)) of the  $1s(A_1) \rightarrow 1s(^3T_2)$  and  $1s(A_1) \rightarrow 1s(T_2)$  transitions of  $\text{Se}^0$  and  $\text{Te}^0$  in  $^{\text{nat}}\text{Si}$  at LHeT [210]. For S, the singlet-triplet transition is not observed

| Line        | $^{\text{nat}}\text{Se}^0$ |               | $^{\text{nat}}\text{Te}^0$ |               | $^{\text{nat}}\text{S}^0$ |                 |
|-------------|----------------------------|---------------|----------------------------|---------------|---------------------------|-----------------|
|             | Energy                     | FWHM          | Energy                     | FWHM          | Energy                    | FWHM            |
| $1s(^3T_2)$ | 266.117<br>(2146.38)       | 0.04<br>(0.3) | 151.059<br>(1218.37)       | 0.05<br>(0.4) |                           |                 |
| $1s(T_2)$   | 272.210<br>(2195.52)       | 0.06<br>(0.5) | 159.658<br>(1287.73)       | 0.36<br>(2.9) | 283.722<br>(2288.37)      | 0.035<br>(0.28) |

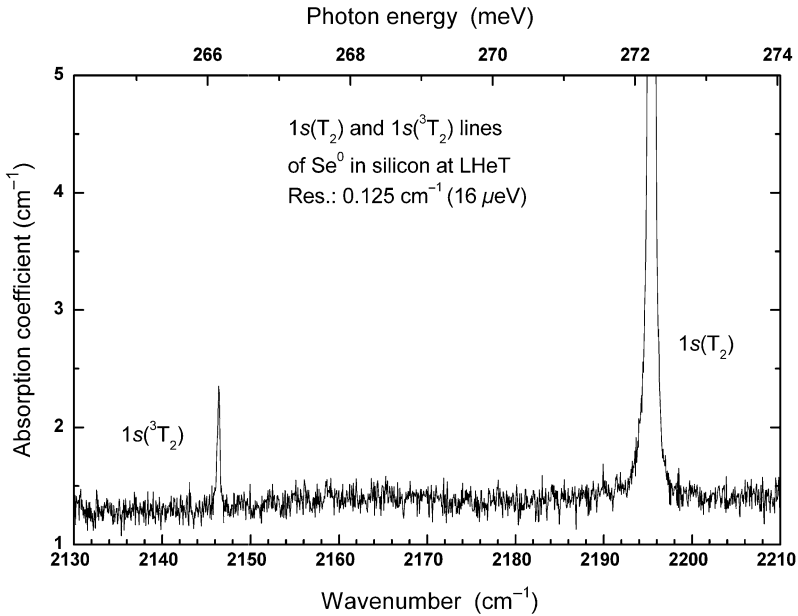


**Fig. 6.15.** Absorption of the  $1s(A_1) \rightarrow 1s(^3T_2)$  and  $1s(A_1) \rightarrow 1s(T_2)$  lines of  $\text{Se}^0$  ( $[\text{Se}] \sim 2.5 \times 10^{16} \text{ at cm}^{-3}$ ) in silicon under band-gap light illumination. The FWHM of the  $1s(^3T_2)$  line is  $\sim 0.3 \text{ cm}^{-1}$  ( $\sim 0.04 \text{ meV}$ ) and its position is  $2146.40 \text{ cm}^{-1}$ . The  $1s(T_2)$  line is truncated and its peak absorption is  $35 \text{ cm}^{-1}$

matrix ISs of  $+223$  and  $+119 \mu\text{eV}$  ( $1.80$  and  $0.961 \text{ cm}^{-1}$ ) are observed for the  $1s(T_2)$  ( $^{32}\text{S}^0$ ) and  $2p_{\pm}$  ( $^{32}\text{S}_2^0$ ) lines, respectively, when a qmi  $^{30}\text{Si}$  host lattice replaces qmi  $^{28}\text{Si}$  [233]. These latter ISs are due to the increase of  $E_g$  in qmi  $^{30}\text{Si}$ .

Table 6.13 summarizes the results of the determination of the first even-parity levels of the isolated  $\text{Ch}^0$  atoms and of the  $\text{Ch}_2^0$  pairs in silicon, as obtained from absorption measurements at LHeT. The EM ground state for a  $\text{He}^0$ -like double donor is  $56.5 \text{ meV}$ , but it can be seen that the  $1s$  split states are already H-like.

**Table 6.13.** Energies (meV) of the first even-parity levels of neutral isolated chalcogens and chalcogen pairs in silicon with respect to the *CB*. The optical ground state energies  $E_{\text{io}}$  is the same as that of the deepest level (first row)

| Level                              | S <sup>0</sup>     | Se <sup>0</sup>     | Te <sup>0</sup>     | EMT <sup>a</sup> | Level                            | S <sub>2</sub> <sup>0</sup> | Se <sub>2</sub> <sup>0</sup> | Te <sub>2</sub> <sup>0</sup> |
|------------------------------------|--------------------|---------------------|---------------------|------------------|----------------------------------|-----------------------------|------------------------------|------------------------------|
| 1s (A <sub>1</sub> )               | 318.340            | 306.675             | 198.869             |                  | 1s(A <sub>1</sub> <sup>+</sup> ) | 187.638                     | 206.469                      | 158.16                       |
| 1s ( <sup>3</sup> T <sub>2</sub> ) |                    | 40.558 <sup>b</sup> | 47.810 <sup>b</sup> |                  | 1s(E <sup>+</sup> )              | 34.4 <sup>d</sup>           | 33.2 <sup>d</sup>            |                              |
| 1s (T <sub>2</sub> )               | 34.618             | 34.465 <sup>b</sup> | 39.211 <sup>b</sup> | 31.26            | 1s(E <sup>-</sup> )              | 31.260                      | 31.317                       | 32.94                        |
| 1s (E)                             | 31.7 <sup>c</sup>  | 31.4 <sup>c</sup>   | 31.6 <sup>d</sup>   | "                | 1s(A <sub>1</sub> <sup>-</sup> ) | 26.53                       | 25.77                        | 25.71                        |
| 2s (A <sub>1</sub> )               | 18.4 <sup>d</sup>  | 18.0 <sup>d</sup>   | 15.2 <sup>d</sup>   | 8.856            | 2s(A <sub>1</sub> <sup>+</sup> ) | 15.3 <sup>d</sup>           | 15.9 <sup>d</sup>            |                              |
| 2s (T <sub>2</sub> )               | 9.37               | 9.270               | 9.67                | "                | 2s(E <sup>-</sup> )              | 8.848                       | 8.851                        |                              |
|                                    |                    |                     |                     |                  | 2s(A <sup>-</sup> )              | 8.247                       | 8.141                        | 8.15                         |
| 3s (T <sub>2</sub> )               |                    | 4.90                | 5.07                | 4.777            | 3s(E <sup>-</sup> )              | 4.792                       | 4.79                         | 4.76                         |
|                                    |                    |                     |                     |                  | 3s(A <sup>-</sup> )              | 4.52                        |                              |                              |
| 3d <sub>0</sub>                    |                    | 3.82                | 3.87                | 3.751            | 3d <sub>0</sub>                  | 3.92 <sup>a</sup>           | 3.89 <sup>a</sup>            | 3.89                         |
| 4s (T <sub>2</sub> )               | 2.84? <sup>a</sup> | 2.99                |                     | 2.911            |                                  |                             | 2.81? <sup>a</sup>           |                              |

<sup>a</sup> [118] for H-like donors, <sup>b</sup> [210], <sup>c</sup> [23], <sup>d</sup> [119]

One notes that the energy of the 1s (A<sub>1</sub><sup>-</sup>) level of the Ch<sub>2</sub> pair is smaller than the 1s EM value and a possible explanation has been proposed [220], quoted by Bergman et al. [23]. The ionization energies of mixed S/Se, S/Te and Se/Te neutral chalcogen pairs reported by Wagner et al. [262] are 191.9, 156.2, and 170.8 meV, respectively. For S/Se and Se/Te, the values are between the energies of the parent homonuclear pairs, but the one for S/Te is slightly less than that of the Te<sub>2</sub><sup>0</sup> pair.

With good <sup>nat</sup>Si samples and stress-free mounting, the lowest FWHMs measured for the neutral S-related complexes are about 25 μeV (0.20 cm<sup>-1</sup>). The FWHM increases with the atomic radius of the donor and is ~0.125 meV (1 cm<sup>-1</sup>) for the Te<sup>0</sup> spectrum. Table 6.14 gives the positions of the first parity-allowed transitions of the Ch-related double donors and of Mg<sup>0</sup> in silicon, to which are added the positions of the lines of the first Ch<sub>c</sub>X<sub>1</sub> complexes. Under high resolution, 2p<sub>0</sub> (S<sub>c</sub>X<sub>1</sub>) is partially resolved into two components in a ratio ~6/1 for the highest energy one, and smaller unresolved splittings are also observed for 3p<sub>0</sub> and 4p<sub>0</sub> of that centre. The positions of the lines of the S<sub>c</sub>X<sub>3</sub> complex have also been added to Table 6.14. A particularity of its spectrum is the splitting of the 2p<sub>±1</sub> line into a doublet.

It is interesting to compare the line spacings of these neutral double donors with those measured for the single donors, given in Table 6.4. The corresponding spacings are given in Table 6.15.

Table 6.15 shows that the level spacings of these He-like donors, when neutral, correspond to H-like centres whose inner core includes the second donor electron. At the spectroscopic level, this second electron manifests itself in the neutral spectra only through its spin, which can be detected in one singlet to triplet transition. There is a noticeable correlation between the  $S_{2p} = 2p_{±1} - 2p_0$  difference for group-V donors of Table 6.4 and for group-VI

**Table 6.14.** Positions (meV) at LHeT of the first parity-allowed lines of the Ch-related and interstitial Mg neutral double donor centres and of the  $S_cX_3$  single donor in silicon

| Line         | $S^0$               | $Se^0$              | $Te^0$               | $S_2^0$             | $Se_2^0$             | $Te_2^0$            | $Mg^{0a}$           | $(Mg,O)^{0a}$       | $S_cX_1$            | $S_cX_3$            | $Se_cX_1$            | $Te_cX_1$           |
|--------------|---------------------|---------------------|----------------------|---------------------|----------------------|---------------------|---------------------|---------------------|---------------------|---------------------|----------------------|---------------------|
| $2p_0$       | 306.873             | 295.173             | 187.322              | 176.136             | 194.914              | 146.55              | 95.83               | 112.99              | 97.83*              | 70.454              | 104.380              | 115.11              |
|              |                     |                     |                      |                     |                      |                     |                     |                     | 97.943              |                     |                      |                     |
| $2p_{\pm 1}$ | 311.938             | 300.275             | 192.492              | 181.235             | 200.082              | 151.81              | 101.15              | 118.27              | 103.140             | 75.769              | 109.637              | 120.57              |
|              |                     |                     |                      |                     |                      |                     |                     |                     |                     | 75.818              |                      |                     |
| $3p_0$       | 312.870             | 301.191             | 193.376              | 182.158             | 200.968              | 152.65              | 101.98              | 119.14              | 104.025             |                     | 110.511              | 121.38              |
| $4p_0$       | 315.035             | 303.360             | 195.579              | 184.330             | 203.152              |                     | 104.19              |                     | 106.214             | 78.84               | 112.70               | 123.14              |
| $3p_{\pm 1}$ | 315.220             | 303.555             | 195.749              | 184.518             | 203.349              | 155.04              | 104.41              | 121.54              | 106.414             | 79.059              | 112.911              | 123.82              |
| $4f_0$       |                     |                     |                      | 185.309             |                      |                     |                     |                     |                     |                     |                      |                     |
| $5p_0$       | 316.114             | 304.437             | 196.684 <sup>†</sup> | 185.406             | 204.289 <sup>†</sup> | 156.03 <sup>†</sup> | 105.34 <sup>†</sup> | 122.46 <sup>†</sup> | 107.292             | 79.985 <sup>†</sup> | 113.850 <sup>†</sup> | 124.79 <sup>†</sup> |
| $4p_{\pm 1}$ | 316.150             | 304.492             |                      | 185.447             |                      |                     |                     |                     | 107.344             |                     |                      |                     |
| $4f_{\pm 1}$ | 316.439             | 304.772             | 196.976              | 185.741             | 204.555              |                     | 105.63              |                     | 107.639             | 80.281              | 114.129              |                     |
| $5f_0$       | 316.702             | 305.00 <sup>b</sup> | 197.243              | 186.001             | 204.82               |                     | 105.86              |                     | 107.889             | 80.53               |                      |                     |
| $5p_{\pm 1}$ | 316.876             | 305.219             | 197.419              | 186.177             | 205.013              |                     | 106.06              | 123.18              | 108.075             | 80.714              | 114.574              |                     |
| $5f_{\pm 1}$ | 317.04 <sup>b</sup> | 305.37 <sup>b</sup> |                      | 186.36              | 205.23               |                     |                     |                     | 108.25              |                     |                      |                     |
| $6f_0$       |                     |                     |                      | 186.387             |                      |                     |                     |                     | 108.277             |                     |                      |                     |
| $6p_{\pm 1}$ | 317.253             | 305.586             | 197.796              | 186.558             | 205.40               |                     | 106.45              |                     | 108.450             | 81.089              |                      |                     |
| $7f_0$       |                     |                     |                      | 186.650             |                      |                     |                     |                     | 108.544             |                     |                      |                     |
| $6h_{\pm 1}$ | 317.444             |                     |                      | 186.738             |                      |                     |                     |                     | 108.635             |                     |                      |                     |
| $7p_{\pm 1}$ | 317.50 <sup>b</sup> | 305.78 <sup>b</sup> | 198.08               | 186.800             | 205.62 <sup>b</sup>  |                     |                     |                     | 108.697             |                     |                      |                     |
| $E_{i0}$     | 318.340             | 306.675             | 198.869              | 187.638             | 206.469              | 158.16              | 107.53              | 124.66              | 109.534             | 82.179              | 116.031              | 126.94              |
|              | 318.32 <sup>b</sup> | 306.63 <sup>b</sup> |                      | 187.61 <sup>b</sup> | 206.44 <sup>b</sup>  |                     |                     |                     | 109.52 <sup>b</sup> | 82.16 <sup>b</sup>  |                      |                     |

$E_{i0}$  is obtained by adding the EM energy (3.120 meV) of the  $3p_{\pm 1}$  level to the position of the line. The positions in  $cm^{-1}$  can be obtained by dividing the meV values by 0.1239842. The semi-empirical energy levels of the final states are the differences between  $E_{i0}$  and the line positions

\* Partially resolved weaker component <sup>†</sup>  $5p_0$  and  $4p_{\pm 1}$  not resolved, <sup>a</sup> [102] <sup>b</sup> [118]

**Table 6.15.** Spacings (meV) between line  $2p_{\pm 1}$  and other lines of Table 6.14 compared with those between the corresponding EM energy levels

| Spacing                   | S <sup>0</sup>    | Se <sup>0</sup>   | Te <sup>0</sup> | S <sub>2</sub> <sup>0</sup> | Se <sub>2</sub> <sup>0</sup> | Te <sub>2</sub> <sup>0</sup> | Mg <sup>0</sup> | (MgO) <sup>0</sup> | S <sub>c</sub> X <sub>1</sub> <sup>0</sup> | S <sub>c</sub> X <sub>3</sub> <sup>*</sup> | Se <sub>c</sub> X <sub>1</sub> <sup>0</sup> | Te <sub>c</sub> X <sub>1</sub> <sup>0</sup> | EMT <sup>a</sup> |
|---------------------------|-------------------|-------------------|-----------------|-----------------------------|------------------------------|------------------------------|-----------------|--------------------|--------------------------------------------|--------------------------------------------|---------------------------------------------|---------------------------------------------|------------------|
| $3p_{\pm 1} - 2p_0$       | 8.347             | 8.382             | 8.427           | 8.382                       | 8.435                        | 8.49                         | 8.58            | 8.55               | 8.471                                      | 8.605                                      | 8.531                                       | 8.71                                        | 8.372            |
| $2p_{\pm 1} - 2p_0$       | 5.065             | 5.103             | 5.171           | 5.100                       | 5.168                        | 5.26                         | 5.32            | 5.28               | 5.198                                      | 5.341                                      | 5.258                                       | 5.47                                        | 5.090            |
| $3p_0 - 2p_{\pm 1}$       | 0.932             | 0.916             | 0.884           | 0.923                       | 0.887                        | 0.84                         | 0.83            | 0.87               | 0.885                                      |                                            | 0.874                                       | 0.81                                        | 0.917            |
| $4p_0 - 2p_{\pm 1}$       | 3.097             | 3.085             | 3.088           | 3.095                       | 3.070                        |                              | 3.04            |                    | 3.074                                      |                                            | 3.07                                        |                                             | 3.093            |
| $3p_{\pm 1} - 2p_{\pm 1}$ | 3.282             | 3.281             | 3.270           | 3.284                       | 3.267                        | 3.24                         | 3.26            | 3.27               | 3.275                                      | 3.267                                      | 3.275                                       | 3.249                                       | 3.282            |
| $4f_0 - 2p_{\pm 1}$       |                   |                   |                 | 4.075                       |                              |                              |                 |                    |                                            |                                            |                                             |                                             | 4.063            |
| $5p_0 - 2p_{\pm 1}$       | 4.176             | 4.163             |                 | 4.171                       |                              |                              |                 |                    | 4.153                                      |                                            |                                             |                                             | 4.167            |
| $4p_{\pm 1} - 2p_{\pm 1}$ | 4.212             | 4.217             | 4.192           | 4.212                       | 4.207                        | 4.23                         | 4.19            | 4.19               | 4.205                                      | 4.192                                      | 4.214                                       | 4.22                                        | 4.215            |
| $4f_{\pm 1} - 2p_{\pm 1}$ | 4.501             | 4.497             | 4.485           | 4.506                       | 4.474                        |                              | 4.48            |                    | 4.500                                      | 4.487                                      | 4.493                                       |                                             | 4.508            |
| $5f_0 - 2p_{\pm 1}$       | 4.764             |                   | 4.752           | 4.767                       | 4.741                        |                              | 4.71            |                    | 4.749                                      |                                            |                                             |                                             | 4.772            |
| $5p_{\pm 1} - 2p_{\pm 1}$ | 4.938             | 4.944             | 4.928           | 4.943                       | 4.931                        |                              | 4.91            | 4.91               | 4.935                                      | 4.921                                      | 4.938                                       |                                             | 4.953            |
| $5f_{\pm 1} - 2p_{\pm 1}$ | 5.11              | 5.13              |                 | 5.13                        | 5.150                        |                              |                 |                    | 5.11                                       |                                            |                                             |                                             | 5.142            |
| $6p_{\pm 1} - 2p_{\pm 1}$ | 5.315             | 5.312             | 5.305           | 5.318                       | 5.323                        |                              | 5.30            |                    | 5.311                                      | 5.297                                      |                                             |                                             | 5.332            |
| $6h_{\pm 1} - 2p_{\pm 1}$ | 5.506             |                   |                 | 5.503                       |                              |                              |                 |                    | 5.496                                      |                                            |                                             |                                             | 5.516            |
| $7p_{\pm 1} - 2p_{\pm 1}$ | 5.57 <sup>a</sup> | 5.54 <sup>a</sup> | 5.58            | 5.565                       | 5.57 <sup>a</sup>            |                              |                 |                    | 5.557                                      |                                            |                                             |                                             | 5.580            |

The  $CB-2p_{\pm 1}$  spacing is the  $3p_{\pm 1}-2p_{\pm 1}$  spacing plus 3.120 meV. For  $S_cX_3$ , the asterisk indicates that the spacings are taken with respect to the arithmetic mean of the two components of  $2p_{\pm 1}$

<sup>a</sup> [118]

neutral donors of the same row of the Periodic Table in Table 6.15, showing the same trend in the local volume variation induced by a foreign atom in the silicon lattice. This correlation has been used to ascertain that the group-VI atoms are located on a substitutional site at a time when it was still argued that they could be interstitial atoms [205]. For the chalcogen-related complexes, the binding energy of the  $2p_0$  level increases with the atomic distortion induced by the complex, but the correlation between the two electrons must also play a role, as shown in the case of  $\text{Mg}^0$ . The global perturbation probed by the  $3p_{\pm 1} - 2p_0$  spacing follows the atomic radius of the chalcogen atom and it increases for the complexes.

In Tables 6.3 and 6.14, the list of the parity-allowed transitions of single donors and neutral double donors in silicon is limited to  $6h_{\pm 1}$  and  $7p_{\pm 1}$ , respectively. For some donor spectra, lines have been detected at higher energies and their positions are given in Table 6.16.

Thus, for P and some neutral S-related complexes in natural silicon, the absorption of about 24 parity-allowed transitions is observed. One can note that while differences exist between the calculated and experimental energy levels, the differences between the corresponding experimental energy spacings

**Table 6.16.** Energies (meV ( $\text{cm}^{-1}$  in parentheses)) at LHeT of the ultimate parity-allowed transitions observed in the donor spectra of P [232],  $\text{S}^0$  [233],  $\text{S}_2^0$  and  $\text{S}_c\text{X}_1^0$  [204] in  $^{\text{nat}}\text{Si}$ . The energies (meV) of the excited states are given in brackets

|                | P                                  | $\text{S}^0$       | $\text{S}_2^0$     | $\text{S}_c\text{X}_1$ | EMT <sup>b</sup>   |
|----------------|------------------------------------|--------------------|--------------------|------------------------|--------------------|
| $7p_{\pm 1}$   | (360.876) 44.7429<br>[0.835]       |                    | 186.800<br>[0.838] | 108.697<br>[0.841]     | 0.822              |
| $7f_{\pm 1}$   | (361.453) 44.8145<br>[0.763]       | 317.582<br>[0.758] | 186.875<br>[0.763] | 108.765<br>[0.773]     | 0.750              |
| $7h_{\pm 1}$   | (362.029) 44.8859<br>[0.692]       | 317.655<br>[0.684] | 186.945<br>[0.693] | 108.840<br>[0.698]     | 0.676              |
| $8p_{\pm 1}^a$ | (362.40) 44.932<br>[0.646]         |                    |                    |                        | 0.636              |
| $8f_{\pm 1}$   | (362.683) 44.9670<br>[0.611]       |                    | 187.031<br>[0.607] | 108.925<br>[0.613]     | 0.596              |
| $8h_{\pm 1}$   | (362.929) 44.9975<br>[0.580]       |                    | 187.065<br>[0.573] | 108.857<br>[0.581]     | 0.566              |
| $9p_{\pm 1}$   | (363.575) 45.0776<br>[0.500]       |                    | 187.132<br>[0.506] | 109.028<br>[0.510]     | 0.498 <sup>c</sup> |
| $9h_{\pm 1}$   | (364.113) 45.1443<br>[0.434]       |                    | 187.204<br>[0.434] | 109.11<br>[0.43]       | 0.438 <sup>c</sup> |
| $a$            | (364.578) 45.2019<br>[0.376]       |                    | 187.27<br>[0.37]   |                        |                    |
| $b$            | $\pm$ (364.957) 45.2489<br>[0.329] |                    |                    |                        |                    |

<sup>±</sup> Reduced accuracy, <sup>a</sup> [275], <sup>b</sup> [204], <sup>c</sup> Broeckx and Clauws, unpublished results

of different donors remain small because it corresponds to differences between nearly perfect EM energy levels: the  $9p_{\pm 1} - 7p_{\pm 1}$  spacing for P,  $S_2^0$  and  $S_cX_1^0$  are 0.335, 0.332 and 0.331 meV, respectively, compared to the EM spacing of 0.324 meV.

### 6.3.1.2 The Singly-Ionized Charge State

In compensated n-type silicon, double donors are in the singly-ionized charge state at thermal equilibrium. The corresponding spectra are observed at about twice the photon energies of those for the neutral charge state (the ratio of the ionization energies of  $He^+$  and  $He^0$  is 2.213) and the line spacings are close to four times the corresponding ones for the neutral charge state, otherwise, the two spectra look similar. The FWHMs of the lines are somewhat larger than those for the neutral charge state, and it is more marked for the lines closer to the ionization limit. This arises partly from an inhomogeneous Stark effect due to the compensation of the samples necessary to ionize the first electron. The spectrum of  $Mg^+$  observed in p-type silicon diffused with Mg is shown in Fig. 6.16.

As for  $Mg^0$ , no even-parity transition is detected in the  $Mg^+$  spectrum, but the Fano resonances involving the  $2s(A_1)$  and  $2s(T_2)$  transitions allow determination of the position of these two levels [130]. This high-resolution

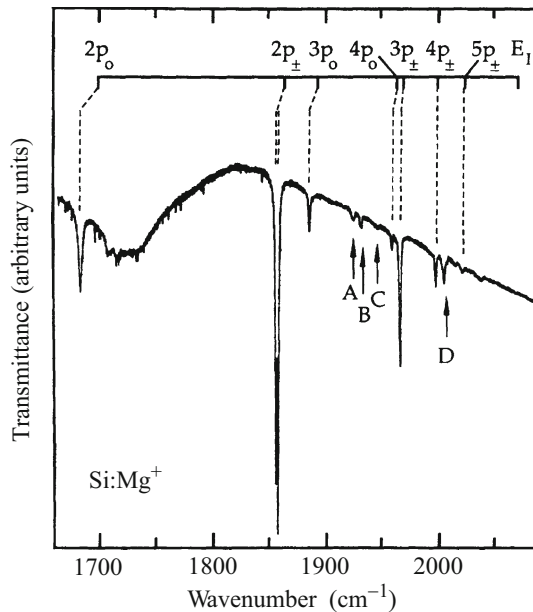


**Fig. 6.16.** Transmittance spectrum of  $Mg^+$  in silicon at LHeT in the  $\sim 205$ – $255$  meV range. Four unidentified lines are denoted A, B, C, and D [249]. Copyright 1994 by the American Physical Society



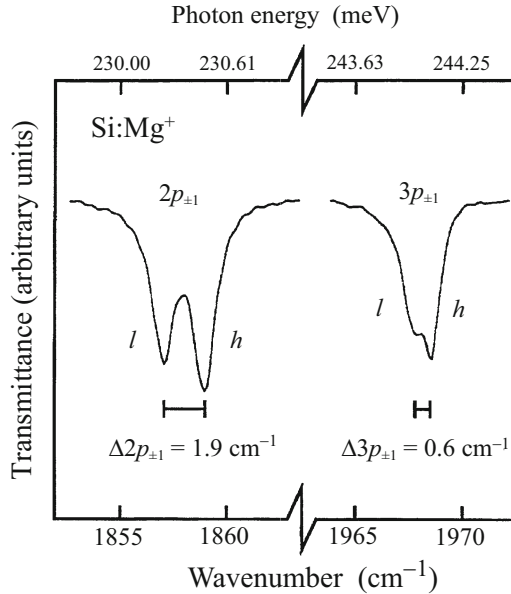


**Fig. 6.17.** Enlargement of the spectral regions of the  $2p_{\pm 1}$  and  $3p_{\pm 1}$  lines of  $\text{Mg}^+$  showing their splitting (236 and 74  $\mu\text{eV}$ , respectively) by valley-orbit and central-cell interactions. The split components are indexed  $l$  and  $h$  in Table 6.18 [249]. Copyright 1994 by the American Physical Society

spectrum is interesting because the  $2p_{\pm 1}$  line is split into two components. This is better seen in Fig. 6.17, which clearly shows the splitting of the  $2p_{\pm 1}$  line (already noted by Ho and Ramdas [103]) and of the  $3p_{\pm 1}$  line.

An EM spectrum attributed to the singly-ionized state of a  $(\text{Mg},\text{O})$  complex has been observed in O-containing B-doped silicon diffused with Mg at higher energy than the  $\text{Mg}^+$  spectrum, and the ionization energy of this centre is 274.90 meV [102]. This seems to show that the  $(\text{Mg},\text{O})$  complex is a double donor.

As for single donors, the spin of the donor electron of  $\text{Ch}^+$  allows for spin-valley coupling and it splits the  $1s(\text{T}_2)$  state into  $1s(\text{T}_2)\Gamma_7$  and  $1s(\text{T}_2)\Gamma_8$  substates, similar to those already observed for Bi and Sb in silicon (Figs. 6.4 and 6.5), but here, because of the larger separation between the levels, it is already observed for  $\text{S}^+$  [82]. This splitting is 0.366, 2.263, and 5.49 meV for  $\text{S}^+$ ,  $\text{Se}^+$ , and  $\text{Te}^+$ , respectively. In a  $^{\text{nat}}\text{Si}$  sample containing sulphur and measured at high resolution, many lines of the  $\text{S}^+$  spectrum have been observed at LHeT, contrary to the parity-allowed transitions, the lines  $1s(\text{T}_2)\Gamma_7$  and  $1s(\text{T}_2)\Gamma_8$  (noted thereafter  $1\Gamma_7$  and  $1\Gamma_8$ ) remain sharp in this sample [206]. This allows the detection of a fine structure, shown in Fig. 6.18, which can only be explained by assuming a combination of Si and S isotopic effects as-

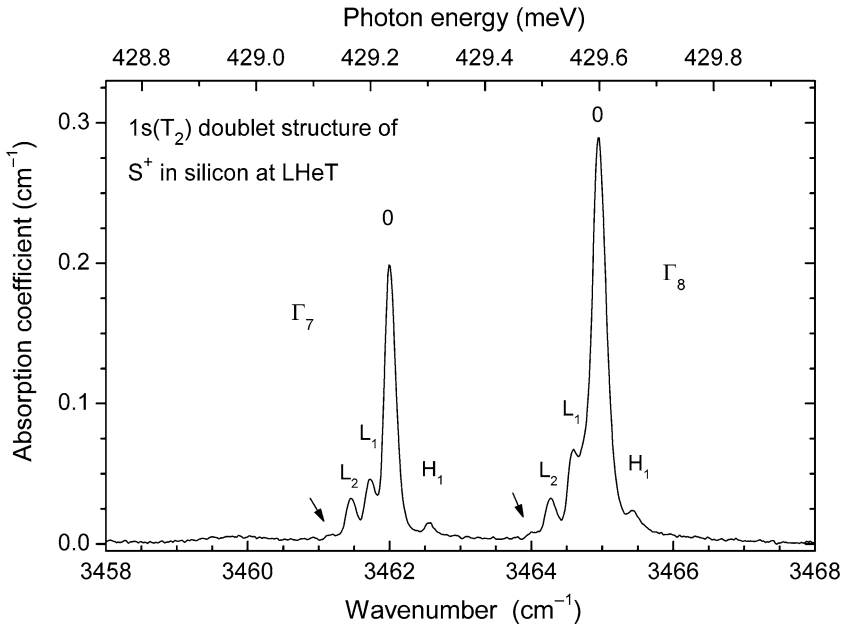


**Fig. 6.18.** High-resolution spectrum (see Table 6.16) of  $1\Gamma_7$  ( $S^+$ ) and  $1\Gamma_8$  ( $S^+$ ) in  $^{nat}\text{Si}$  at LHeT showing components associated with different  $\text{SSi}_4$  isotopic combinations. The FWHMs of 0 ( $\Gamma_7$ ) and of 0 ( $\Gamma_8$ ) are 22 and 30  $\mu\text{eV}$  (0.18 and 0.24  $\text{cm}^{-1}$ ), respectively. The features attributed to  $^{28}\text{Si}_2^{29}\text{Si}^{30}\text{Si}$  are indicated by arrows [206]. Copyright 2004 by the American Physical Society

sociated with the S atom and its four Si  $nn$ , viewed as some kind of  $\text{SSi}_4$  pseudo-molecule.

This attribution is confirmed by the observation of an expected isotope component (unresolved) of the  $1\Gamma_7$  line in a silicon sample doped with sulphur enriched with isotope  $^{33}\text{S}$  [206]. The isotope shifts observed for  $1\Gamma_7$  and  $1\Gamma_8$  with respect to the strongest component, noted 0 in Fig. 6.18, are given in Table 6.17.

This IS is negative for larger Si atomic masses, but positive for larger S masses. The magnitude of the S IS is slightly larger for  $1\Gamma_7$  (+34  $\mu\text{eV}/\text{amu}$ ) than for  $1\Gamma_8$  (+30  $\mu\text{eV}/\text{amu}$ ), but it is the inverse for the Si IS (−34 and −73  $\mu\text{eV}/\text{amu}$ , respectively).

The  $1\Gamma_7$  and  $1\Gamma_8$   $1s(T_2)$  lines of  $S^+$  have recently been observed at 1.5 K in qmi  $^{28}\text{Si}$  at a resolution of 0.3  $\mu\text{eV}$  (0.0024  $\text{cm}^{-1}$ ) by Steger et al. [233]. The isotopic effect due to silicon is absent as well as the broadening of the lines due to isotopic randomness existing in  $^{nat}\text{Si}$ . The FWHMs of  $1\Gamma_7$  and  $1\Gamma_8$  observed for  $^{34}\text{S}$  are 1.0 and 2.7  $\mu\text{eV}$ , respectively (0.008 and 0.022  $\text{cm}^{-1}$ ), compared to 22 and 30  $\mu\text{eV}$  in  $^{nat}\text{Si}$  at  $\sim 6$  K in Fig. 6.18. A FWHM of 1  $\mu\text{eV}$  is presently the smallest one ever reported for an electronic impurity absorption line in silicon and probably in any bulk semiconductor. The FWHMs reported

**Table 6.17.** Values of the shifts ( $\mu\text{eV}$ ) from the 0 component of the isotope satellites of  $1\Gamma_7$  ( $\text{S}^+$ ) and  $1\Gamma_7$  ( $\text{S}^+$ ) in  $^{\text{nat}}\text{Si}$  (accuracy:  $\pm 7 \mu\text{eV}$ )

| Satellite    | $1\Gamma_7$ shift | $1\Gamma_8$ shift | Attribution                                                       |
|--------------|-------------------|-------------------|-------------------------------------------------------------------|
| $\text{H}_1$ | +69               | +59               | $^{34}\text{S}^{28}\text{Si}_4$                                   |
|              | +35               |                   | $^{33}\text{S}^{28}\text{Si}_4$                                   |
| 0            | —                 | —                 | $^{32}\text{S}^{28}\text{Si}_4$                                   |
| $\text{L}_1$ | −34               | −44               | $^{34}\text{S}^{28}\text{Si}_3$ $^{29}\text{Si}$                  |
| $\text{L}_2$ | −69               | −84               | $^{34}\text{S}^{28}\text{Si}_3$ $^{30}\text{Si}$                  |
|              | −100              | −120              | $^{34}\text{S}^{28}\text{Si}_2$ $^{29}\text{Si}$ $^{30}\text{Si}$ |

The same value of  $+35 \mu\text{eV}$  is obtained for the  $^{33}\text{S}$  shift of line  $\Gamma_7$  either by linear interpolation between the  $^{32}\text{S}$  and  $^{34}\text{S}$  values or by direct measurement in a sample enriched with  $^{33}\text{S}$ . The last row is an estimation of the shifts of the components denoted by arrows in Fig. 6.18 [206]. For the positions of  $0(\Gamma_7)$  and  $0(\Gamma_8)$ , see Table 6.18

for the  $np_{\pm 1}$  transitions in qmi  $^{28}\text{Si}$  in Table 6.1 are more than twice as large as the FWHM of  $1\Gamma_7$  of  $\text{S}^+$  and this must also be related to the longer natural lifetime of the parity-forbidden  $1s$  ( $\text{T}_2$ ) transitions.

At high resolution, the absorption of  $1\Gamma_7$  ( $\text{Se}^+$ ) in  $^{\text{nat}}\text{Si}$  shows a pronounced asymmetry, with a FWHM of  $60 \mu\text{eV}$  ( $0.48 \text{ cm}^{-1}$ ), but no fine structure is observed (see Fig. 6.19). This profile can, however, be explained by the existence of six Se isotopes (the most abundant ones are  $^{76}\text{Se}$ ,  $^{77}\text{Se}$ ,  $^{78}\text{Se}$ ,  $^{80}\text{Se}$  and  $^{82}\text{Se}$  with natural abundances of 0.094, 0.076, 0.238, 0.496, and 0.087, respectively), and it has been shown [206] that it could be reasonably fitted to the individual isotopic components with FWHM of  $27 \mu\text{eV}$  ( $0.22 \text{ cm}^{-1}$ ).<sup>5</sup>

The IS for Si resulting from this fit is  $-34 \mu\text{eV}/\text{amu}$ , the same as that for  $\text{S}^+$ , but the chalcogen IS decreases from  $+34$  to  $+11 \mu\text{eV}/\text{amu}$  between S and Se, in qualitative agreement with the mass increase. On this basis, a Te IS of  $\sim 5 \mu\text{eV}/\text{amu}$  and the same Si IS as that for the  $\text{S}^+$  and  $\text{Se}^+$  lines is a reasonable estimate for the  $1\Gamma_7$  ( $\text{Te}^+$ ) line. On this premise, the global FWHM of the  $1\Gamma_7$  ( $\text{Te}^+$ ) line in  $^{\text{nat}}\text{Si}$  is expected to be comparable to those for  $\text{Se}^+$  (the natural abundances (%) of  $^{122}\text{Te}$ ,  $^{124}\text{Te}$ ,  $^{125}\text{Te}$ ,  $^{126}\text{Te}$ ,  $^{128}\text{Te}$  and  $^{130}\text{Te}$  are 2.6, 4.7, 7.1, 18.8, 31.7, and 34.1, respectively). Now, the true FWHM of the  $1\Gamma_7$  ( $\text{Te}^+$ ) line measured at LHeT in  $^{\text{nat}}\text{Si}$  is  $\sim 0.2 \text{ meV}$  ( $1.6 \text{ cm}^{-1}$ ) and the line is rather symmetric. These differences with  $1\Gamma_7$  ( $\text{Se}^+$ ) seem to rule out for  $1\Gamma_7$  ( $\text{Te}^+$ ) a profile determined by an isotope effect [206].

<sup>5</sup> An IS of all the parity-allowed transitions of the B shallow acceptor in silicon ( $^{10}\text{B}$  and  $^{11}\text{B}$ ), opposite to those for  $\text{S}^+$ , has been observed by Karauskaj et al. [126] in qmi  $^{28}\text{Si}$ . Thus, the statement made by Pajot et al. [206] that the ISs reported for  $\text{S}^+$  and  $\text{Se}^+$  were the first ones observed for EM-like donor and acceptor absorption spectra in semiconductor was partially incorrect.

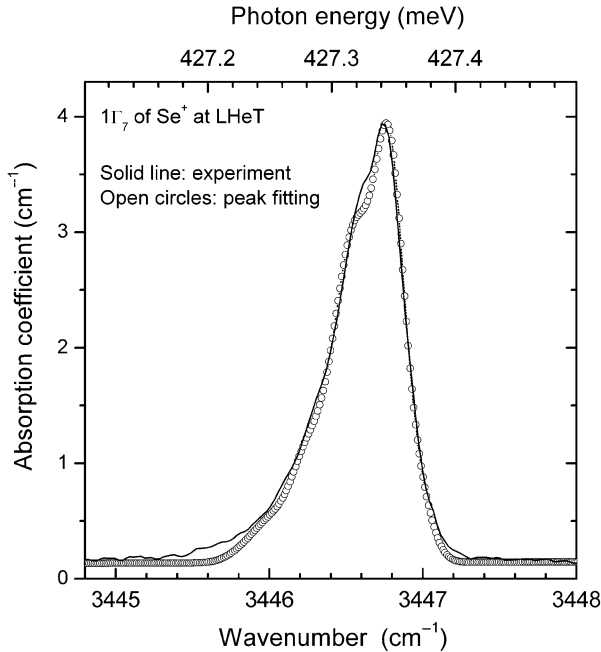


**Fig. 6.19.** Peak fitting of the  $1\Gamma_7$  ( $\text{Se}^+$ ) profile with Si and Se ISs in  $^{\text{nat}}\text{Si}$  obtained by summing the intensities of the 18 strongest  $\text{SeSi}_4$  isotopic combinations and fitting the peak absorption and energy of the  $^{80}\text{Se}^{28}\text{Si}_4$  component to  $3.28 \text{ cm}^{-1}$  and  $427.346 \text{ meV}$  [206]. Copyright 2004 by the American Physical Society

The  $1\Gamma_7$  ( $\text{Se}^+$ ) component has recently been measured in a  $^{\text{nat}}\text{Si}$  sample doped with  $^{77}\text{Se}$  and in qmi  $^{28}\text{Si}$  samples doped with  $^{\text{nat}}\text{Se}$  or  $^{77}\text{Se}$  [248]. With  $^{77}\text{Se}$ , the absorption of  $1\Gamma_7$  ( $\text{Se}^+$ ) in  $^{\text{nat}}\text{Si}$  shows three components with a FWHM  $\sim 25 \mu\text{eV}$  ( $0.2 \text{ cm}^{-1}$ ), close to the value obtained from the fit used in Fig. 6.19. This is due to the Si isotope effect involving the  $^{77}\text{Se}^{28}\text{Si}_4$ ,  $^{77}\text{Se}^{28}\text{Si}_3^{29}\text{Si}$  and  $^{77}\text{Se}^{28}\text{Si}_3^{30}\text{Si}$  combinations. In the qmi  $^{28}\text{Si}$  sample doped with  $^{\text{nat}}\text{Se}$ , the lines of the fine structure observed are only due to the Se isotope effect, with FWHMs  $\sim 1.0 \mu\text{eV}$  ( $0.008 \text{ cm}^{-1}$ ), and relative intensities matching the Se natural abundance. With such small FWHMs, the Se IS of  $+9 \mu\text{eV}/\text{amu}$  can be measured directly and is in reasonable agreement with the fitted value of Fig. 6.18 ( $+11 \mu\text{eV}/\text{amu}$ ). In the qmi  $^{28}\text{Si}$  sample doped with  $^{77}\text{Se}$ , the structure simplifies, but two lines are still observed separated by  $0.056 \text{ cm}^{-1}$  ( $\sim 7 \mu\text{eV}$ ), the hyperfine splitting due to the coupling of the spin  $\frac{1}{2}$  of  $^{77}\text{Se}$  nucleus with the electron spin. This  $1s$  ( $A_1$ ) ground state hyperfine splitting can be determined by optical absorption spectroscopy because of the very small FWHM of the  $1\Gamma_7$  ( $\text{Se}^+$ ) component in qmi silicon. In natural material, it is obtained more easily (and more accurately) from ESR measurements. The value actually obtained by this method for  $^{77}\text{Se}$  in  $^{\text{nat}}\text{Si}$

is  $(5.532 \pm 0.002) \times 10^{-2} \text{ cm}^{-1}$  [81]. When a magnetic field is applied, the electronic and nuclear spin contributions can be separated and the  $g$ -factors of the  $1s(A_1)$  and  $1s(T_2)\Gamma_7$  states be determined [233].

The Si IS is explained by considering the S-Si bond softening effect of the  $\text{SSi}_4$  pseudo-molecule in the electronic ground state, which is larger than that in the excited state. The positive IS of S is attributed to the effect of a vibronic coupling in the electronic excited state with the  $\tau_2$  mode of vibration of  $\text{SSi}_4$  within the bond softening framework.

With the exception of the  $1s(T_2)\Gamma_7$  and  $1s(T_2)\Gamma_8$  lines of  $\text{S}^+$  and  $\text{Se}^+$ , the lines of the spectra of the singly-ionized chalcogen-related donors are broader than those of the neutral donors. One reason for this is the inhomogeneous Stark broadening due to the ionized donors themselves and the compensating ionized acceptors; this usually reduces the number of lines observed. As already mentioned, the spacing between corresponding lines of singly-ionized He-like donors is multiplied by a factor of four ( $Z^2$ ) compared to the neutral H-like donors. Hence, level splitting induced by the atomic structure of non-cubic donor centres produces detectable line splittings which were barely observed in the neutral state. The positions of the lines observed in the  $\text{S}^+$ ,  $\text{Se}^+$ , and  $\text{Te}^+$  spectra are given in Table 6.18, together with the energies of the corresponding excited levels.

**Table 6.18.** Positions (meV) of the first lines of singly-ionized isolated chalcogen and Mg spectra in silicon at LHeT

| Line              | $\text{S}^+$                | $\text{Se}^+$             | $\text{Te}^+$             | $\text{Mg}^{+a}$                                           | EMT    |
|-------------------|-----------------------------|---------------------------|---------------------------|------------------------------------------------------------|--------|
| $1s(T_2)\Gamma_7$ | 429.233* (184.56)           | 427.341 (162.1)           | 234.574 (176.2)           |                                                            | 125.05 |
| $1s(T_2)\Gamma_8$ | 429.599* (184.19)           | 429.594 (159.8)           | 240.06 (170.7)            |                                                            | "      |
| $2p_0$            | 568.03 (45.76)              | 547.15 (42.2)             | 364.4 <sup>b</sup> (46.4) | 208.66 (48.02)                                             | 45.96  |
| $2s(T_2)$         | 573.14 (40.65)              |                           | 374.4 <sup>b</sup> (36.4) |                                                            | 35.44  |
| $2p_{\pm 1}$      | 588.01 (25.78)              | 563.8 <sup>c</sup> [25.6] | 385.2 <sup>b</sup> [25.6] | <sup>l</sup> 230.25 (26.43)<br><sup>h</sup> 230.48 (26.20) | 25.61  |
| $3p_0$            | 592.27 (21.52)              |                           |                           | 233.91 (22.77)                                             | 21.92  |
| $3s(T_2)$         | 593.04 (20.75)              |                           |                           |                                                            | 19.12  |
| $3d_0$            | 598.52 <sup>d</sup> (15.27) |                           |                           |                                                            | 15.00  |
| $4p_0$            |                             |                           |                           | 243.05 (13.63)                                             | 13.24  |
| $3p_{\pm 1}$      | 601.32 [12.48]              | 578 <sup>c</sup>          |                           | <sup>l</sup> 243.98 (12.70)<br><sup>h</sup> 244.06 (12.62) | 12.48  |
| $4s(T_2)$         | 601.99 (11.80)              |                           |                           |                                                            | 11.64  |
| $4p_{\pm 1}$      | 605.8 <sup>†</sup> (8.0)    |                           |                           | 247.93 [8.75]                                              | 8.75   |
| $5p_{\pm 1}$      | 608.07 (5.73)               |                           |                           | 250.87 (5.81)                                              | 5.80   |
| $E_{\text{io}}$   | 613.80                      | 589.4 <sup>c</sup>        | 410.8 <sup>b</sup>        | 256.68                                                     |        |

The energies of the excited levels (in parentheses) are normalized to four times the calculated EM energy of the  $3p_{\pm 1}$  state for  $\text{S}^+$ , of the  $2p_{\pm 1}$  state for  $\text{Se}^+$  and  $\text{Te}^+$ , and of the  $4p_{\pm 1}$  state for  $\text{Mg}^+$ , noted in brackets. The energies of the last column are four times the EMT values of [118] for neutral single donors

\* Lines 0 of Fig. 6.18, <sup>†</sup> Blended with  $5s(T_2)$ , <sup>a</sup> [249], <sup>b</sup> [81], <sup>c</sup> [243], <sup>d</sup> [142]

The positions (meV) of the  $(\text{Mg}, \text{O})^+$  lines given by Ho [102] are 227.07 ( $2p_0$ ), 248.83 ( $2p_{\pm 1}$ ), 252.38 ( $3p_0$ ), 262.42 ( $3p_{\pm 1}$ ), and 266.36 ( $4p_{\pm 1}$ ), resulting in  $E_{\text{io}} = 274.90$  meV.

Lines due to  $5f_0$ ,  $5f_{\pm 1}$ , and  $6h_{\pm 1}$  are observed in the  $\text{S}^+$  spectrum at 607.50, 608.07, 608.76, and 610.32 meV, respectively, and the energy levels obtained for the excited states are in good agreement with the EMT values [206]. The  $2s(\text{T}_2)$  line of  $\text{S}^+$  at 573.14 meV is relatively broad, due to unresolved spin-valley splitting. The profile of  $2p_{\pm}(\text{S}^+)$  is asymmetric and the  $^{34}\text{S} - ^{32}\text{S}$  IS of that line has been measured to be  $-175 \mu\text{eV}$  ( $-1.41 \text{ cm}^{-1}$ ) in  $^{\text{nat}}\text{Si}$ . The asymmetry persists in qmi  $^{28}\text{Si}$  and  $^{30}\text{Si}$ , but in qmi  $^{28}\text{Si} : ^{77}\text{Se}$ , the  $2p_{\pm} (^{77}\text{Se}^+)$  transition shows a splitting of  $166 \mu\text{eV}$  ( $1.34 \text{ cm}^{-1}$ ) [233], which can be compared with the one for  $\text{Mg}^+$ .

In  $^{\text{nat}}\text{Si}$  samples diffused with  $^{34}\text{S}$ , an IS of  $-0.14$  meV ( $-1.1 \text{ cm}^{-1}$ ) with respect to  $^{32.07}\text{S}$  (natural S) has been measured for the parity-allowed transitions of the  $^{34}\text{S}^+$  spectrum by Forman [64] and a comparable value ( $-0.175$  meV or  $-1.41 \text{ cm}^{-1}$ ) has been reported by Steger et al. [233]. The sign of IS, which is in agreement with the model of [132] is the opposite of the above-reported one for the parity-forbidden  $1s(\text{T}_2)$   $\Gamma_7$  and  $\Gamma_8$  transitions of  $\text{S}^+$  and  $\text{Se}^+$ , which is related to different vibronic coupling effects.

Some lines associated with the deepest donor excited states of the  $\text{S}_2^+$  and  $\text{Se}_2^+$  pairs and of  $\text{S}_c\text{X}_1^+$  and  $\text{Se}_c\text{X}_1^+$  have also been observed and their positions are given in Table 6.19. By analogy with the  $1s(\text{T}_2)$  state of the  $\text{Ch}^+$  donors, the  $1s(\text{E}^-)$  state of the  $\text{Ch}_2^+$  donors with  $D_{3d}$  symmetry can be assumed to be split by spin-valley interaction into  $1s\Gamma_5^-$  and  $1s\Gamma_6^-$ , where  $\Gamma_5^-$  and  $\Gamma_6^-$  are single-valued IRs of the double group of  $D_{3d}$ . In Table 6.19, the two first low-energy lines of  $\text{S}_2^+$  and  $\text{Se}_2^+$  are labelled accordingly.

The position of the line attributed to  $3p_{\pm 1}(\text{Se}_c\text{X}_1^+)$  is of rather lower energy than expected by EMT and the reason for this is not clear. A spectrum of  $\text{Se}_2^+$  is displayed in Fig. 6.20. In this spectrum, the low-energy  $1s$  components are globally denoted  $1s(\text{E}^-)$ . This spectrum is partially superimposed on the photoionization spectrum of  $\text{Se}^0$  and the transitions of  $\text{Se}_2^+$  above  $3p_0$  are severely broadened.

The high- and low-energy component of the  $2p$  lines of the  $\text{Ch}_2^+$  pairs have been tentatively attributed to  $2p(\text{E}^-)$  and  $2p(\text{A}_1^-)$ , respectively.

It is interesting to compare the ratio of the ionization energies of the chalcogen-related double donors and Mg in the singly ionized and neutral states. For the isolated chalcogens, it is 1.96, 1.93 and 2.07 for S, Se and Te, respectively, but it rises to 2.39 for Mg and 2.56 for  $\text{S}_c\text{X}_1$ , compared to an EM ratio of 2.21. The  $2p_{\pm 1}$  and  $3p_{\pm 1}$  lines of the  $\text{Ch}_2^+$  spectra are split into a doublet attributed, for  $\text{Mg}^+$ , to the valley-orbit splitting. This splitting, which is not observed for the isolated  $\text{Ch}^+$  donors, is larger for  $\text{Se}_2^+$  than for  $\text{S}_2^+$ , and larger for  $2p_0$  than for  $2p_{\pm 1}$ . While the lines of the  $\text{S}_2^+$  spectrum can be identified up to  $4p_{\pm 1}$ , the  $3p_{\pm 1}(\text{Se}_2^+)$  transition is broad and no line is observed at higher energy for that centre.

**Table 6.19.** Positions (meV) of lines of the singly-ionized  $S_2^+$ ,  $Se_2^+$ ,  $S_cX_1^+$ , and  $Se_cX_1^+$  donors in silicon at LHeT

| Line           | $S_2^+$                     | $Se_2^+$                  | $S_cX_1^{+a,b}$    | $Se_cX_1^{+c}$     | EMT <sup>b</sup> |
|----------------|-----------------------------|---------------------------|--------------------|--------------------|------------------|
| $1s\Gamma_5^-$ | 220.98 (150.14)             | 264.55 (124.9)            | 163.2 (84.0)       | 154.3              | 125.05           |
| $1s\Gamma_6^-$ | 221.54 (149.58)             | 270.9 (118.6)             |                    |                    |                  |
|                | 221.93 (149.19)             | 272.88 (116.6)            |                    |                    |                  |
|                | 225.77 (145.35)             |                           |                    |                    |                  |
| $1s(A_1^-)$    | 274.9 <sup>b</sup> (96.2)   | 296.64 (92.9)             |                    |                    |                  |
| $2p_0$         | 323.45 (47.67)              | 340.34 (49.2)             | 201.6 (46.3)       | 166.3 (47.4)       | 45.96            |
|                | 324.74 (46.38)              | 342.51 (47.0)             |                    |                    |                  |
| $2s$           | 340.01 (31.11)              | 358.34 (31.2)             | 220.8 (26.4)       |                    | 35.44            |
| $2p_{\pm 1}$   | 344.51 (26.61)              | 362.52 (27.0)             | 222.0 (25.9)       | 188.1 [25.6]       | 25.61            |
|                | 344.84 (26.28)              | 363.29 (26.2)             |                    |                    |                  |
|                |                             | 362.3 <sup>c</sup> (27.2) |                    |                    |                  |
| $3p_0$         | 348.48 (22.64)              | 365.98 (23.5)             | 225.3 (22.6)       |                    | 21.92            |
|                | 349.0 (22.1)                | 367.1 (22.4)              |                    |                    |                  |
| $3d_0$         | 355.51 <sup>d</sup> (15.61) |                           |                    |                    | 15.00            |
| $3p_{\pm 1}$   | 358.64 [12.48]              | 377.0 <sup>c</sup> [12.5] | 235.4 [12.5]       | 197.2 (16.5)       | 12.48            |
| $4s$           | 362.58 (8.54)               |                           |                    |                    | 11.64            |
| $E_{io}$       | 371.12                      | 389.5*                    | 247.9 <sup>b</sup> | 213.7 <sup>c</sup> |                  |

$E_{io}$  is obtained by adding 12.48 meV to the position of the  $3p_{\pm 1}$  line. The energies of the excited states are indicated in parentheses. There are interferences between the  $1s(S_2^+)$  and  $2p_{\pm 1}(S_cX_1^+)$  lines

<sup>a</sup> [262], <sup>b</sup> [118], <sup>c</sup> [243], <sup>d</sup> [142]

### 6.3.1.3 Other Chalcogen-Related Donors

Spectra due to other Ch-related donor complexes in silicon have also been reported [118, 243, 262] and these complexes have been denoted  $Ch_cX_n$  where index c represents complex and  $n = 2, 3, 4$ , and 5. The spectroscopic data of the  $Ch_cX_1$  complexes and of  $S_cX_3$  are already included in Tables 6.14 and 6.15. The spectra of the other complexes show only a few lines and their main characteristics are given in Table 6.20. Each chalcogen is given in order of decreasing ionization energies and a correlation between the indices and the atomic structure of the complexes has not been established.

The  $3p_{\pm 1} - 2p_0$  spacings of the  $Te_cX_i$  complexes other than  $Te_cX_1$  are close to the EM value. This has also been observed in other measurements (Pajot, unpublished results) and the reason for this is not clear. An increase in the ionization energies of the corresponding complexes from S to Te, at the inverse of those of Table 6.14 for the isolated neutral chalcogens and chalcogen pairs are observed. The positions of the lines of complex  $S_cX_2$ , whose concentration is low in most S-doped samples, are not indifferent, in connection with the partial passivation of  $S^0$  by hydrogen discussed below. The values deduced by Janzén et al. [118] for the  $2p_{\pm 1}$ ,  $3p_{\pm 1}$  and  $4p_{\pm 1}$  lines of  $S_cX_2$  are 690.4, 716.9 and 724.3  $cm^{-1}$  (85.60, 88.88 and 89.80 meV), respectively. Line

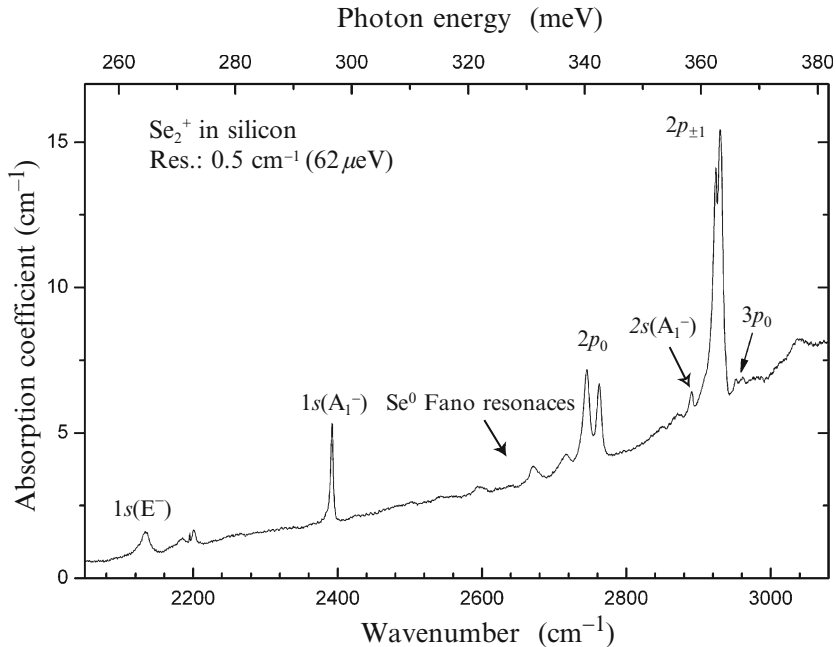


**Fig. 6.20.** Spectrum of  $\text{Se}_2^+$  in silicon under TEC at LHeT. The sample contains a small concentration of  $\text{Se}^0$ . Due to the experimental conditions, the only  $\text{Se}^0$  line observed is the sharp  $1s(\text{T}_2)$  line at 272.2 meV ( $2195\text{ cm}^{-1}$ ), barely visible, plus Fano resonances of the same transition

**Table 6.20.**  $2p_{\pm 1} - 2p_0$  spacings and ionization energies (meV) of  $\text{Ch}_c\text{X}_i$  chalcogen complexes in silicon [262]

|                     | $\text{S}_c\text{X}_2$ | $\text{S}_c\text{X}_3$ | $\text{S}_c\text{X}_4$ | $\text{S}_c\text{X}_5$ | $\text{Se}_c\text{X}_2$ | $\text{Se}_c\text{X}_3$ | $\text{Te}_c\text{X}_2$ | $\text{Te}_c\text{X}_3$ | $\text{Te}_c\text{X}_4$ | EM   |
|---------------------|------------------------|------------------------|------------------------|------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|------|
| $3p_{\pm 1} - 2p_0$ |                        | 8.6                    | 8.7                    | 8.7                    | 8.66 <sup>b</sup>       |                         | 8.4                     | 8.4                     | 8.3                     | 8.37 |
| $E_{\text{io}}$     | 92.00 <sup>a</sup>     | 82.1                   | 80.6                   | 56.5                   | 94.22                   | 53.1                    | 109.8                   | 93.3                    | 73.1                    |      |

<sup>a</sup> [118], <sup>b</sup> Pajot, unpublished results

$2p_0(\text{S}_c\text{X}_2)$  must be close to a transition toward a  $1s$  excited state of  $\text{S}_c\text{X}_1$  and to  $4f_{\pm 1}(\text{S}_c\text{X}_3)$ , though it has not been identified with certainty.

In silicon, the electrical activity of group-V donors can be passivated by hydrogen, when a Si – H bond involving the donor electron is formed on a Si atom *nn* of the donor. For double donors, IR absorption allows one to make a difference between full passivation of the electrical activity of the double donor centre, resulting in a decrease or a disappearance of the electronic spectra, and partial passivation of the centre, where the same effect is accompanied by the appearance of the spectrum of a new single donor. While



DLTS measurements have concluded the full hydrogen passivation of the electrical activity of the isolated chalcogen donors and donor pairs [212], IR measurements have demonstrated partial hydrogen passivation of the S-related donors [211]. In the S-doped hydrogenated samples, the intensity of the  $S_cX_2$  spectrum, very weak in the spectra of the non-hydrogenated samples, was found to increase by more than one order of magnitude after hydrogenation. In addition, four new EM single-donor spectra were observed, together with a small decrease of the intensities of the S-related spectra measured before hydrogenation. These results show a small, but effective passivation by hydrogen. In hydrogenated samples, the lines of the spectrum of  $S_cX_2$  show a shift of  $-2.2 \text{ cm}^{-1}$  ( $-0.27 \text{ meV}$ ) when  $^1\text{H}$  is replaced by  $^2\text{H}$ , indicating that a hydrogen atom is part of this complex. This proves that  $S_cX_2$ , relabelled  $(S, H)_c$  [92 meV] by Peale et al. [211], with the indication of the ionization energy, and here more simply  $(S, H)_{c1}$ , is a partially hydrogen-passivated double donor centre existing in a small concentration in as-doped samples. The four new  $(S, H)$  spectra denoted  $(S, H)_c$  [135.07 meV],  $(S, H)_c$  [135.45 meV],  $(S, H)_c$  [82.4 meV], and  $(S, H)_c$  [82.6 meV] in the original reference (here,  $(S, H)_{c2}$ ,  $(S, H)_{c3}$  and  $(S, H)_{c4}$ ,  $(S, H)_{c5}$ , respectively) are divided into two pairs,  $(S, H)_{c2}-(S, H)_{c3}$  and  $(S, H)_{c4}-(S, H)_{c5}$ , with relatively close ionization energies. It is assumed that the lowest-energy spectrum of each pair is derived from the split upper ground state of the same centre, but differences observed in relative intensities of the corresponding lines of the pair for different cooling-down procedures after high-temperature hydrogenation indicate that the two spectra of each pair are due to two distinct centres. As for  $(S, H)_{c1}$ , the  $(S, H)_{c2}-(S, H)_{c3}$  pair shows a  $^1\text{H}/^2\text{H}$  isotope effect, displayed in Fig. 6.21 for the  $2p_0$  lines, confirming the presence of hydrogen in the atomic structure of  $(S, H)_{c2}$  and  $(S, H)_{c3}$ . This residual passivation can also be present for other chalcogens and be related to other complexes of Table 6.20.

The lines of the  $(S, H)_{c4}-(S, H)_{c5}$  pair are close to those of  $S_cX_3$  (see Table 6.20), but they do not show any  $^1\text{H}/^2\text{H}$  isotope effect. The ionization energies of the above-discussed  $(S, H)$  complexes are summarized in Table 6.21.

The first spectroscopic evidence of the presence of  $(S, H)$  and  $(S, D)$  centres in hydrogenated S-doped silicon was actually provided by Love et al. [155] in a study of spectral hole burning in the  $2p_0$  and  $2p_{\pm 1}$  lines of the  $(S, H)_{c2}$  and  $(S, H)_{c3}$  spectra inhomogeneously broadened in  $\text{Si}_{0.999}\text{Ge}_{0.001}$  alloy samples.

In the absence of absorption measurements under uniaxial stress, there has been no correlation between the spectra and specific hydrogenated double donors. Two spin  $1/2$  ESR spectra, Si-NL54 and Si-NL55, have been reported in hydrogenated S-doped silicon [277]. They are due to centres with  $\langle 111 \rangle$  axial symmetry, and the corresponding ENDOR measurements on samples enriched with  $^{33}\text{S}$  isotope and on samples where  $^2\text{H}_2$  is used for hydrogenation, show that each centre contains one S and one H atom.

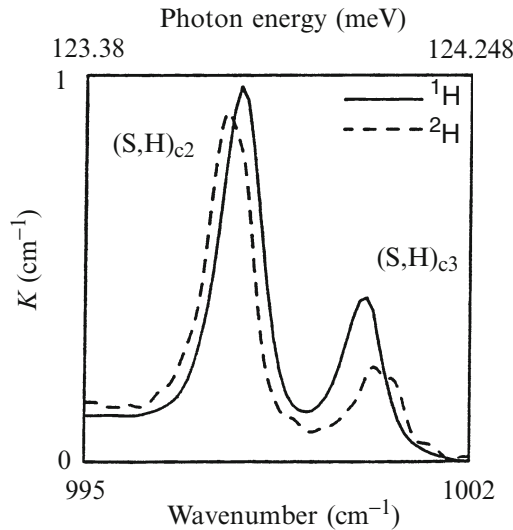


**Fig. 6.21.**  $^1\text{H}/^2\text{H}$  isotope effect of the  $2p_0$  lines of the centres  $(\text{S,H})_{\text{c}2}$  and  $(\text{S,H})_{\text{c}3}$  in silicon at 1.7 K. The resolution is  $0.5\text{ cm}^{-1}$  ( $62\mu\text{eV}$ ) (after [211]). Reproduced with permission from Trans Tech Publications

**Table 6.21.** Ionization energies (meV ( $\text{cm}^{-1}$  in parentheses)) of the  $(\text{S,H})$  EM donor complexes in silicon with the above-defined notations (after [211]). No line positions were given in that reference

| $(\text{S,H})_{\text{c}1}(\text{S}_\text{c}\text{X}_2)$ | $(\text{S,H})_{\text{c}2}$ | $(\text{S,H})_{\text{c}3}$ | $(\text{S,H})_{\text{c}4}$ | $(\text{S,H})_{\text{c}5}$ |
|---------------------------------------------------------|----------------------------|----------------------------|----------------------------|----------------------------|
| 92.0 (742)                                              | 135.07 (1089.4)            | 135.45 (1092.5)            | 82.4 (665)                 | 82.6 (666)                 |

### 6.3.2 Germanium

There has been much less work on the properties of chalcogens in germanium than in silicon. The review by Grimmeiss et al. [84] shows that a larger difference between the ionization energies of the group-V and -VI donors is observed in germanium than in silicon: the ratios of the ionization energies of the  $(\text{S}^0/\text{P})$ ,  $(\text{Se}^0/\text{As})$ , and  $(\text{Te}^0/\text{Sb})$  pairs are  $\sim 22$ , 19, and 9, respectively, in germanium compared to  $\sim 7$ , 5.7, and 4.7, respectively, in silicon. This difference in the ionization energies is also mirrored in the singly-ionized charge state. A comparison between the energy levels measured for the Se and Te donor in germanium and those for P is given in Table 6.22. The results of [192] for  $\text{Se}^0$  are obtained from germanium samples enriched with 74%  $^{76}\text{Ge}$  doped with  $^{77}\text{Se}$  by NTD (see Table 2.1). In this reference, the level denoted  $4p_{\pm 1}$ , following [30], corresponds to  $4f_{\pm 1}$  in Faulkner’s notation (used throughout the book).

**Table 6.22.** Comparison of the first energy levels measured for  $\text{Se}^0$ ,  $\text{Te}^0$ , and  $\text{Se}^+$  in germanium with the calculated EM values [30] and those measured for P (meV units). The values for  $\text{Se}^+$  are divided by four except for  $1s(A_1)$ . FR stands for Fano resonance

| Level                 | $\text{Se}^{0a}$ | $\text{Se}^{0b}$ | $\text{Te}^{0b}$ | $\text{Se}^{+b}$ | P     | EMT  |
|-----------------------|------------------|------------------|------------------|------------------|-------|------|
| $1s(T_2)$             | 9.99             | 9.95             |                  |                  | 10.08 | 9.84 |
| $2s(A_1)$             |                  | 7.4 (FR)         |                  |                  |       | 3.60 |
| $2p_0$                | 4.78             | 4.75             | (4.7)            | 4.80 (FR)        | 4.75  | 4.78 |
| $2s(T_2)$             |                  | 3.58             |                  |                  |       | 3.60 |
| $3p_0$                | 2.63             | 2.57             |                  | 2.55 (FR)        | 2.56  | 2.59 |
| $2p_{\pm 1}$          | 1.73             | 1.73             | 1.73             | 1.73             | 1.73  | 1.73 |
| $3p_{\pm 1}$          | 1.07             | $1.04 \pm 0.03$  |                  | 0.98             | 1.04  | 1.04 |
| $4f_{\pm 1}$          | 0.65             |                  |                  |                  | 0.61  | 0.61 |
| $1s(A_1)$ or $E_{i0}$ | 268.85           | 268.22           | 93.4             | 512.4            | 12.89 |      |

<sup>a</sup> [192], <sup>b</sup> [84]

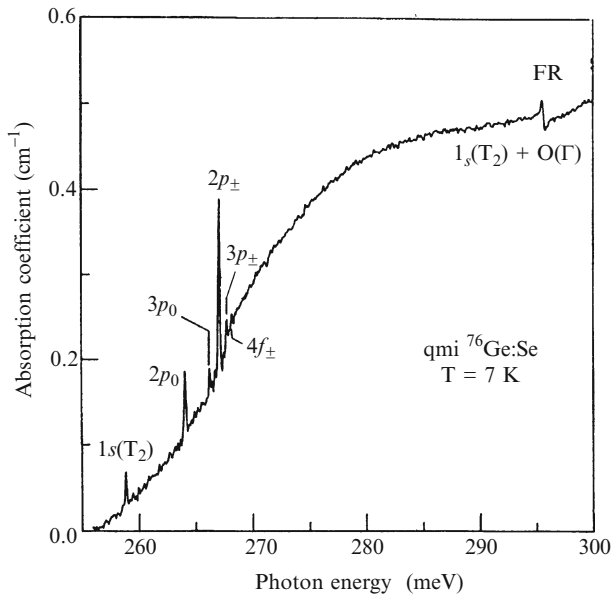


**Fig. 6.22.** Absorption between 2055 and  $2420\text{ cm}^{-1}$  of  $^{77}\text{Se}^0$  in a qmi Ge sample with  $[^{77}\text{Se}] = 3 \times 10^{15}\text{ cm}^{-3}$ . FR is the Fano resonance. The energy of the O ( $\Gamma$ ) phonon is  $37.7\text{ meV}$  ( $304\text{ cm}^{-1}$ ) (after [192]). Copyright 1998, with permission from Elsevier

The positive difference ( $+0.63\text{ meV}$ ) between the values of  $E_{i0}(\text{Se}^0)$  in the sample enriched with  $^{76}\text{Ge}$  and  $^{\text{nat}}\text{Ge}$  sample could be attributed to the increase of  $E_g$  in qmi  $^{76}\text{Ge}$ .

The absorption spectrum of  $^{77}\text{Se}^0$  obtained at LHeT by Olsen et al. [192] in the germanium sample enriched with  $^{76}\text{Ge}$  is shown in Fig. 6.22.

An evoked possibility of n-type doping of diamond with sulphur [219] has aroused an interest for the electronic properties of this element in diamond. It is now well established that, as expected from the properties of chalcogens in silicon and germanium, S behaves in diamond as a deep donor, with an ionization energy of  $\sim 1$  eV for  $S^0$ , predicted from the *ab initio* DFT calculations [177]. However, the existence of S-related complexes with native defects or impurities like B is a possibility which could explain some appealing experimental results ([37], and references therein).

## 6.4 O-Related Donors in Group IV Crystals

In silicon with relatively high  $O_i$  content, thermal annealings at temperatures between  $\sim 400$  and  $600^\circ\text{C}$  produce what is known as oxygen-related thermal donors. Some of them have only O and Si as constituents and they are double donors, with electronic absorption comparable to the Ch-related centres and Mg. Similar centres have also been observed in O-containing germanium. In CZ silicon, containing appreciable concentrations of nitrogen and/or hydrogen, other donors with lower ionization energies, known as shallow thermal donors, include FAs other than O and Si, and H has been identified with certainty as one of these atoms. Other donors with still smaller ionization energies, known as ultrashallow thermal donors, seem to also involve carbon. The electronic spectroscopy of these donors is presented below.

### 6.4.1 The Thermal Double Donors

Half a century ago, Fuller and Logan [68] published the first evidence of the production of donors in oxygen-containing silicon heat-treated between  $350$  and  $500^\circ\text{C}$ . It has been pointed out in Sect. 2.2.2.1 that CZ silicon was oversaturated with  $O_i$  at RT. Annealing this material at higher temperatures is expected to induce modifications in the oxygen distribution, and this correlation was recognized in a detailed study by Kaiser et al. [124], who proved that annealing CZ silicon between  $350$  and  $550^\circ\text{C}$  produced donor centres associated with oxygen. They were logically called thermal donors or more precisely  $450^\circ\text{C}$  thermal donors, as their production rate was maximum near from  $450^\circ\text{C}$ , and also because later, new O-related centres were found to be produced by annealing between  $650$  and  $800^\circ\text{C}$ . The  $450^\circ\text{C}$  thermal donors have a limited stability domain and become unstable when temperature rises above  $550^\circ\text{C}$ . They can be totally removed by a relatively short time ( $\sim 10$  mn) annealing at temperatures above  $800^\circ\text{C}$ , followed by quenching at RT. During the post-growth cooling-down, the CZ silicon crystals spend some time in a temperature range where TDs can be produced and hence, the as-grown CZ crystals already contain these thermal donors at a concentration, which depends on the cooling rate. These crystals, therefore, require a thermal treatment to reach their initially-planned resistivity. Because of its importance in the electrical properties of silicon, the production kinetics of

thermal donors has been widely investigated. For instance, in annealing experiments in the temperature range known to produce these centres, their maximum concentration was found to be proportional to the 3<sup>rd</sup> power of the initial  $O_i$  concentration, and their initial formation rate to the 4<sup>th</sup> power of the same concentration [124]. This latter fact was the reason why it was then proposed that these centres involved four O atoms (a  $SiO_4$  entity).

The n-type doping observed in germanium, accidentally polluted by air admission during zone refining, led to assume that, like chalcogens, the O element was a n-type dopant in germanium [57]. This assumption was clarified by the work of Bloem et al. [27], which proved the existence of O-related donor complexes containing several O atoms.

#### 6.4.1.1 Silicon

The first IR measurements on silicon samples saturated with oxygen near the melting point, either as-prepared or further annealed at 430°C, produced electronic spectra similar to those of the group-V donors, showing the simultaneous presence of several different new EM donors [106]. Renewed interest for these TDs was triggered by Wruck and Gaworzewski [271], confirming the presence of several TDs and demonstrating that they were in fact double donors. They were relabelled thermal double donors or TDDs, identified by index  $i = 1, 2$ , etc. by order of decreasing ionization energy [263]. The different varieties of TDDs can be obtained in CZ silicon by varying the duration of the 350–550°C annealing and the post-annealing thermal treatments. In as-grown CZ crystals, only the TDDs up to  $\sim i = 4$  are produced, with TDD2 and TDD3 being predominant. The variation of the contributions of different TDDs as a function of annealing time can be estimated from Figs. 6, 7, and 8 of [263]. The absorption spectra associated with the neutral  $TDDi^0$  (or  $TDi^0$ ) have been reported up to  $i = 16$ , with ionization energies ranging from 69.3 to 41.9 meV (558 to 338  $cm^{-1}$ ) and those associated with the singly-ionized  $TDDi^+$  up to  $i = 9$ , with ionization energies ranging from 156.3 to 116 meV (1260 to 935  $cm^{-1}$ ).

A centre, called the  $\alpha$  trap in connection with the study by Haynes and Hornbeck [98], has been reported to be the first TDD species, but without giving data on its ionization energies [159]. The electronic properties of this centre, labelled BTDD- $\alpha$  for bistable thermal donor, or alternatively TDD0, have remained elusive for some time and they will be discussed with the metastability properties of the TDDs. To avoid any confusion in the following, the ionization energies of the different TDDs in the neutral and singly-ionized states are listed in Table 6.23. Apparently, no data have been reported for  $TDDi^+$  above TDD9.

A thermal donor denoted TDD7', with an ionization energy of 55.8 meV when neutral, has been added to this list by Emtsev et al. [58]. The ratio  $E_{i+}/E_{i0}$  varies from 2.25 for  $i = 1$  and stabilizes to 2.19 for  $i = 7$ , close to the EM ratio 2.21 for He-like donors. As the energy spans of the parity-allowed

**Table 6.23.** Ionization energies (meV) of the thermal double donors TDDi in silicon, denoted here i, and indexed 0 and + in the neutral and singly-ionized states

|          |                 |                 |                 |                 |                 |                 |                 |                |                |                |
|----------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|----------------|----------------|----------------|
| i        | 0 <sup>a</sup>  | 1 <sup>b</sup>  | 2 <sup>b</sup>  | 3 <sup>b</sup>  | 4 <sup>b</sup>  | 5 <sup>b</sup>  | 6 <sup>b</sup>  | 7 <sup>b</sup> | 8 <sup>b</sup> | 9 <sup>b</sup> |
| $E_{i0}$ | 72.4            | 69.2            | 66.8            | 64.6            | 62.2            | 60.1            | 58.0            | 56.5           | 54.5           | 53.0           |
| $E_{i+}$ | 164.1           | 156.3           | 149.7           | 143.8           | 138.2           | 133.0           | 128.3           | 123.6          | 119.3          | 116.0          |
| i        | 10 <sup>b</sup> | 11 <sup>b</sup> | 12 <sup>c</sup> | 13 <sup>c</sup> | 14 <sup>c</sup> | 15 <sup>c</sup> | 16 <sup>c</sup> |                |                |                |
| $E_{i0}$ | 51.4            | 49.9            | 48.3            | 46.6            | 45.0            | 43.4            | 41.9            |                |                |                |

<sup>a</sup> [176], <sup>b</sup> [263], <sup>c</sup> [77]

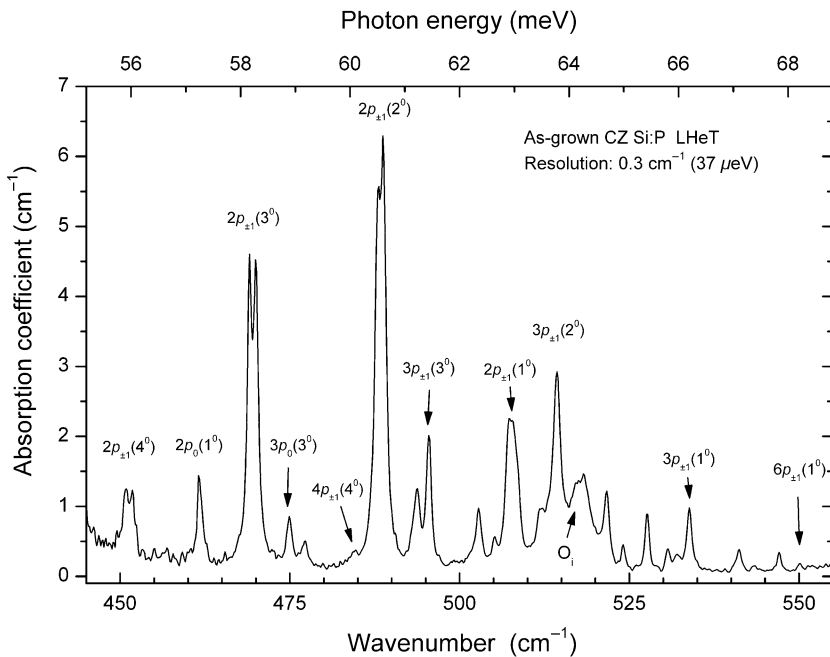


**Fig. 6.23.** Absorption of the first TDDi<sup>0</sup>, denoted here i<sup>0</sup>, in as-grown CZ Si:P with [P] = 3 × 10<sup>14</sup> at cm<sup>-3</sup>, cooled and recorded under band-gap-light illumination. The mixing of the spectra produces in some cases near coincidences of lines pertaining to the spectra of different TDDs. A broad O<sub>i</sub> vibrational feature at 517 cm<sup>-1</sup> is superimposed on the electronic spectra

neutral and singly-ionized EMT donor spectra are about 12 and 48 meV, respectively, one can infer from Table 6.23 that the spectra of the different TDDs superimpose on each other. This can be seen in Fig. 6.23, showing the electronic absorption of the first TDD<sup>0</sup>s in an as-grown P-doped silicon sample.

This figure also shows the splitting of the 2p<sub>±1</sub> lines of TDD2<sup>0</sup>, TDD3<sup>0</sup> and TDD4<sup>0</sup>. Despite the proximity of the 5p<sub>±1</sub> (TDD3<sup>0</sup>) line seen as a high-frequency elbow, the value of the splitting estimated for 2p<sub>±1</sub> (TDD1<sup>0</sup>) is in

**Table 6.24.** Positions (meV ( $\text{cm}^{-1}$  in parentheses)) at LHeT of the lines of the first TDD<sup>0</sup>s in silicon

| Line                | TDD0 <sup>0a</sup> | TDD1 <sup>0</sup> | TDD2 <sup>0</sup> | TDD3 <sup>0</sup>       | TDD4 <sup>0</sup>       |
|---------------------|--------------------|-------------------|-------------------|-------------------------|-------------------------|
| $2p_0$              | 60.5 (488)         | 57.231 (461.60)   | 54.807 (442.05)   | 52.5 (423) <sup>b</sup> | 50.2 (405) <sup>b</sup> |
| $2p_{\pm 1}^l$      | 66.15 (533.5)      | 62.91 (507.3)     | 60.516 (488.03)   | 58.162 (469.05)         | 55.91 (450.9)           |
| $2p_{\pm 1}^h$      |                    | 62.97 (507.8)     | 60.603 (488.73)   | 58.280 (470.00)         | 56.028 (451.84)         |
| $3p_0$              |                    | 63.67 (513.5)     | 61.223 (493.73)   | 58.893 (474.94)         | 56.5 (456) <sup>b</sup> |
| $3p_{\pm 1}$        | 69.3 (559)         | 66.197 (533.85)   | 63.779 (514.35)   | 61.441 (495.49)         | 59.178 (477.24)         |
| $4p_{\pm 1}$        |                    | 67.103 (541.15)   | 64.688 (521.68)   | 62.347 (502.80)         | 60.09 (484.6)           |
| $4f_{\pm 1}$        |                    | 67.37 (543.3)     | 64.983 (524.06)   | 62.635 (505.12)         |                         |
| $5p_{\pm 1}$        |                    | 67.837 (547.07)   | 65.425 (527.62)   | 63.08 (508.7)           |                         |
| $6p_{\pm 1}$        |                    | 68.215 (550.12)   | 65.802 (530.66)   | 63.45 (511.7)           |                         |
| $6h_{\pm 1}$        |                    |                   | 65.97 (532.0)     | 63.6 (513) <sup>*</sup> |                         |
| $5p_{\pm 1} - 2p_0$ | 8.8                | 8.97              | 8.97              | 8.9                     | 9.0                     |
| $E_{\text{io}}$     | 72.4               | 69.30             | 66.88             | 64.53                   | 62.30                   |

Except for TDD0, the uncertainty varies between  $\pm 0.1$  and  $0.2 \text{ cm}^{-1}$  (13 and  $25 \mu\text{eV}$ ). The ionization energy  $E_{\text{io}}$  is obtained by adding to the  $3p_{\pm 1}$  line position the calculated EM value ( $3.120 \text{ meV}$ ) of the  $3p_{\pm 1}$  state

<sup>\*</sup> Elbow or near-coincidence, <sup>a</sup> [176], <sup>b</sup> [263]

good agreement with those ( $0.5 \text{ cm}^{-1}$  or  $62 \mu\text{eV}$ ) reported by Marinchenko et al. [161] from measurements with  $0.1 \text{ cm}^{-1}$  ( $13 \mu\text{eV}$ ) resolution (no line position is given in this reference). Table 1 of [263] is supplemented by Table 6.24, which gives the  $2p_{\pm 1}$  splitting of the first TDDs<sup>0</sup> and the positions of a few lines not included in the former tables.<sup>6</sup> Some of the isolated lines of Table 6.24, like  $2p_0$  (TDD2<sup>0</sup>), show asymmetry and the positions indicated, which can vary slightly with resolution, are those of the maximums for a spectral resolution of  $0.3 \text{ cm}^{-1}$  ( $37 \mu\text{eV}$ ). For TDD5<sup>0</sup> and TDD6<sup>0</sup>, which are seemingly the lowest energy donors for which a splitting of the  $2p_{\pm 1}$  line has been measured, the splitting for both donors is  $1.5 \text{ cm}^{-1}$  ( $0.186 \text{ meV}$ ). The splitting of  $2p_{\pm 1}$  into two components  $2p_{\pm 1}^l$  and  $2p_{\pm 1}^h$  ( $l$  for low and  $h$  for high) seems to be obvious, but a deconvolution analysis of the profile of  $2p_{\pm 1}$  (TDD5<sup>0</sup>) has revealed, at least for that thermal donor, a triplet structure with components at  $433.5$ ,  $434.0$  and  $435 \text{ cm}^{-1}$  [161]. The absorption spectrum of TDD0 has been reported by Murin et al. [176] under specific conditions which will be discussed later.

Considering the He-like ionization energies of the TDDs and their electronic degeneracy, no parity-forbidden transition equivalent to the  $1s(T_2)$  line is observed in the TDD spectra.

The comparison of the lines spacings of the TDD1<sup>0</sup> and TDD2<sup>0</sup> spectra with those of the group-V, neutral group-VI and  $\text{Mg}^0$  spectra shows an EM behaviour of the unsplit  $np_{\pm 1}$  lines with  $n > 2$ . For  $i > 4$ , reliable values of the TDDi<sup>0</sup> ionization energies depend on accurate measurements and identifi-

<sup>6</sup> The positions of the lines of TDD12 to TDD16 are given in Table 1 of Götz et al. [77].

cations of  $3p_{\pm 1}$  or  $4p_{\pm 1}$  lines, a difficult task because of their weak intensities and already mentioned coincidences with other lines. The energy of the  $2p_0$  level of the TDD1-TDD12 donors varies around 12.0 meV compared to the EM value of 11.49 meV, but starting with TDD12<sup>0</sup>, a decrease of the energy of this level is measured, which reaches 11.3 meV for TDD16<sup>0</sup>. The  $3p_{\pm 1}$ – $2p_0$  spacings of the first TDDi<sup>0</sup> are significantly larger than the EM value (8.37 meV), indicating a strong perturbation with respect to a point charge model.

In CZ silicon doped with acceptors and turned n-type by the production of TDDs either during cooling-down or during annealing at  $\sim 350$ – $550^\circ\text{C}$ , one can observe TDD<sup>+</sup>s spectra similar to the singly-ionized chalcogen spectra of Sect. 6.3.1.2. In p-type material, the observation requires external band-gap radiation pumping for partial neutralization of the TDD<sup>++</sup>s. It must be pointed out that the TDD<sup>+</sup>s spectra can also be observed at LHeT under TEC in samples where these centres are supposed to be neutral. This effect is due to the photoionization of the TDD<sup>0</sup>s by the RT background radiation coming through the optical windows and from the sampling beam itself. The TDD<sup>+</sup> spectra are characterized by a splitting of the  $2p_{\pm 1}$  lines, which is larger than the one in the TDD<sup>0</sup> spectra, and also by a splitting of the  $3p_{\pm 1}$  lines, reported earlier for  $3p_{\pm 1}$  (Mg<sup>+</sup>). An overall spectrum of the TDD<sup>+</sup>s in a p-type CZ silicon sample with a B concentration near  $10^{15}\text{cm}^{-3}$ , annealed for 1 h at  $450^\circ\text{C}$ , is shown in Fig. 6.24. The total TDD<sup>++</sup>s concentration is

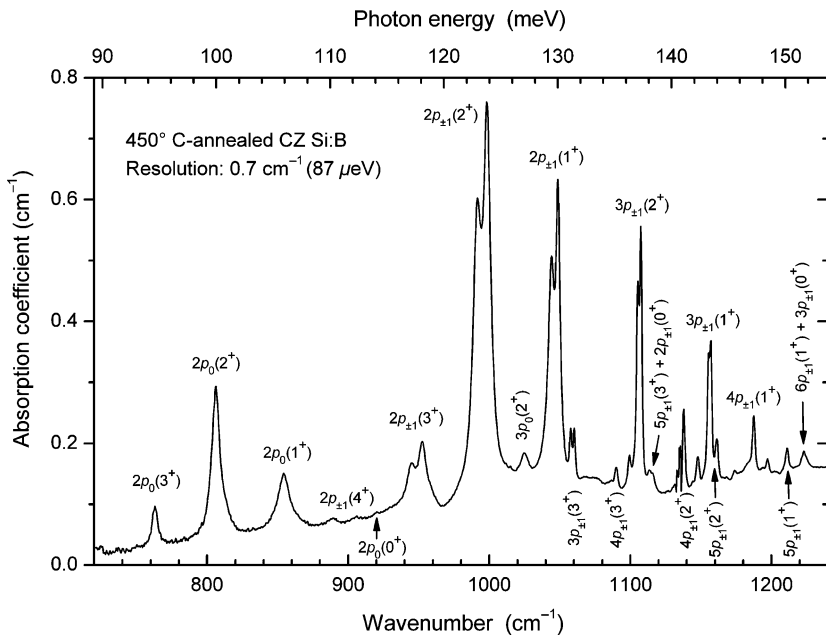


**Fig. 6.24.** Absorption spectrum at LHeT under band-gap-light illumination of the first TDDi<sup>+</sup>, denoted here i<sup>+</sup>, after short-term annealing. The same sample, p-type under TEC, is used as a reference



about  $2.5 \times 10^{14} \text{ cm}^{-3}$  and thus, the sample is still p-type. As mentioned before, partial neutralization of the TDDs is achieved here by controlling the intensity of the pumping band-gap radiation [203].

It is interesting to note that weak lines of  $\text{TDD0}^+$  are observed in this spectrum, superimposed for two of them on lines of other TDDs. Above  $1240 \text{ cm}^{-1}$ , the  $4p_{\pm 1}$ ,  $4f_{\pm 1}$ , and  $5p_{\pm 1}$  lines of  $\text{TDD0}^+$  reported by Murin et al. [176] are also observed in this spectrum.

Table 6.25 gives the positions of the lines of singly-ionized TDDs in silicon.

The positions of  $2p_0$  line for  $\text{TDD7}^+$  and  $\text{TDD8}^+$  are  $613.8$  and  $585.1 \text{ cm}^{-1}$  ( $76.10$  and  $72.54 \text{ meV}$ ), respectively. The splitting of the  $2p_{\pm 1}$  transition for the higher  $\text{TDDi}^+$  is rather large ( $29 \text{ cm}^{-1}$  for  $\text{TDD9}^+$ ) and is given in Table 1-b of [263]. The  $3p_{\pm 1}$  transition of these centres is also split and superimposed on other lines, making its detection very difficult.

**Table 6.25.** Positions ( $\text{meV}$  ( $\text{cm}^{-1}$  in parentheses)) at LHeT of the lines of the singly-ionized TDDs in silicon. Up to  $\text{TDD4}^+$ , the ionization energy  $E_{i0}$  is obtained by adding to the  $4p_{\pm 1}$  line position the calculated energy level ( $8.75 \text{ meV}$ ) of the  $4p_{\pm 1}$  state. The uncertainty is  $\pm 0.2 \text{ cm}^{-1}$  ( $\pm 25 \text{ } \mu\text{eV}$ )

| Line           | TDD0 <sup>+</sup> <sup>a</sup>            | TDD1 <sup>+</sup>            | TDD2 <sup>+</sup>  | TDD3 <sup>+</sup>            | TDD4 <sup>+</sup>  | TDD5 <sup>+</sup>           | TDD6 <sup>+</sup>           |
|----------------|-------------------------------------------|------------------------------|--------------------|------------------------------|--------------------|-----------------------------|-----------------------------|
| $2p_0$         | 114.39<br>(922.6)<br>(920.6) <sup>c</sup> | 105.93<br>(854.4)            | 99.97<br>(806.3)   | 94.58<br>(762.8)             | 88.502<br>(713.82) | 84.20<br>(679.1)            | 79.97<br>(645.0)            |
| $2p_{\pm 1}^l$ | 137.87<br>(1112)                          | 129.48<br>(1044.3)           | 122.96<br>(991.7)  | 117.17<br>(945.0)            | 110.22<br>(889.0)  | 105.03<br>(847.1)           | 99.07 <sup>b</sup><br>(804) |
| $2p_{\pm 1}^h$ | 138.34<br>(1115.8)                        | 130.01<br>(1048.6)           | 123.76<br>(998.2)  | 118.07<br>(952.3)            | 112.16<br>(904.6)  | 106.89<br>(862.1)           | 102.32<br>(825.3)           |
| $3p_0$         |                                           |                              | 127.06<br>(1024.8) |                              |                    |                             |                             |
| $3p_{\pm 1}^l$ | 151.4<br>(1221)                           | 143.24<br>(1155.3)           | 137.04<br>(1105.3) | 131.14<br>(1057.7)           | 125.45<br>(1011.8) | 120.0 <sup>b</sup><br>(968) |                             |
| $3p_{\pm 1}^h$ | 151.5<br>(1222)                           | 143.39<br>(1156.5)           | 137.28<br>(1107.2) | 131.42<br>(1060.0)           | 125.79<br>(1014.6) | 120.5 <sup>b</sup><br>(972) |                             |
| $4p_{\pm 1}$   | 155.4<br>(1253)                           | 147.22<br>(1187.4)           | 141.11<br>(1138.0) | 135.17<br>(1090.1)           | 129.4<br>(1044)    |                             |                             |
| $4f_{\pm 1}$   | 156.6<br>(1263)                           | 148.45<br>(1197.3)           | 142.21<br>(1147.0) | 136.30<br>(1099.3)           |                    |                             |                             |
| $5p_{\pm 1}$   | 158.3<br>(1277)                           | 150.16<br>(1211.1)           | 143.92<br>(1160.8) | 138.0 <sup>†</sup><br>(1113) |                    |                             |                             |
| $6p_{\pm 1}$   |                                           | 151.6 <sup>†</sup><br>(1223) | 145.51<br>(1173.6) |                              |                    |                             |                             |
| $E_{i0}$       | 164.1                                     | 155.97                       | 149.84             | 143.90                       | 138.2              | 133.0 <sup>b</sup>          | 128.3 <sup>b</sup>          |

<sup>†</sup> Superimposed on  $3p_{\pm 1}$  ( $0^+$ ), <sup>‡</sup> Superimposed on  $2p_{\pm 1}$  ( $0^+$ ), <sup>a</sup> [176], <sup>b</sup> [263],

<sup>c</sup> Pajot, unpublished

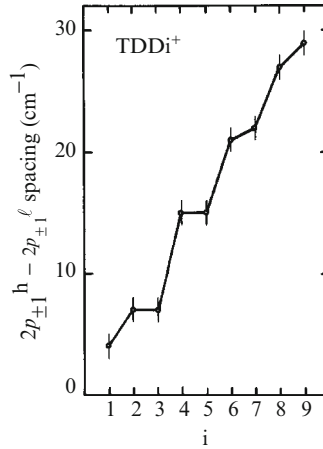


**Fig. 6.25.** Spacing  $2p_{\pm 1}^h - 2p_{\pm 1}^l$  of the components of the  $2p_{\pm 1}$  lines of the  $\text{TDDi}^+$  spectra for increasing values of  $i$  [263]

**Table 6.26.** Energies (meV) of the  $2p_0$  levels of  $\text{TDDi}^+$  donors, identified as  $i^+$ , compared to the  $\text{He}^+$ -like EM value (Pajot, unpublished, [263])

| $0^+$ | $1^+$ | $2^+$ | $3^+$ | $4^+$ | $5^+$ | $6^+$ | $7^+$ | $8^+$ | $\text{He}^+$ -like |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|---------------------|
| 50.0  | 50.04 | 49.84 | 49.33 | 49.8  | 49.0  | 48.4  | 47.6  | 46.8  | 46.0                |

The step-like increase of the spacings between the observed components of the  $2p_{\pm 1}$  ( $\text{TDDi}^+$ ) lines for increasing values of  $i$  can be seen in Fig. 6.25.

The energies of the  $2p_0$  levels of the  $\text{TDDi}^+$  donors are significantly larger than the EM value, taken as four times the H-like value. This is shown in Table 6.26, but their values tend to decrease with  $i$ , a trend already observed for the  $\text{TDDi}^0$  donors, but for larger values of  $i$ .

The  $\text{TDDi}^+$ s should be paramagnetic and an ESR spectrum labelled NL8 has been related to the  $\text{TDDi}^+$ s [174]. This will be discussed further in Chap. 8 in connection with the piezospectroscopic results on the TDDs.

In samples annealed at  $450^\circ\text{C}$  for a considerable time, lines whose intensities increase with the  $\text{TDDi}^+$ s concentration, but whose positions do not fit a  $\text{He}^+$ -like EM level scheme have been reported [203, 263]. The positions of these unattributed lines are, by order of increasing energies, 77.16, 80.33, 82.45, 86.23, 89.90, 91.59, and 97.02 meV (622.3, 647.9, 665.0, 695.8, 725.1, 738.7 and 782.5  $\text{cm}^{-1}$ ) and they are displayed in Fig. 6.26. Broad vibrational lines at 724, 728, 734, 744 and 748  $\text{cm}^{-1}$ , related to other lines at 988, 999, 1006, 1012 and 1015  $\text{cm}^{-1}$  have been attributed to TDDs [153], but they seem distinct from the unidentified lines of Fig. 6.26.

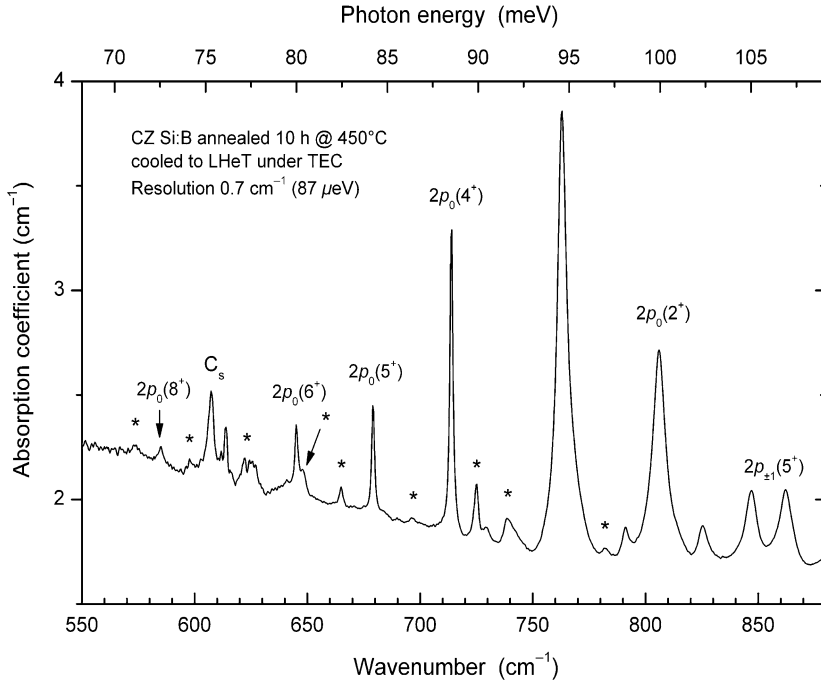


**Fig. 6.26.** Part of the absorption spectrum of a silicon sample showing low-energy  $\text{TDDi}^+$  lines and unidentified lines denoted by an asterisk. A high-purity FZ silicon sample used as a reference allows the subtraction of the silicon two-phonon absorption. Line  $\text{C}_s$  is the vibrational mode of residual carbon at  $607.4 \text{ cm}^{-1}$

The possibility of passivation of the TDDs by hydrogen has been investigated, but this point and the results obtained by optical spectroscopy will be discussed in the next section, with the properties of the shallow thermal donors.

The exact structure of TDDs in silicon and the origin of the double donor behaviour has been a matter of controversy for many years. The ESR measurement indicates that these centres are oriented in the crystal along the  $\langle 110 \rangle$  axes. ENDOR measurements have also shown that they involved O atoms. The consensus is that they are complexes whose atomic constituents are O and Si atoms, and that their atomic structure is dominated by Si-O-Si zigzag chains along the  $\langle 110 \rangle$  direction. This will be discussed in Chap. 8, where the results of electronic absorption measurements under uniaxial stress are presented.

### *Metastability*

Electrical experiments have shown that the TDDs with the highest ionization energies are metastable, with two different arrangements of the atoms. The

stable form (denoted sometimes X) is electrically inactive and the metastable form gives the TDDs [255]; similar results were also reported in germanium [154]. Metastability manifests itself in n-type material cooled under TEC from RT to temperatures of the order of 100 K or below. When the free-carrier concentration is measured at these temperatures, it is found to be smaller in the samples cooled under TEC than the one expected from the ionization energies of the TDDs [255]. When the TDDs spectra are measured at low temperature in n-type samples cooled under TEC or quasi-TEC, the TDD1 and TDD2 contributions are reduced compared to those measured in the same sample cooled under band gap light illumination, indicating that part of these centres is in the X form [151, 263, 272]. Occurrence of metastability depends on the Fermi level position in the sample and it is not observed in p-type material containing TDDs. For initially high resistivity or moderately p-type samples, it depends on the duration of the annealing producing TDDs. Metastability of TDD1 is always observed in n-type samples, and the consequence is shown in Fig. 6.27: in (a), the sample has been cooled from room temperature in the dark (quasi-thermal-equilibrium conditions (quasi-TEC)) and the contribution of TDD1 is missing as this centre turned into a stable electrically-inactive X configuration; in (b) before recording the spectrum,

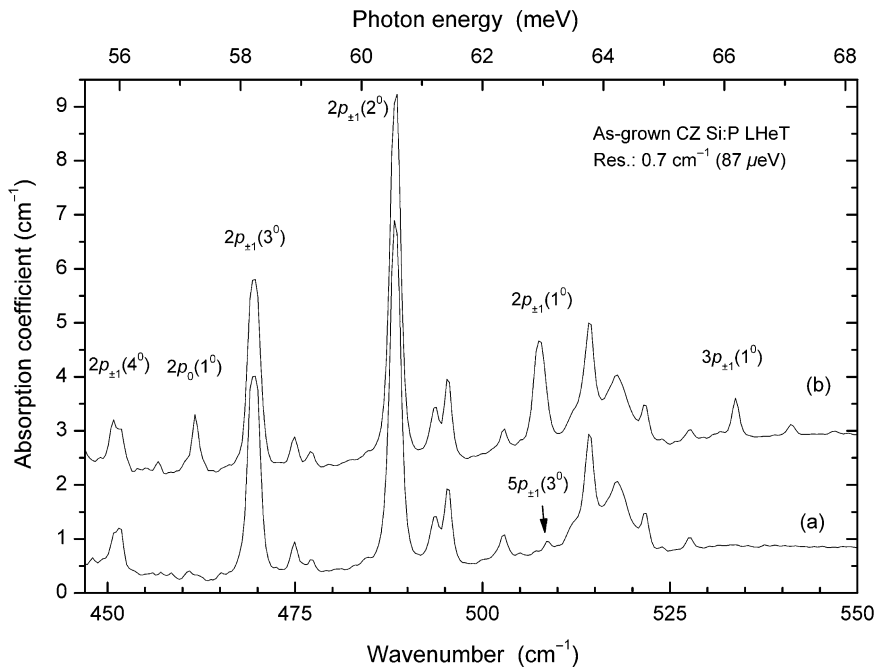


**Fig. 6.27.** Changes in the absorption spectrum of TDD1<sup>0</sup> (1<sup>0</sup>) in a CZ Si:P sample ([P] = 3 × 10<sup>14</sup> cm<sup>-3</sup>) due to metastability (a): cooled under TEC (b): cooled from 200 K under band-gap light illumination (same notations as in Fig. 6.23)

the sample has been warmed from LHeT to 200 K and after 10 min at this temperature, cooled-down again to LHeT under band-gap light illumination. After this latter treatment, the centre has turned into the metastable donor state and the associated TDD1 spectrum is then visible. Both spectra are recorded without external excitation. An interesting point is that the absence of  $2p_{\pm 1}(1^0)$  in (a) allows one to observe the weak  $5p_{\pm 1}(3^0)$  line.

The observation of the metastability of TDD2 requires further production of thermal donors to raise the Fermi level position. The limiting value of  $E_F$  is  $E_c - 0.25$  eV at room temperature and for samples with  $E_F$  in this energy region, partial metastability of TDD2 may be observed, as in Fig. 6.28.

When a metastable sample has been cooled from room temperature to LHeT under TEC, band-gap light illumination at LHeT cannot turn the X form into the metastable TDD form, as expected for a thermally-activated process. Absorption experiments at LHeT have been performed to determine the temperature where switching on band-gap illumination after cooling under TEC to this temperature does not produce the metastable form. A value of  $\sim 110$  K is obtained for both TDD1 and TDD2 [263].

The complementary experiment consists in measuring the thermal stability of the metastable forms TDD1 and TDD2, whose initial absorptions  $K_0$  have

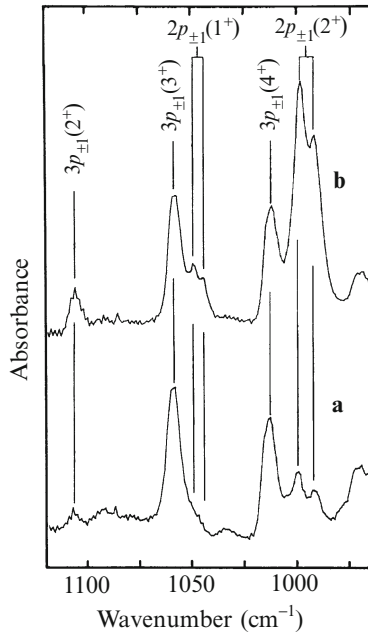


**Fig. 6.28.** Metastability effect in the LHeT absorption of TDD1<sup>+</sup> and TDD2<sup>+</sup> lines in a CZ Si:B sample ( $[B] = 4 \times 10^{15} \text{ cm}^{-3}$ ) annealed for 30 h at 460°C (a): cooled under TEC; (b): cooled under band-gap light illumination (same notations as in Fig. 6.24) (after [263])

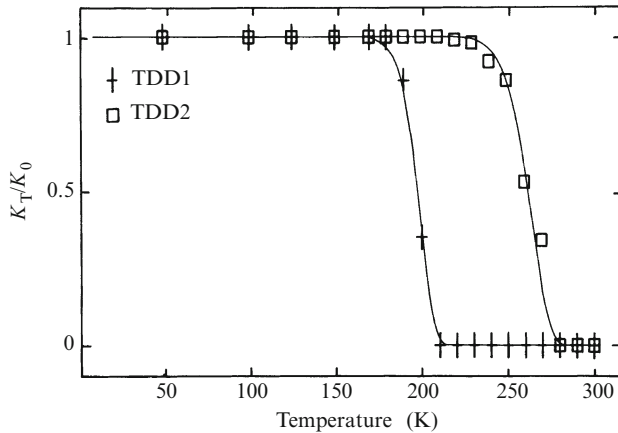


**Fig. 6.29.** Fraction measured at LHeT of metastable TDDs remaining after 5 mn isochronal annealing of a silicon sample from LHeT under TEC at different temperatures (after [263])

been measured at LHeT after cooling-down under band-gap-light illumination. For this, the temperature of the sample is raised under TEC to a value  $T$ , where it stays for a given time and lowered back under TEC to LHeT, where the absorption  $K_T$  of TDD1 and TDD2 is measured again. The variation of the ratio  $K_T/K_0$  with  $T$  for both TDDs is displayed in Fig. 6.29 for a hold time of 5 mn at temperature  $T$ .

From the first kind of experiment, an activation energy of 0.16 eV and attempt frequencies in the range  $10^5$ – $10^6$  s $^{-1}$  are derived for the transformation from the stable to the metastable state for both thermal donors. Metastability implies that the activation energies for the inverse transformations are not the same and the second kind of experiment yields values of 0.54 and 0.71 eV for TDD1 and TDD2, respectively, with the same order of magnitude of  $10^{10}$ – $10^{11}$  s $^{-1}$  for the attempt frequencies [263]. The energy barrier measured for TDD0 $^0$  is only 0.28 eV [176], and when in the metastable state at LHeT, this centre is turned back into the X state at a temperature lower than that required for TDD1 $^0$  and TDD2 $^0$ . The observation of the TDD0 $^0$  spectrum [176] has then been made possible by recording first the spectrum of a n-type CZ Si sample cooled under band-gap light illumination, producing TDD0 $^0$ , TDD1 $^0$ , and TDD2 $^0$ . The sample is then annealed at 200 K under TEC to turn TDD0 $^0$  into the X state, leaving TDD1 $^0$  and TDD2 $^0$  in the metastable state.<sup>7</sup> The difference between the initial spectrum and those at LHeT after this annealing is displayed in Fig. 6.30 and it shows three weak

<sup>7</sup> From Fig. 6.29, one would think that a 200 K annealing would also turn TDD1 $^0$  into the X state, but after a single annealing cycle at 200 K, this is apparently not the case.

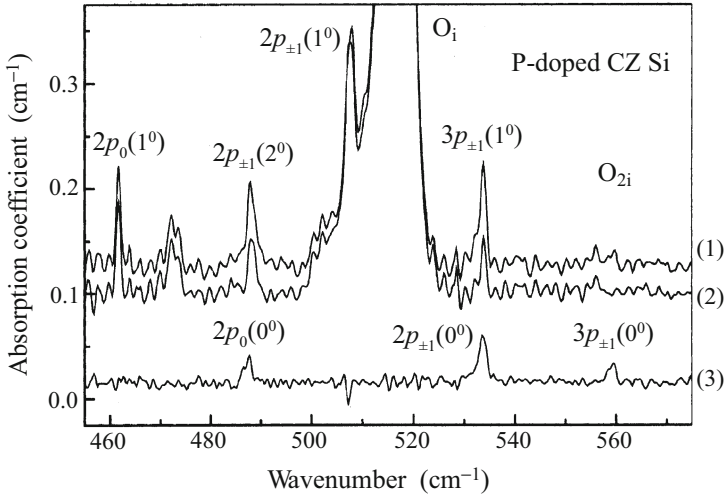


**Fig. 6.30.** Part of spectra between 56.4 and 71.3 meV of an as-grown CZ silicon sample with  $[O_i] = 9 \times 10^{17} \text{ cm}^{-3}$  cooled (1) under band-gap light illumination and (2) under TEC from 200 K. The difference (3) between spectra 1 and 2 (same notations as in Fig. 6.23) shows the weak absorption of TDD0<sup>0</sup> (after [176]). Copyright 2003, with permission from Elsevier

lines whose relative intensities and spacings are the signature of a new TDD identified as TDD0.

A spectrum including a signature attributed to TDD0<sup>+</sup> has been obtained from the difference spectrum of a CZ p-type sample annealed at 1250°C for 40 min in H<sub>2</sub> gas ambient and of the same sample after supplementary annealing at 300°C for 2 h [176].

#### 6.4.1.2 Germanium

As-grown CZ germanium contains a very small O concentration ( $\sim 10^{12}$ – $10^{13} \text{ cm}^{-3}$ ) compared to CZ silicon because of its smaller reactivity with O and its melting point of 937°C. It can, however, be doped with O whose solubility is comparable to that in silicon, by adding for instance oxygen gas or water vapour to the growth atmosphere. When O-doped germanium is annealed in the range 300–500°C, the same kind of thermal double donors as in CZ silicon are produced, but their rate of formation is about 500 times larger than in silicon. A consequence is that for the same value of  $[O_i]$ , the TDDs concentration is about one order of magnitude larger in germanium than in silicon ([45], [44], and references therein).

The ground state energies of these thermal donors extend from 18.1 to 14.3 meV when neutral and from 40.5 to 31.0 meV when singly ionized. When comparing the energy spacing between the  $2p_0$  and  $2p_{\pm 1}$  EM levels in germanium ( $\sim 4 \text{ meV}$ ) with the ionization energies spanning the TDDs, it can be

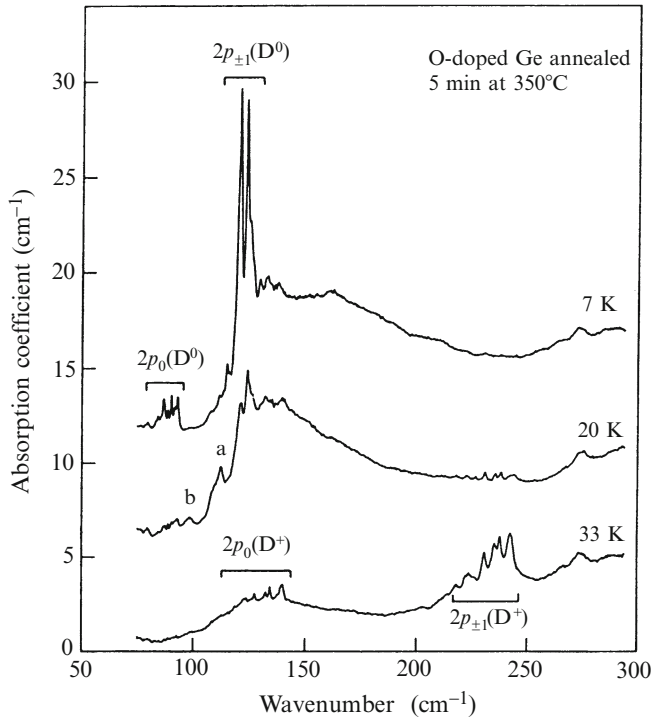


**Fig. 6.31.** Absorption spectra between  $\sim 9.3$  and  $36$  meV of the first TDDs in a  $^{\text{nat}}\text{Ge}$  sample with  $[\text{O}_i] = 2.5 \times 10^{17} \text{ cm}^{-3}$  at three temperatures. At  $33 \text{ K}$ , the thermal ionization of the neutral donors  $\text{D}^0$  allows one to observe the absorption of the singly-ionized donors  $\text{D}^+$ . There is a near-coincidence between the  $2p_0(\text{D}^+)$  and  $2p_{\pm 1}(\text{D}^0)$  transitions. The spectra have been displaced vertically for clarity [45]. Copyright 1996, with permission from Elsevier

seen in Fig. 6.31 that the  $2p_0$  transitions are relatively well separated from the higher energy ones.

The TDD $^0$ -related spectra in germanium are denoted  $\text{D}^0$ ,  $\text{E}^0$ ,  $\text{F}^{0'}$ ,  $\text{F}^0$ ,  $\text{G}^0$ ,  $\text{H}^0$ ,  $\text{I}^0$  and  $\text{J}^0$  in order of decreasing ionization energies and the TDD $^+$ -related spectra  $\text{A}^+$ ,  $\text{B}^+$ ,  $\text{C}^+$ ,  $\text{D}^+$ ,  $\text{E}^+$ ,  $\text{F}^+$ ,  $\text{G}^+$ ,  $\text{H}^+$  and  $\text{I}^+$  [44]. There is a correlation between the presence of Cu, a fast-diffusing acceptor impurity and contaminant in germanium, and the observation of the  $\text{A}^+$ ,  $\text{B}^+$  and  $\text{C}^+$  spectra (The acceptor Cu doping was used for partial compensation of n-type germanium to observe the TDD $^+$  spectra at LHeT). As can be seen later, the  $\text{D}^0$ ,  $\text{E}^0$ ,  $\text{F}^{0'}$ ,  $\text{D}^+$  and  $\text{E}^+$  spectra correspond to the neutral and singly-ionized charge states of the same centre denoted usually TD1; the  $\text{F}$ ,  $\text{G}$ ,  $\text{H}$ ,  $\text{I}$  and  $\text{J}$  spectra are identified with the double-donor centres denoted TD2, TD3, TD4, TD5 and TD6, respectively, by Clauws [45]. The different spectra related to the TDDs are not easy to sort because their ground-state energies are close



**Table 6.27.** Positions (meV (cm<sup>-1</sup> in parentheses)) at LHeT of the first lines of the TDD<sup>0</sup>s spectra in germanium

| Line         | $D^0$                                    | TD1<br>$E^0$       | $F'^0$                                   | TD2<br>$F^0$                           | TD3<br>$G^0$                           | TD4<br>$H^0$                                            | TD5<br>$I^0$                  | TD6<br>$J^0$ |
|--------------|------------------------------------------|--------------------|------------------------------------------|----------------------------------------|----------------------------------------|---------------------------------------------------------|-------------------------------|--------------|
| $2p_0$       | 12.305<br>(99.23)                        | 11.961<br>(96.46)  | 11.492<br>(92.68)                        | 11.370<br>(91.69)<br>11.536<br>(93.03) | 10.996<br>(88.68)<br>11.189<br>(90.23) | 10.45<br>(84.3)<br>10.76<br>(86.8)<br>10.819<br>(87.25) | 9.5<br>(77)<br>9.92<br>(80.0) | 9.2<br>(74)  |
| $2p_{\pm 1}$ | 16.366<br>(131.98)<br>16.410<br>(132.34) | 15.874<br>(128.02) | 15.516<br>(125.13)<br>15.558<br>(125.47) | 15.593<br>(125.75)                     | 15.362<br>(123.89)                     | 14.897<br>(120.14)<br>14.985<br>(120.85)                | 14.3<br>(115)                 |              |
| $3p_{\pm 1}$ | 17.093<br>(137.85)                       | 16.529<br>(133.30) | 16.238<br>(130.95)                       |                                        | 16.088<br>(129.74)                     | 15.752<br>(127.03)                                      |                               |              |
| $4p_{\pm 1}$ | 17.386<br>(140.21)                       | 16.812<br>(135.58) | 16.529<br>(133.30)                       |                                        | 16.392<br>(132.19)                     |                                                         |                               |              |
| $4f_{\pm 1}$ | 17.525<br>(141.33)                       | 16.955<br>(136.73) | 16.679<br>(134.51)                       |                                        | 16.518<br>(133.21)                     |                                                         |                               |              |
| $E_{i_o}$    | 18.13                                    | 17.57              | 17.28                                    | 17.3<br>1.7<br>3.3                     | 17.13<br>1.7                           | 16.79<br>~1.6                                           | 16.0                          | 15.2         |

The ionization energy  $E_{i_o}$  is obtained by adding to the line position the calculated energy level (1.04 meV) of the  $3p_{\pm 1}$  state except for  $F^0$  where the value for the  $2p_{\pm 1}$  state (1.73 meV) is used. Lines from split upper 1s states have been observed for TD2, TD3 and TD4. The separation of these 1s states from  $E_{i_o}$  is indicated in the last row [44]

and sometimes nearly degenerate, and also because of a multiplet splitting of the ground state for some of them. The identification of the first lines of the main spectra of the neutral centres, given in Table 6.27, illustrate these points.

The splitting for these lines is assumed to originate from the final state. One observes a splitting of the  $2p_{\pm 1}$  transition in the  $D$  and  $F'$  spectra, which could be reminiscent of the situation in silicon, but the splitting of the  $2p_0$  lines is new. The identification of the first lines of the spectra in the singly-ionized state is given in Table 6.28. These spectra include  $A^+$ ,  $B^+$  and  $C^+$ , assumed to be Cu-related.

Distinct ESR spectra correlated with the IR spectra  $F^0$ ,  $G^0$ ,  $H^0$ , and  $I^0$  have been reported at 1.6 K and below 10 K [19, 47]. This situation contrasts with the one in silicon, where no ESR spectrum can be correlated with the TDDi<sup>0</sup>. For silicon, this absence is explained by a “normal” neutral configuration with antiparallel electron spins and resultant total spin 0. In germanium, the low-temperature ESR spectra are observed under conditions where TDD<sup>+</sup>s centres are absent. They have been attributed to the

**Table 6.28.** Positions (meV ( $\text{cm}^{-1}$  in parentheses)) at LHeT of the first lines of the spectra related to the TDD<sup>+</sup>s and to Cu-related centres in germanium [44]

| Line         | Cu-related |       |         | TD1   |         | TD2   | TD3     | TD4     | TD5   |
|--------------|------------|-------|---------|-------|---------|-------|---------|---------|-------|
|              | $A^+$      | $B^+$ | $C^+$   | $D^+$ | $E^+$   | $F^+$ | $G^+$   | $H^+$   | $I^+$ |
| $2p_0$       | 21.0       | 20.1  | 19.28   | 18.7  | 17.94   | 17.4  | 16.43   | 15.4    | 14.1  |
|              | (169)      | (162) | (155.5) | (151) | (144.7) | (140) | (132.5) | (124)   | (114) |
|              |            |       |         |       |         |       | 16.68   | 15.81   | 14.8  |
| $2p_{\pm 1}$ | 33.6       | 32.9  | 32.0    | 31.5  | 30.6    | 30.1  | 29.20   | 28.09   | 27.0  |
|              | (271)      | (265) | (258)   | (254) | (247)   | (243) | (235.5) | (226.5) | (218) |
|              |            |       |         |       |         | 30.3  | 29.5    | 28.6    | 27.59 |
| $3p_{\pm 1}$ | 36.3       | 35.6  |         | 34.2  | 33.4    | 32.9  | 32.2    | 31.4    |       |
|              | (293)      | (287) |         | (276) | (269)   | (265) | (260)   | (253)   |       |
| $E_i$        | 40.5       | 39.8  | 38.9    | 38.4  | 37.5    | 37.0  | 36.3    | 35.3    | 34.2  |
|              |            |       | 36.4    | 35.9  | 35.0    | 34.7  | 36.8    |         |       |
|              |            |       |         |       |         | 32.1  |         |         |       |

Lines from split upper  $1s$  states have been observed for TD1, TD2 and TD3. The separations of these  $1s$  states from  $E_{\text{io}}$  is indicated in the last row

presence of TDD<sup>0</sup>s with parallel spins and total spin 1, which seems to be the equilibrium configuration [112]. No ESR spectrum has, however, been correlated with the set of  $D^0$ ,  $E^0$  and  $F^{0'}$  spectra.

In silicon, the Si-NL8 ESR spectrum can be correlated with the TDDi<sup>+</sup>, but because of the relatively small anisotropy of the electron spin  $g$ -factors, all the ESR responses of the different thermal donors are superimposed on the Si-NL8 signal (Fig. 8.17a). This is not the case in germanium for the spin 1 spectra because of the larger value of the spin-orbit coupling coefficient, allowing one to discriminate the ESR signals of different donors and determine their symmetry in the crystal. In germanium, an ESR spectrum due to the  $S = 1/2$  singly-ionized thermal donors, equivalent to the Si-NL8 spectrum, can also be observed in properly compensated samples [47].

### Metastability

As for the TDDs in silicon, Fermi-level-dependent metastability has been observed in the TDD-related spectra in germanium depending on the cooling-down conditions. This effect is illustrated for the neutral charge state in Fig. 6.32. It represents the  $2p_0$  lines corresponding to different thermal donors in three different samples measured at 7 K for cooling-down conditions 1 and 2. In 1, the samples are cooled from room temperature under TEC, and in 2, they are cooled under band-gap light pumping. Sample (a) with  $[\text{O}_i] = 5 \times 10^{16} \text{ cm}^{-3}$  is as-grown ( $n = 2 \times 10^{14} \text{ cm}^{-3}$ ) and the dominant centre is TD1, giving the  $D^0$ ,  $E^0$  and  $F^{0'}$  lines. A comparison between conditions 1 and 2 shows that this centre is 100% metastable in the given sample,

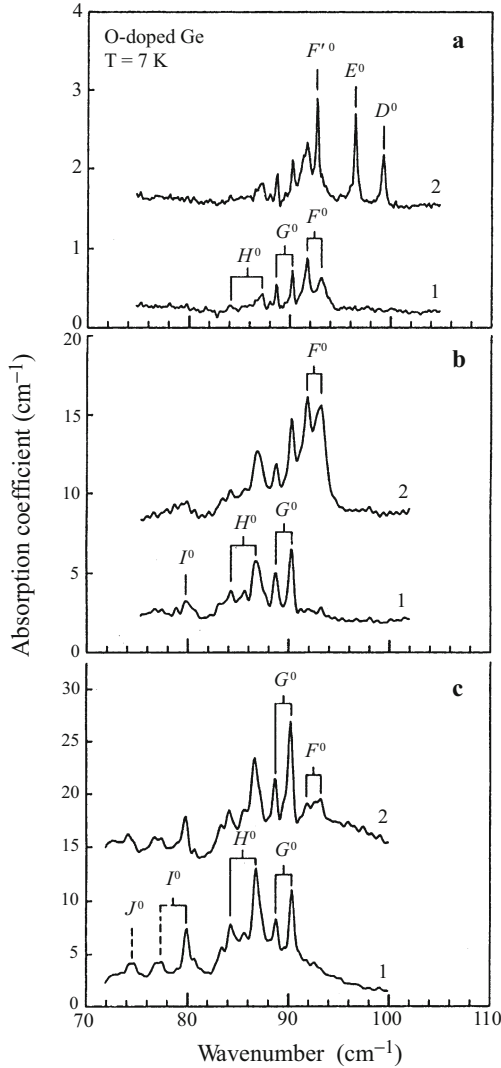


**Fig. 6.32.** Metastability effects of the neutral thermal donor spectra ( $2p_0$  lines) between 8.9 and 12.4 meV observed in three O-doped germanium samples with free-carrier concentrations increasing from (a) to (c) (see text). The spectra denoted 1 are obtained after cooling-down from RT under TEC and those denoted 2 after cooling-down under band-gap light illumination (after [47])

while the other centres are stable. Sample (b) with  $[O_i] = 2 \times 10^{17} \text{ cm}^{-3}$  has been annealed at  $350^\circ\text{C}$  for 22 mn ( $n = 3 \times 10^{15} \text{ cm}^{-3}$ ), and the early-formed TD1 centre is absent, but TD2 ( $F^0$  lines), now the dominant centre, is 100% metastable. Sample (c) is an as-grown sample with  $[O_i] = 2 \times 10^{17} \text{ cm}^{-3}$  and

a rather large free-carrier concentration ( $n = 3 \times 10^{16} \text{ cm}^{-3}$ ). In this sample, TD2 is still metastable, but TD3 ( $G^0$  lines), now the dominant centre, is partially metastable as the Fermi level is closer to the  $CB$ .

These infrared metastability experiments have been correlated with ESR measurements, and the comparison has allowed a fair understanding of these donors. Also, some differences exist with the situation in silicon where the point group symmetries of the different TDDs are either  $C_{2v}$  or  $C_{2h}$ . In germanium, if TD2 and TD5 display  $C_{2v}$  symmetry, TD3 and TD4 display axial  $\langle 111 \rangle$  symmetry ( $C_{3v}$ ).

When the same measurements as those of Fig. 6.32 are repeated at 34 K with sample (a), the only contribution observed is that of the singly-ionized charge states at higher energies, with metastability. A noticeable difference, however, is that if full metastability is observed for the  $D^+$  and  $E^+$  lines, no equivalent of the  $F'^0$  line is detected in any spectrum. It has been suggested that despite the fact that no ESR signal can be related with TD1, the  $F'^0$  spectrum could be due to  $S = 1$  configuration [48].

Vibrational absorption of the O atoms of the TDDs in silicon and germanium has been observed and will be discussed in [201].

#### 6.4.2 The Shallow Thermal Donors in Silicon

Shallow donor spectra in the  $230\text{--}290 \text{ cm}^{-1}$  ( $\sim 28\text{--}36 \text{ meV}$ ) range were reported for CZ silicon samples annealed at  $450^\circ\text{C}$  after a short annealing at  $770^\circ\text{C}$  in nitrogen [184]. Similar spectra observed in N-containing CZ silicon, but absent in N-lean CZ silicon and in N-doped FZ silicon, were attributed to shallow thermal donors (STDs) involving oxygen and nitrogen [238, 239]. Similar results were also reported by Griffin et al. [80]. Pulling CZ silicon under a nitrogen atmosphere had become a common practice at the end of the 1980s to improve the mechanical strength of the material and to enhance the O precipitation rate near  $800^\circ\text{C}$  for technological uses. This explains the detection of presence of these STDs in as-grown CZ silicon by Hu et al. [109]. The observation in an as-grown FZ silicon sample with a relatively high  $O_i$  concentration for a FZ material ( $4 \times 10^{16} \text{ cm}^{-3}$ ) of the spectra of two shallow donors at a small concentration level was also reported by Yu et al. [275] using high-resolution PTIS ( $0.06 \text{ cm}^{-1}$ ).

These STDs are characterized by a larger production range and a higher thermal stability than the TDDs discussed in Sect. 6.4.1.1: they can be produced at temperatures up to  $600^\circ\text{C}$  [231] and some of them can survive thermal annealing at  $900^\circ\text{C}$  [238]. Several labels have been used for these STDs. They have been denoted N-O- $n$  ( $n = 1, 2, 3, \dots$ ) by Suezawa et al. [239], and STD- $N$  with  $N = A, B, C, \dots$  by Griffin et al. [80] or D(N,O)- $n$  with  $n = 1, 2, 3, \dots$  by Hara [92]. In a paper by Newman et al. [187] where a parallel is made with the TDDi donors because of the possibility of their partial passivation by hydrogen, they were denoted STD(i) (actually STD( $N$ )) with  $i = 1, 2, 3, \dots$ . The relations between the different labels are given in Table 6.29.

**Table 6.29.** Relation between the different labels of the N-related STDs in CZ silicon. The average position of  $2p_{\pm 1}$  line of their spectra at LHeT is indicated

| Ref. a | Ref. b | Ref. c    | Ref. d | $2p_{\pm 1}$ (cm <sup>-1</sup> ) |
|--------|--------|-----------|--------|----------------------------------|
|        |        |           | STD(7) | 226.1                            |
| STD-A  | N-O-6' |           | STD(6) | 230.6                            |
| STD-B  | N-O-1  |           | STD(5) | 233.8                            |
| STD-C  | N-O-2  | D (N,O)-1 |        | 237.8                            |
|        |        |           | STD(4) | 238.4                            |
| STD-D  | N-O-3  | D (N,O)-2 |        | 240.4                            |
|        | N-O-8  |           |        | 241.5                            |
| STD-E  | N-O-4  |           |        | 242.5                            |
| STD-F  | N-O-6  | D (N,O)-3 | STD(2) | 247.0                            |
| STD-G  | N-O-5  | D (N,O)-4 |        | 249.8                            |
|        |        |           | STD(1) | 253.6                            |

<sup>a</sup> [80], <sup>b</sup> [239], <sup>c</sup> [92], <sup>d</sup> [187]

**Table 6.30.** Positions (meV (cm<sup>-1</sup> in parentheses)) at 10 K of the first parity-allowed transitions of the N-induced STDs in silicon [6]. NSD1 and NSD2 were reported from PTIS measurements at 17 K in a FZ sample with a RT resistivity of 1000  $\Omega$  cm [275]. The cm<sup>-1</sup>/meV conversion factor used is 0.124

|            | $2p_0$        | $2p_{\pm 1}$               | $3p_{\pm 1}$    | $3p_{\pm 1}-2p_0$ | $E_{io}$ |
|------------|---------------|----------------------------|-----------------|-------------------|----------|
| STD labels |               |                            |                 |                   |          |
| N-O-6'     | 23.30 (187.9) | 28.59 (230.6)              | 31.86 (256.9)   | 8.56              | 34.97    |
| N-O-1      | 23.65 (190.8) | 28.99 (233.8)              | 32.25 (260.1)   | 8.60              | 35.37    |
| N-O-2      | 24.16 (194.9) | 29.49 (237.8)              | 32.76 (264.2)   | 8.60              | 35.88    |
| N-O-3      | 24.51 (197.7) | 29.81 (240.4)              | 33.08 (266.8)   | 8.57              | 36.20    |
| N-O-8      | 24.69 (199.1) | 29.94 (241.5)              | 33.25 (268.2)   | 8.56              | 36.37    |
| N-O-4      | 24.82 (200.2) | 30.07 (242.5)              | 33.35 (269.0)   | 8.53              | 36.47    |
| NSD1       |               | 30.230 (243.79)            | 33.492 (270.10) |                   | 36.612   |
| NSD2       |               | 30.586 (270.10)            | 33.856 (273.03) |                   | 36.976   |
| N-O-6      | 25.34 (204.4) | 30.62 (247.0)              | 34.00 (274.2)   | 8.66              | 37.12    |
| N-O-5      | 25.71 (207.4) | 30.97 <sub>5</sub> (249.8) | 34.27 (276.4)   | 8.56              | 37.39    |

Families of STDs involving H, Al and another ingredient X, with very close ionization energies, have been labelled STD- $N(H)$ , STD- $N(Al)$ , and STD- $N(X)$ , respectively [216]. There has, however, been no evidence of the presence of N in the atomic core of these STDs. Nevertheless, on the basis of recent correlations between the intensities of the electronic lines of some of them and the N concentration, it has been concluded that at least four of them each contain one N atom Alt et al. [6].

The positions of the first lines of the N-induced STDs spectra and of the SDs reported by Yu [275] are listed in Table 6.30. [6] reported a new STD spectrum (N-O-8), close to N-O-4, detected because of the smaller FWHMs in these samples.

The  $3p_{\pm 1}-2p_0$  spacing in the STD spectra is  $\sim 8.57$  meV, significantly larger than the EM and average group-V donor values (8.37 and  $\sim 8.4$  meV, respectively), but smaller than that for the TDDi<sup>0</sup>. As expected, the  $3p_{\pm 1}-2p_{\pm 1}$  spacing in the STD spectra is close to the EM value (3.28 meV) but the one for N-O-6 is slightly larger (3.38 meV), and this can be due to unresolved components.

No transitions which could be associated with a second donor electron have been observed for the N-related STDs. Therefore, it is concluded that they are single donors [80] and this is probably also true for the other STDs [216]. This single-donor behaviour of the STDs is associated with an ESR signature known as Si-NL10 [79] and the ESR results indicate a  $C_{2v}$  symmetry for these centres, the same as that of the TDDs.

The attribution of all these centres to N-related complexes is questionable. It is worth noting, for instance, that [76] reported the presence of centers E and F with corrected ionization energies of 36.6 and 35.4 meV in FZ silicon samples containing lithium and oxygen, which correspond to N-O-1 and NSD1 of Table 6.30. Different STDs can have ionization energies very close to each other, and there are also small discrepancies between the positions/attributions of the lines reported from the absorption and PTIS measurements. This is partly due to the uncertainty of the measurements, but also to genuine differences in the constituents of the STDs, and it will be discussed later in this section. A  $1s-2s$  energy difference of 27.95 meV has been deduced for N-O-5 from two-electron PL measurements [231], giving an energy of 9.42 meV for the  $2s$  level of this centre, slightly larger than the EM value (8.86 meV). Absorption experiments between LHeT and 45 K down to  $\sim 110\text{ cm}^{-1}$  ( $\sim 14$  meV) show the existence of STDs spectra originating from split  $1s$  states [226]. Evidence for a  $1s$  excited state split by about 10 meV from the ground state has been obtained for five STDs, but because of the small differences between the ground state energies of the different donors, it has not been possible to ascribe a definite value of the splitting to a given STD. For two STDs, spectra originating from what appears to be a second  $1s$  excited state separated from the first one by 3–4 meV have also been reported in the same reference.

Possible atomic compositions of (N,O) STDs have been proposed by Alt et al. [6] from the measurements of the intensities of their spectra as a function of  $[O_i]$ , in relation with the theoretical calculations of [69] on the (N,O) complexes in silicon. In this study, N-O-5 and N-O-3 are attributed to NO and ONO structures, respectively. The NO structure is similar to the split nitrogen pair of Fig. 2.6, where one O atom replaces one N atom, and the tricoordinated O atom accounts for the donor behaviour of this pair [69]. The N-O-6 spectrum is elusive and it is only observed in the CZ samples with the highest values of  $[O_i]$ . A recent IR study of the (N,O) STDs, focused on the N-O-3, N-O-5, and N-O-6 spectra, has been reported by Ono [193]. It is shown that N-O-6 anneals at a temperature ( $\sim 600^\circ\text{C}$ ) lower than that for the two other STDs, and that the thermal regeneration of the STDs after

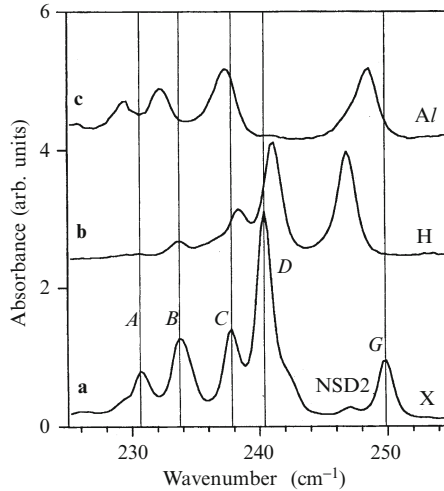


**Fig. 6.33.** LHeT absorption spectra between 27.9 and 31.6 meV centred on the  $2p_{\pm 1}$  lines of different STDs produced in (a) CZ silicon pre-heated in  $N_2$  gas and annealed at  $550^\circ\text{C}$  (same notation as in Table 6.29 (Ref. a) with STD omitted), (b) hydrogenated CZ silicon annealed at  $470^\circ\text{C}$  and (c) Al-doped CZ silicon pre-heated in argon gas and annealed at  $470^\circ\text{C}$ . The vertical lines are included as a guide for the eye (after [216]). Reproduced with permission from the Institute of Physics

high-temperature annealing fails to produce N-O-6 again. In the same study, from calculations of the formation energies of NO and of different ONO configurations, it is suggested that the N-O-6 corresponds to NO.

The observation of STDs in annealed N-free CZ silicon nominally suggests that other families of STDs may exist. This is indeed the case in hydrogenated CZ silicon and CZ Al-doped silicon [158,216]. In these materials, STD spectra with lines slightly shifted in position from those in silicon not containing these impurities are observed, as shown in Fig. 6.33.

The unknown constituent in the STDs whose spectra are observed in N-containing CZ silicon is denoted X in this figure. The measured shifts depend on the STD considered and on the accuracy with which a peak position can be measured. The FWHMs of most of the STD lines are between 1 and  $2\text{ cm}^{-1}$  (0.124 and 0.25 meV) and it is reasonable to assume an uncertainty of one tenth of the FWHM. A complete list of the STD(X), STD(Al) and STD(H) line positions is given in Ammerlaan's contribution on STDs in silicon [7]. When considering the positions of the lines of the STD(X)-N spectra as references, the lines of the STD(Al)-N spectra are found to be red-shifted. The values of the most significant Al-induced shifts of the  $2p_{\pm 1}$  lines with respect to the positions in Table 6.29 are (in  $\text{cm}^{-1}$ ) for STD-A:  $-1.4$ , STD-B:  $-1.5$ , STD-C:  $-0.5$ , STD-G:  $-0.9$ , and this seems to imply that an Al atom is present in the core of these donor centres. The values of the shifts (positive) of the STD(H) spectra are smaller or non-existent. The largest ones are  $+0.5$

and  $+0.7 \text{ cm}^{-1}$  for *C* and *D*, respectively, giving for STD(H)*D* the same ionization energy of 36.3 meV as that of D(N,O)-2, implying that the donors are the same.

The existence of a shift between the lines of STD(X) and STD(H) spectra is an indication that H can be a constituent of these centres. The absence of a shift of the spectra of other STD(H) centres with respect to other STD(X) centres can also be an indication that some of the STD(X) centres, like the D(N,O)-1 and D(N,O)-2 centres, are indeed H-related STDs and that hydrogen is either present in as-grown CZ silicon or introduced during the nitridation process.

A definite proof of the presence of hydrogen in these centres has been obtained by using  $^2\text{H}$  instead of  $^1\text{H}$  in the hydrogenation process: this substitution has been correlated with a small, but unmistakable negative IS of some of the STD(H) lines, visible in Fig. 6.34. The values of the  $^2\text{H}$  shifts are  $-0.18$  and  $-0.15 \text{ cm}^{-1}$  ( $-22$  and  $-15 \mu\text{eV}$ ) for SPD-*D* and SPD-*F*, respectively.

It must be noted that the  $^2\text{H}$  IS of the STD(H)-*D* and STD(H)-*F* donors is negative, as those for the *D*(H,O) donor in germanium discussed in Sect. 6.2.2.

The observation of three STD absorption spectra has been reported in H-doped n-type CZ silicon samples irradiated with 3 MeV electrons after annealing in the 300–600°C temperature range [96]. The values of  $E_{\text{io}}$  for two of these STDs (*D2* and *D3*) are 37.0 and 36.3 meV, respectively, very

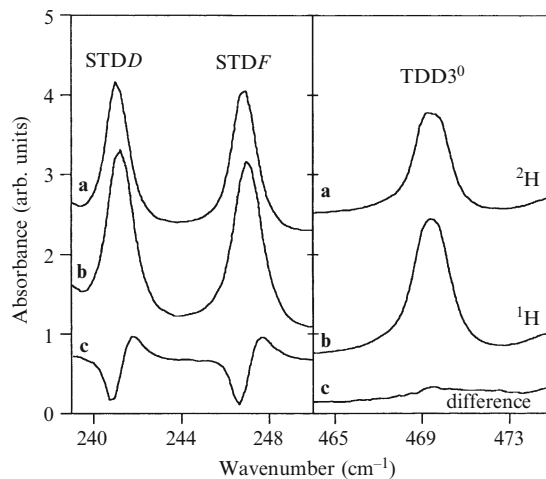


**Fig. 6.34.**  $2p_{\pm 1}$ (STD(H)-*D*) and  $2p_{\pm 1}$ (STD(H)-*F*) lines (*left*) and  $2p_{\pm 1}$  ( $\text{TDD3}^0$ ) line (*right*) in the LHeT spectra of a pair of P-doped CZ silicon samples heated (a) in a deuterium plasma for 34 h and (b) in a hydrogen plasma for 17 h. The  $^1\text{H}/^2\text{H}$  IS is visible in the difference spectrum in (c) (*left*), obtained after renormalization (the absorbance of the deuterated sample is weaker than that of the hydrogenated sample) (after [187]). In this reference, the STD(H) A, B, C, D, and F centres are denoted STD(6), (5), (4), (3) and (2), respectively. The positions of the lines are given in Tables 6.29 and 6.24



close to those of D(N,O)-3 and D(N,O)-2 of Table 6.30, and they correspond to the same centres, but the  $D1$  STD, with  $E_{\text{io}} = 42.6$  meV is reported for the first time and is tentatively attributed to an oxygen-hydrogen-vacancy centre.

One of the interests of a spectroscopic study of hydrogenated CZ silicon was a search for electronic spectra associated with partially passivated TDD<sup>0</sup>s similar to those observed for sulphur in silicon. DLTS measurements have proved the passivation of the electrical activity of TDDs in silicon after exposure to a hydrogen plasma at relatively low temperature (100–150°C) [42, 120]. The reduction of the TDDs concentration indicates that in the region closest to the surface, full passivation is achieved. The thermal stability of the (TDD,H) complexes thus created has been found to be moderate, and full electrical recovery takes place at about 200°C. The passivation efficiency depends on the TDDi considered, but this is not discussed here. It has been suggested that some of the STD(H) centers could be H-passivated TDDi [187]. However, the temperature difference between the reactivation of the H-passivated TDDi ( $\sim 200^\circ\text{C}$ ) and the temperature of dissociation of STD(H) centres ( $\sim 500^\circ\text{C}$ ) has led to abandon this assumption [216].

### 6.4.3 The Ultrashallow Thermal Donors in Silicon

The observation at LHeT of absorption spectra between  $\sim 230$  and  $130\text{ cm}^{-1}$  ( $\sim 28$ – $16$  meV) has been reported by Hara [92] in N- and C-rich CZ silicon samples, when annealed between 500 and  $600^\circ\text{C}$  for typically 20 h or longer. They correspond to EM donors with ionization energies between 35 and 28 meV, distinct from the above-discussed STD centres, whose production is hindered by the presence of carbon. They have, however, a stability domain comparable to the STDs, limited to about  $700^\circ\text{C}$ . These donors are known as ultrashallow thermal donors (USTDs) as their ionization energies vary between 27.90 and 34.85 meV, compared to the EMT value of 31.3 meV. Spectra associated with 12 such donors have been identified by Hara [92], and the shallowest line for a donor electronic transition from the ground state in silicon seems to be  $2p_0(\text{USTD1})$  at  $\sim 128.0\text{ cm}^{-1}$  (15.87 meV). Table 6.31 gives spectroscopic values for the USTDs (the  $3p_{\pm 1}$  line has not been reported for these centres).

**Table 6.31.** Positions of the  $2p_{\pm 1}$  lines, values (meV) of the  $2p_{\pm 1} - 2p_0$  spacings and ionization energies of the USTDs in silicon obtained from LHeT spectra

| USTD                | 1     | 2     | 3     | 4    | 5     | 6     | 7     | 8     | 9     | 10    | 11    |
|---------------------|-------|-------|-------|------|-------|-------|-------|-------|-------|-------|-------|
| $2p_{\pm 1}$        | 21.49 | 21.82 | 22.23 | 25.0 | 25.09 | 25.99 | 26.77 | 26.88 | 27.49 | 28.17 | 28.42 |
| $2p_{\pm 1} - 2p_0$ | 5.62  | 5.40  | 5.40  | 5.36 | 5.31  | 5.24  |       |       |       |       |       |
| $E_{\text{io}}$     | 27.90 | 28.24 | 28.65 | 31.4 | 31.51 | 32.40 | 33.19 | 33.30 | 33.89 | 34.57 | 34.82 |
| CCC                 | -3.36 | -3.02 | -2.61 | 0.14 | 0.25  | 1.14  | 1.93  | 2.04  | 2.63  | 3.31  | 3.56  |

The central-cell correction (CCC) is the difference between the ionization energy  $E_{\text{io}}$  of the donor and the EM value taken as 31.26 meV. The EM value of the  $2p_{\pm 1} - 2p_0$  spacing is 5.09 meV (after [92])

A negative value of the central-cell correction indicates a central-cell potential which is repulsive for electrons.

It must also be mentioned that evidence for USTDs with ionization energies down to  $\sim 23$  meV has been obtained by low-temperature admittance spectroscopy and thermally-stimulated capacitance measurements in standard CZ silicon samples annealed at  $470^\circ\text{C}$  in oxygen ambient for up to 500 h [1].

## 6.5 Other Shallow Donors Involving Hydrogen

The interaction of hydrogen with impurities can assume several characteristics, one of which is the electrical passivation of the shallow acceptors and donors in several semiconductors. It has also been shown at the end of Sect. 6.3.1 that partial passivation by hydrogen of double chalcogen donors produced single donors with EM spectra. New acceptors and donors can also be produced by thermal treatments involving hydrogen and electrically inactive impurities, like the already-mentioned  $D(\text{H},\text{O})$  donor in germanium grown in a hydrogen or deuterium atmosphere, discussed in Sect. 6.2.2, and the O-related STD(H)- $D$  and STD(H)- $F$  donors in silicon discussed in Sect. 6.4.2. Another contribution arises from the interaction between hydrogen and lattice defects. This is illustrated by the observation of shallow donor spectra in as-irradiated NTD FZ silicon after different hydrogen-plasma treatments at temperatures between  $\sim 240$  and  $400^\circ\text{C}$  for a few hours [95]. These treatments produce a n-type layer, typically a few  $\mu\text{m}$ -thick with a resistivity allowing one to perform PTIS measurements. Besides the P spectrum associated with NTD, several shallow EM donor spectra, denoted HDi, are observed. They are characterized by a splitting of the  $2p_{\pm 1}$  line, already observed for some TDD<sup>0</sup>i, like TDD<sup>0</sup>3, but the interesting point is the observation in these spectra of a positive IS of the donor lines when  $^1\text{H}$  is replaced by  $^2\text{H}$  in the plasma. This shift is rather small ( $0.1\text{--}0.2\text{ cm}^{-1}$  or  $\sim 12\text{--}24\text{ }\mu\text{eV}$ ) and comparable in value to the one reported for the STD(H)- $D$  and STD(H)- $F$  donors by Newman et al. [187]. However, a noticeable difference with two other kinds of donors is that the  $^2\text{H}$  IS of the HDi donors is opposite to the one observed for the STD(H) $D$  and STD(H) $F$  donors (the  $^2\text{H}$ -related lines of the HDi donors are at energies higher than the  $^1\text{H}$ -related one). The origin of these donors has not been elucidated, but they must be related to the complexing of defects with hydrogen during the dissociation of the radiation damages produced by the neutron irradiation. These thermal donors are stable up to  $\sim 500^\circ\text{C}$  and the positions of the first lines of their spectra are given in Table 6.32. As the measurements were performed by PTIS, the transitions toward the  $np_0$  levels are not observed.

The first values of  $E_{i0}$  of Table 6.32 are in the same energy range as those of Table 6.30, but considering the accuracy of the measurement, they correspond to different donor centres, in which oxygen is probably not involved. Moreover, the opposite hydrogen ISs clearly speaks for a difference.

**Table 6.32.** LHeT positions (meV (cm<sup>-1</sup> in parentheses)) of lines of HDi spectra in as-irradiated NTD FZ silicon after annealing in the 240–400°C range in a <sup>1</sup>H<sub>2</sub> plasma

| Line                            | HD3     | HD4     | HD5     | HD6     | HD7     |
|---------------------------------|---------|---------|---------|---------|---------|
| $2p_{\pm 1}$                    | 27.70   | 29.37   | 32.19   | 37.86   | 46.05   |
|                                 | (223.4) | (236.9) | (259.6) | (305.4) | (371.4) |
|                                 | 27.86   | 29.46   | 32.26   | 37.99   | 46.20   |
| $3p_{\pm 1}$                    | (224.7) | (237.6) | (260.2) | (306.4) | (342.6) |
|                                 | 30.97   | 32.66   | 35.46   | 41.16   | 49.32   |
|                                 | (249.8) | (263.4) | (286.0) | (332.0) | (397.8) |
| $4p_{\pm 1}$                    | 31.86   | 33.57   | 36.39   | 42.08   | 50.26   |
|                                 | (257.0) | (270.8) | (293.5) | (339.4) | (405.4) |
| $5p_{\pm 1}$                    |         | 34.31   | 37.12   | 42.79   |         |
|                                 |         | (276.7) | (299.4) | (345.1) |         |
| $E_{i0}$                        | 34.09   | 35.78   | 38.58   | 44.28   | 52.44   |
| $^2\text{H} - ^1\text{H}$ (μeV) |         | + 19    | + 25    | + 12    | + 19    |

$E_{i0}$  is obtained by adding 3.12 meV to the position of the  $3p_{\pm 1}$  line. The last row gives average values of the  $^2\text{H} - ^1\text{H}$  energy difference (accuracy  $\pm 6 \mu\text{eV}$ ) (after [95])

## 6.6 TMs, Group-I Elements and Pt in Silicon

### 6.6.1 Interstitial Iron

In its isolated form, iron is incorporated in silicon at a tetrahedral interstitial site ( $\text{Fe}_i$ ). This configuration is moderately stable and thermal annealings show that atomic migration of Fe starts for temperatures of about 170°C [189]. The absorption spectrum between  $\sim 5700$  and  $6450 \text{ cm}^{-1}$  ( $\sim 0.71$  and  $0.80 \text{ eV}$ ) shown in Fig. 6.35 is associated with  $\text{Fe}_i$  as all the spectral features decrease at the same rate under thermal annealing [250].

The lines observed in the h-e region have spacings and relative intensities typical of EM donor spectra. In order to understand the origin of this spectrum, a brief introduction to transition metals (TMs) at tetrahedral interstitial states is necessary. When submitted to a tetrahedral crystal field, the one-electron  $d$  states of a TM are split into an orbital triplet  $t_2$  state and an orbital doublet  $e$  state and for an interstitial location, the  $t_2$  state is deeper in energy compared to the continuum. It must be noted that these  $e$  and  $t_2$  states are not pure  $d$  states, but also contain contributions from the  $p$ -like host state (covalency). The orbital momentum is totally quenched by the crystal field for an electron in an  $e$ -state whereas an effective orbital momentum  $\ell = 1$  corresponding to a manifold of  $p$  orbitals can be associated with an electron in a  $t_2$ -state. As first evidenced by Ludwig and Woodbury [157], the outermost  $s$  electrons of a TM are incorporated in the  $d$  shell when the atom enters the crystal interstitially. For Fe with electronic configuration  $\text{Ar}d^6s^2$ , this leads to an  $\text{Ar}d^8$  configuration. Following the first two Hund's rules and the convention for the multi-electron atomic notations, an isolated  $d^8$  configuration is represented by a  $^3\text{F}$  ground state. In a crystal field with tetrahedral symmetry, this

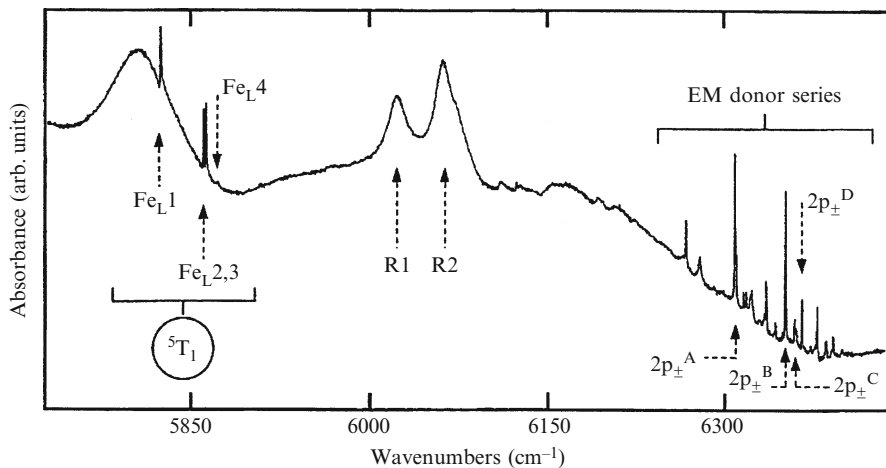
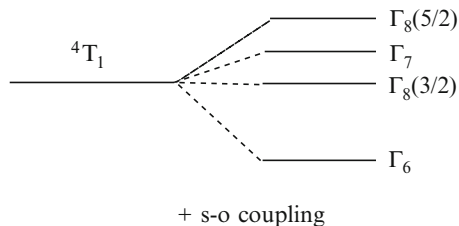


**Fig. 6.35.** Absorption between  $\sim 713$  and  $800$  meV at a resolution of  $0.3 \text{ cm}^{-1}$  ( $37 \mu\text{eV}$ ) of a Fe-diffused n-type silicon sample at LHeT (after [250]). Reproduced with permission from Trans Tech Publications

state is split into three substates:  $^3A_2$  (ground state), which corresponds to 6  $d$ -electrons in  $t_2$  orbitals and 2  $d$ -electrons in  $e$  orbitals ( $t_2^6 e^2$  configuration),  $^3T_1$  and  $^3T_2$  [240]. ESR experiments have proved that for  $\text{Fe}_i^0$  in silicon,  $^3A_2$  was indeed the ground state [157]. This deep state is the fundamental state of the transitions shown in Fig. 6.35.



In its excited state,  $\text{Fe}_i^0$  consists of a  $\text{Fe}^+ d^7$  core<sup>8</sup> plus an electron weakly bound ( $e_{\text{wb}}$ ) to this core. This  $e_{\text{wb}}$  is then considered adequately decoupled from the  $\text{Fe}^+$  core for its eigenstates to be described by EMT. However, in order to arrive at a more detailed interpretation of the different EM spectra apparent in Fig. 6.35, one must get some insight of the level structure of the  $d^7$  core responsible for this diversity. This  $d^7$  core is considered as an isolated entity. Its configuration is thus represented by a  $^4F$  ground state, split by the “weak” crystal field of the tetrahedral interstitial site, giving a  $^4T_1$  high-spin

<sup>8</sup> The term “core” usually refers to the electrons of the closed shells and it is used here in a slightly different meaning.

ground state corresponding to a  $t_2^5 e^2$  configuration [240]. Under s-o coupling, the  $^4T_1$  state splits as shown in the diagram on the preceding page.

Of course, the  $^4T_1$  state being an orbital triplet, can be affected by Jahn-Teller coupling and therefore, the energies of the sublevels are not necessarily in agreement with those calculated in the frame of pure s-o coupling.

Figure 6.36 is a blow-up of Fig. 6.35 in the region of the EM donor spectra, whose relative intensities and line spacings are comparable to those observed for shallow donors. The spectrum labelled A in Fig. 6.36 corresponds to transitions from the  $^3A_2$  ( $d^8$ )  $Fe_i^0$  ground state to a series of EM excited donor states ( $d^7$  + weakly-bound electron) with the  $d^7$  core in the  $\Gamma_6$  state. Similarly, the spectra labelled B, C, and D correspond to transitions from the  $^3A_2$  ground state to a series of EM donor excited states with the  $d^7$  core in the  $\Gamma_8$  ( $3/2$ ),  $\Gamma_7$  and  $\Gamma_8$  ( $5/2$ ) states, respectively [252]. The positions of the lines of spectra A, B, C and D are given in Table 6.33. The antepenultimate row of the table gives the EM ionization energies of the weakly bound electron from the  $d^8$  ( $^3A_2$ ) state leaving  $Fe_i^+$  in the  $d^7\Gamma$  (i) states indicated in the penultimate row.

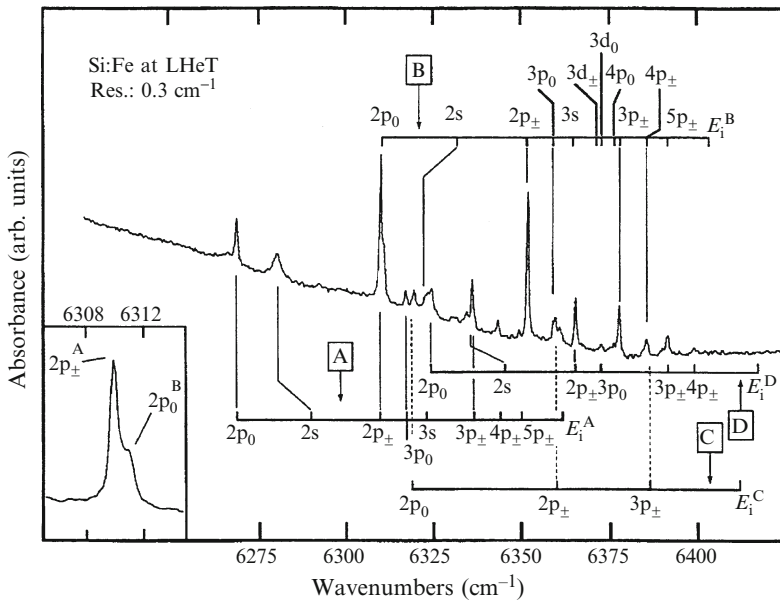


**Fig. 6.36.** EM-like donor spectra of interstitial  $Fe^0$  in silicon at LHeT between  $\sim 775$  and  $797$  meV. Four distinct donor spectra denoted A, B, C and D can be identified, and the resulting level patterns are shown, with the indication of the ionization energies  $E_i$ . The lines are labelled as usual by the EM final states. As shown in the inset,  $2p_0^B$  nearly coincides with  $2p_{\pm 1}^A$ . For the attribution, see text (after [251]). Copyright 1990, with permission from World Scientific Publishing Co. Pte. Ltd, Singapore

**Table 6.33.** Positions (meV (cm<sup>-1</sup> in parentheses)) of the lines of spectra of the A, B, C and D series of Fe<sup>0</sup> in silicon near LHeT

| Line                                                      | Series A                      | Series B                            | Series C                      | Series D                            | EMT <sup>a</sup> |
|-----------------------------------------------------------|-------------------------------|-------------------------------------|-------------------------------|-------------------------------------|------------------|
| 2p <sub>0</sub>                                           | (6268.21)                     | (6310.83)                           | (6318.73)                     | (6324.34)                           |                  |
|                                                           | 777.159 <i>11.55</i>          | 782.443 <i>11.49</i>                | 783.423 <i>11.51</i>          | 784.118 <i>11.51</i>                | 11.492           |
| 2s (A <sub>1</sub> )                                      | (6280.14)                     | (6323.42)                           |                               |                                     |                  |
|                                                           | 778.638 <i>10.07</i>          | 784.004 <i>9.93</i>                 |                               |                                     | 8.856            |
| 2p <sub>±1</sub>                                          | (6309.72)                     | (6351.85)                           | (6359.89)                     | (6365.58)                           |                  |
|                                                           | 782.306 [6.40]                | 787.529 [6.40]                      | 788.526 [6.40]                | 789.231 [6.40]                      | 6.402            |
| 3p <sub>0</sub>                                           | (6317.11)                     | (6359.34)                           | (6367.20)                     | (6372.95)                           |                  |
|                                                           | 783.222 <i>5.49</i>           | 788.458 <i>5.47</i>                 | 789.432 <i>5.50</i>           | 790.145 <i>5.48</i>                 | 5.485            |
| 3s(A <sub>1</sub> )                                       | (6319.54)                     | (6361.14)                           |                               |                                     | 4.777            |
|                                                           | 783.523 <i>5.19</i>           | 788.681 <i>5.25</i>                 |                               |                                     |                  |
| 4p <sub>0</sub>                                           | (6334.55)                     | (6376.68)                           |                               | (6390.42)                           | 3.309            |
|                                                           | 785.384 <i>3.33</i>           | 790.608 <i>3.32</i>                 |                               | 792.311 <i>3.32</i>                 |                  |
| 3p <sub>±1</sub>                                          | (6336.11)                     | (6378.20)                           | (6386.2)                      | (6391.88)*                          |                  |
|                                                           | 785.578 <i>3.13</i>           | 790.796 <i>3.13</i>                 | 791.79 <i>3.14</i>            | 792.492 <i>3.14</i>                 | 3.120            |
| 4p <sub>±1</sub>                                          | (6343.61)                     | (6385.74)                           |                               | (6399.37)                           | 2.187            |
|                                                           | 786.507 <i>2.20</i>           | 791.731 <i>2.20</i>                 |                               | 793.421 <i>2.21</i>                 |                  |
| 5p <sub>±1</sub>                                          | (6349.37)                     | (6391.88)*                          |                               |                                     | 1.449            |
|                                                           | 787.222 <i>1.49</i>           | 792.492 <i>1.44</i>                 |                               |                                     |                  |
| 3p <sub>±1</sub> - 2p <sub>0</sub>                        | 8.42                          | 8.353                               | 8.37                          | 8.374                               | 8.372            |
| E <sub>i</sub> <sup>j</sup>                               | 788.71                        | 793.93                              | 794.93                        | 795.63                              |                  |
|                                                           | d <sup>7</sup> Γ <sub>6</sub> | d <sup>7</sup> Γ <sub>8</sub> (3/2) | d <sup>7</sup> Γ <sub>7</sub> | d <sup>7</sup> Γ <sub>8</sub> (5/2) |                  |
| E <sub>i</sub> <sup>j</sup> - E <sub>i</sub> <sup>A</sup> | —                             | 5.22                                | 6.22                          | 6.92                                |                  |

The semi-experimental energy levels are in italics, and the reference energy in brackets. The E<sub>i</sub><sup>j</sup> values are obtained by adding 6.402 meV to the position of the 2p<sub>±1</sub> lines. The corresponding states of the d<sup>7</sup> Fe<sup>+</sup> configuration are given in the penultimate row. The estimated accuracy of the line positions vary between 0.05 and 0.3 cm<sup>-1</sup> (6 and 37 μeV) and the ionization energies have been rounded up accordingly (after [252])

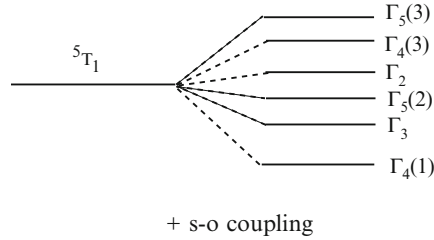
\* Superimposed lines, <sup>a</sup> [118]

In the framework of EMT, the true ionization energy of Fe<sub>i</sub><sup>0</sup>, leaving Fe<sub>i</sub><sup>+</sup> in its lowest energy d<sup>7</sup> substate is the one corresponding to the A series (788.71 meV). Considering a band gap of 1.170 eV at LHeT for silicon, one can then locate the Fe<sup>0</sup>/Fe<sup>+</sup> donor level at E<sub>v</sub> + 0.371 eV at LHeT, in good agreement with the value of E<sub>v</sub> + (0.375 ± 0.015) eV near 100 K obtained by a combination of ESR and Hall measurements [63].

From the comparison of the observed 3p<sub>±1</sub> - 2p<sub>0</sub> spacings with the EM donor at the interstitial Fe site, it can be seen that the local perturbation felt by the excited states is very small.

Until now, we only considered the EM excited states with n ≥ 2, but the electron bound to the d<sup>7</sup> core can also be found in the 1s state. In this state, the electron is more localized around the d<sup>7</sup> core, and therefore, more affected by the local potential. The d<sup>7</sup> core and the 1s electron ground states being represented by <sup>4</sup>T<sub>1</sub> and <sup>2</sup>A<sub>1</sub>, respectively, their coupling gives T<sub>1</sub> states with a

total spin 2 and 1 ( $^5T_1$  and  $^3T_1$ ) with the  $^5T_1$  high-spin ground state. Under s-o coupling with  $\ell = 1$  effective angular momentum, the  $^5T_1$  level splits as shown in the diagram below.



With the help of absorption experiments under magnetic field, [250] have shown that the lines at  $5824.39$ ,  $5860.77$ , and  $5862.64 \text{ cm}^{-1}$  ( $722.123$ ,  $726.643$ , and  $726.875 \text{ meV}$ ), labelled respectively  $\text{Fe}_L1$ ,  $\text{Fe}_L2$ , and  $\text{Fe}_L3$  in Fig. 6.35, are due to the transitions from the  $d^8 (^3A_2)$  state to the  $\Gamma_4(1)$ ,  $\Gamma_3$  and  $\Gamma_5(2)$  substates of  $^5T_1$ , respectively. It is assumed that the weak line at  $5872.8 \text{ cm}^{-1}$  ( $728.13 \text{ meV}$ ), labelled  $\text{Fe}_L1$  in Fig. 6.35 is due to a transition from the  $d^8 (^3A_2)$  state to one of the remaining sublevels of  $^5T_1$ .

The spectrum in Fig. 6.35 also displays a broadband around  $5800 \text{ cm}^{-1}$  and two resonances R1 and R2. These features have the same annealing behaviour as the sharp lines described until now, suggesting that they are also due to  $\text{Fe}_i$  [250]. Transitions between the  $d^8 (^3A_2)$  ground state and the  $d^8 (^3T_2)$  and  $d^8 (^3T_1)$  states could be potential candidates for these bands.

### 6.6.2 Ag, Au, and Pt

Ag and Au are substitutional group-I elements in silicon. These atoms are amphoteric, giving an acceptor and a donor state. The absorption related to the donor state is discussed here and that of the acceptor state in Chap. 7. Pt is also included here as it displays the same amphoteric behaviour.

In the transmission spectrum of Ag-diffused silicon, a series of sharp lines is observed at LHeT in the  $6200\text{--}6700 \text{ cm}^{-1}$  ( $770\text{--}830 \text{ meV}$ ) range [190]. This series does not fit a classical EM donor or acceptor spectrum, but the h-e limit is not too different from the Ag donor ( $\text{Ag}(D)$ ) level located at  $E_v + 0.34 \text{ eV}$  ( $E_c - 0.83 \text{ eV}$ ) in the Si band gap [12]. A comparison of this spectrum with the spectrum of  $\text{Te}^0$  in silicon has made possible a few correlations which seemingly allow to ascribe the Ag spectrum to a modified EM donor spectrum where the  $np_{\pm 1}$  lines are absent, the  $np_0$  lines very weak and the  $ns(T_2)$  lines predominant (see Fig. 6.37).

The  $ns(T_2)$  lines observed in some donor spectra are denoted  $ns(E + T_2)$  for  $\text{Ag}(D)$  in this reference because the observed splitting of the  $1s(E + T_2)$  line implies a non-cubic symmetry of the Ag atom site. In this symmetry, the  $1s(E)$  level of the  $T_d$  symmetry, to which no IR active transition from

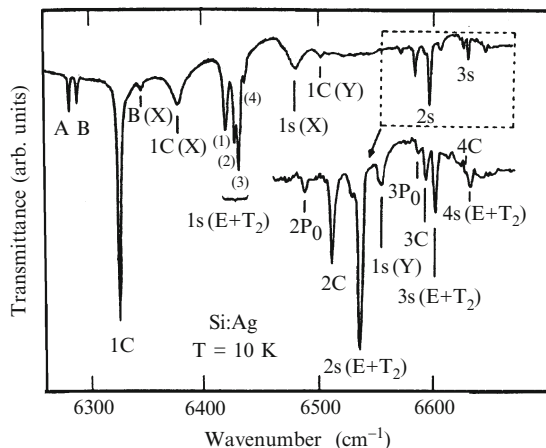


**Fig. 6.37.** Transmission spectrum between 775 and 828 meV of Ag in silicon at LHeT. The section in the *dotted rectangle* is shown below an expanded scale [190]. Copyright 1988 by the American Physical Society

the  $1s(A_1)$  ground state is possible, splits into sublevels which can be the final states of some symmetry-allowed transitions. The  $nC$  lines ( $n = 1, 2, 3, 4$ ) of Fig. 6.37 have been interpreted by assuming some s-o interaction between the electrons of the donor core and the weakly-bound electron. For the Se and Te substitutional double donors, this interaction is responsible for the extra  $1s(^3T_2)$  state and the corresponding  $1s(^3T_2)$  line. For Ag(*D*), the corresponding transitions should be  $1C$ . This is substantiated by the average spacing between the  $nC$  and  $ns(E + T_2)$  lines, which decreases as  $1/n^3$ , as expected for such a kind of interaction [189]. Fano resonances are, in general, more clearly observed in PTIS than in standard absorption. With this method, Fano resonances have been observed in the Ag photoionization spectrum. For a donor, the phonons involved in these resonances should be  $fTO$ ,  $gLO$  and  $fLA$  inter-valley phonons, and replicas of the  $1C$  and  $1s(E + T_2)$  transitions involving the  $fTO$  and  $gLO$  phonons have been observed in the  $6800\text{--}6950\text{ cm}^{-1}$  ( $\sim 840\text{--}860\text{ meV}$ ) range [190]. The lines with (X) or (Y) added in Fig. 6.37 are phonon-assisted replicas of the original lines and their spacings ( $50\text{ cm}^{-1}$  ( $6.2\text{ meV}$ ) for (X) and  $180\text{ cm}^{-1}$  ( $22.3\text{ meV}$ ) for (Y)) indicate that the phonons involved are resonant with the silicon acoustic phonon branches.

The energies of the transitions of the Ag(*D*) spectrum are listed in Table 6.34.

The value of the Ag(*D*) level deduced from  $E_{io}$  is in very good agreement with the value  $E_v + 0.34\text{ eV}$ , obtained from DLTS measurements [12]. Lines A, B and C have also been observed in PL experiments and Ag-isotope effects have been identified; it has been pointed out that the decay time of these lines is consistent with their attribution to an exciton bound to an isoelectronic



**Table 6.34.** Positions (meV ( $\text{cm}^{-1}$  in parentheses)) of the transitions of  $\text{Ag}(D)$  in silicon at LHeT

| Line                                               | Position                                      | Level  | EMT <sup>a</sup> |
|----------------------------------------------------|-----------------------------------------------|--------|------------------|
| <i>A</i>                                           | 778.91 (6282.3)                               | 47.23  |                  |
| <i>B</i>                                           | 779.85 (6289.9)                               | 46.29  |                  |
| <i>1C</i>                                          | 784.35 (6326.2)                               | 41.79  | 31.262           |
| <i>1s</i> ( <i>E</i> + <i>T</i> <sub>2</sub> ) (1) | 795.79 (6418.5)                               | 30.35  | "                |
| " (2)                                              | 796.73 (6426.1)                               | 29.41  | "                |
| " (3)                                              | 797.17 (6429.6)                               | 28.97  | "                |
| " (4)                                              | 797.76 (6434.4)                               | 28.38  | "                |
| <i>2p</i> <sub>0</sub>                             | 814.56 (6569.9)                               | 11.58  | 11.492           |
| <i>2C</i>                                          | 816.06 (6582.0)                               | 10.08  | 8.856            |
| <i>2s</i> ( <i>E</i> + <i>T</i> <sub>2</sub> )     | 817.58 (6594.2)                               | 8.56   | "                |
| <i>3p</i> <sub>0</sub>                             | 820.65 (6619.0)                               | [5.49] | 5.485            |
| <i>3C</i>                                          | 821.06 (6622.3)                               | 5.08   | 4.477            |
| <i>3s</i> ( <i>E</i> + <i>T</i> <sub>2</sub> )     | 821.54 (6626.2)                               | 4.60   | "                |
| <i>4s</i> ( <i>E</i> + <i>T</i> <sub>2</sub> )     | 823.38 (6641.0)                               | 2.76   | 2.911            |
| <i>E</i> <sub>io</sub>                             | 826.14<br>( <i>E</i> <sub>v</sub> + 0.344 eV) |        |                  |

The energies of the levels are calculated using *3p*<sub>0</sub> as a reference (after [190]), <sup>a</sup> [118]

centre [258]. At first sight, the LHeT absorption of the Au donor in silicon seems to limit to the four components A, B, B' and C of a structure centred at  $6395 \text{ cm}^{-1}$  or  $793 \text{ meV}$  [267], also observed by PL [244], very similar to the *1s* (*E* + *T*<sub>2</sub>) multiplet of Ag. The results of piezospectroscopic and Zeeman measurements on this spectrum confirm the substitutional location of Au, with a static <100> tetragonal distortion [244, 267].

The only absorption which has been ascribed to a donor-like state for Pt in silicon is a set of three lines near  $8000 \text{ cm}^{-1}$  (992 meV) investigated by Olajos et al. [191], denoted the T-lines and shown on the h-e side of Fig. 7.19.

## 6.7 Pseudo-Donors and Isoelectronic Donors

It was mentioned in Sect. 1.3.2 that in semiconductors, isoelectronic impurity centres could present a relatively strong attracting potential for electrons or holes. Excitons can be trapped by or created at these isoelectronic centres to form an isoelectronic bound exciton (IBE). The electron (hole) of this exciton is also more strongly bound to the isoelectronic centre than in classical excitons and the second constituent of the exciton, hole (electron) can be considered to be bound to a compound negative or positive ion. These structures are similar to those of neutral donors or acceptors and they are called isoelectronic donors or acceptors [104]. When formed by near band-gap or above band-gap laser illumination, the long lifetimes of these IBEs result in sharp PL lines, and this has for some time aroused interest for these centres as potential near IR radiation emitters.

This seems to be also valid for excitons bound to deep neutral centres not necessarily isoelectronic, giving pseudo-donors or pseudo-acceptors.

This section is devoted to the absorption of excitons bound to isoelectronic or deep centres with a strong attracting potential for holes (isoelectronic donors (IDs) and pseudo-donors), but for a more general description, it will be referred to the PL and PLE results. A point to consider is the interaction between the deep hole and the shallow electron of the IBE or BE, mediated by the competition between s-o coupling and the local attracting potential for hole. This often results in a quenching of the hole orbital momentum, with the only coupling of the electron spin with the hole pseudo-spin, giving a spin 1 triplet state, the lowest in energy, and a spin 0 singlet state split by electron-hole exchange [168]. Spectroscopically, the IBEs or BE are characterized in the near IR by a sharp no-phonon line which can be observed by absorption or by PL, respectively, due to the creation or recombination of the exciton in its fundamental state. These fundamental lines can be accompanied by phonon replicas at lower or higher energies depending on both the temperature and the detection mode. At higher energies, weaker no-phonon transitions related to the fundamental line can also be observed by PL above LHeT and by PLE spectroscopy or absorption at LHeT. In PLE experiments, where photoluminescence is observed at the energy of the fundamental line as a function of the illumination with a tunable excitation source, the exciton can be created in an EM excited state of the weakly bound electron and de-excite into the ground state, where it recombines radiatively [260]; in absorption, the lines are simply due to the creation of an IBE or of a BE in an excited state (the binding energies  $E_{\text{IBE}}$  or  $E_{\text{BE}}$  of the exciton to the specific centres are the difference between  $E_{\text{g}}$  and the position of the fundamental lines). Another spectroscopic possibility consists in producing the exciton in the near IR under an appropriate illumination and in observing simultaneously the induced absorption of the shallow ID or pseudo-donor in the far IR ([18], and references therein). Near IR spectra related to IBE or BE have been observed in silicon and two examples of such centres in silicon are considered.

### 6.7.1 The “C” and “P” Centres in Silicon

In electron-irradiated CZ silicon annealed at different temperatures, two of the PL lines studied at the end of the 1960s (see [254], and references therein), the *C*- and *P*-lines, have been thoroughly investigated, in relation with the study of the (C,O) complexes and of some O-related thermal donors. The *C*-line, at 789.6 meV, also known as the 0.79 eV line, is observed in CZ silicon irradiated with electrons in the 1 – 3 MeV energy range, preferably after annealing near 200°C, while the *P*-line, at 767.2 meV (also called the 0.767 eV line) is observed in the same samples after annealing in the 300–400°C range. From IS studies, these lines have been shown to be C- and O-related [50, 147]. The absorption of the *C*-line under a uniaxial stress measured by Foy [66] was consistent with  $C_{1h}$  symmetry of the related centre. Weak lines associated with the *C*-

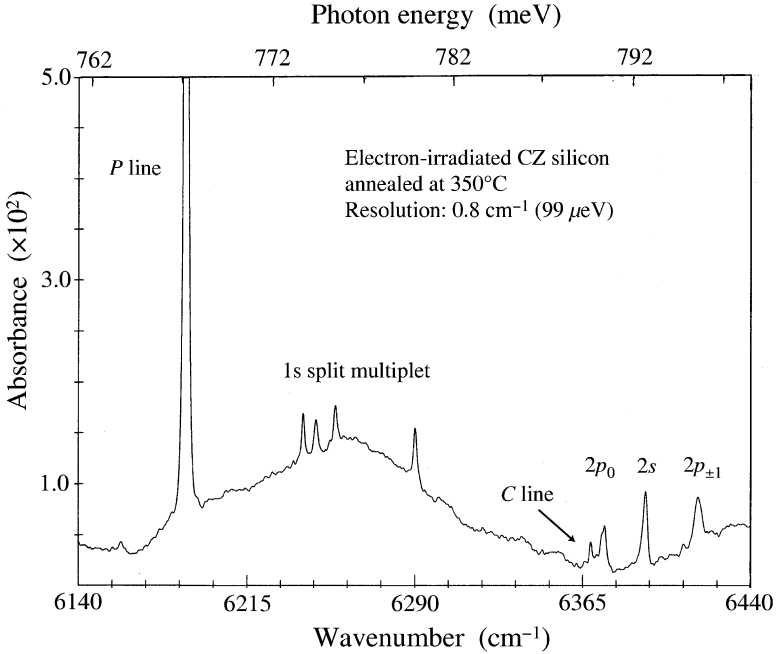


**Fig. 6.38.** Absorbance of the *P*-line (truncated) and of EM excited states of the IBE to the (C,O) complex (see text) in p-type CZ silicon under TEC at LHeT. A weak absorption due to the C-line can still be observed. The peak absorbance of the *P*-line is 0.15

and *P*-lines have been observed at higher energies in PL or PLE experiments [260] and in absorption [66, 203], and they have been found to correspond to BE transitions associated with electrons excited mostly to the even-parity EM states (a few lines corresponding to electrons excited to odd-parity states have also been observed). The spectrum in Fig. 6.38 shows the *P*-line and the weak absorptions due to the creation of the BE in EM excited states.

The positions of the pseudo-donor lines of the *C*- and *P*-line centres are given in Table 6.35. The Ag(D) lines of Table 6.34 are close to those of the “*C*” and “*P*” centres.

In absorption, a value of 0.184 meV ( $1.48 \text{ cm}^{-1}$ ) has been measured for the FWHM of the *P* line at LHeT in CZ<sup>nat</sup>Si. In <sup>30</sup>Si, the energies of the fundamental lines are found to increase by about 0.8 meV [97].

The identification of the spectra as those of pseudo-donors with a ground state corresponding to the fundamental line allows determination of the electron binding energy (the ionization energy of the ID). For the BEs associated with the “*C*” and “*P*” centres, the electron binding energies of the pseudo-donors are very similar (38.26 and 34.77 meV, respectively). The binding energies of the holes to the neutral centres are the differences between  $E_{BE}$

**Table 6.35.** Energies (meV (cm<sup>-1</sup> in parentheses)) and attributions of the lines associated with the “C” and “P” centres in <sup>nat</sup>Si, showing the importance of the even-parity transitions

|                        | “P” centre              |                     | “C” centre              |                     |
|------------------------|-------------------------|---------------------|-------------------------|---------------------|
|                        | Absorption <sup>a</sup> | PLE <sup>b</sup>    | Absorption <sup>a</sup> | PLE <sup>c</sup>    |
| Triplet ?              | 763.54 (6158.4)         |                     |                         |                     |
| Fundamental            | 767.189<br>(6187.80)    | 767.15 <sup>d</sup> | 789.607<br>(6368.61)    | 789.57 <sup>d</sup> |
|                        | <i>P</i> -line          | 767.2               | <i>C</i> -line          |                     |
| 1s multiplet           | 773.71                  | 773.7               | 794.99                  | 795.2               |
| ”                      | 774.43                  | 774.4               | 800.17                  | 800.4               |
| ”                      | 775.48                  | 775.5               | 801.34                  | 801.8               |
| ”                      | 779.89                  | 779.9               | 805.36                  | 805.6               |
| 2p <sub>0</sub>        | 790.27 (6374.0)         | 790.1               | 816.32                  | 816.8               |
| 2s multiplet           | 792.69                  | 792.5               | 818.11                  | 818.6               |
| ”                      |                         | 793.4               | 818.75                  | 819.2               |
| ”                      |                         | 794.1               |                         |                     |
| 2p <sub>±1</sub>       | 795.56                  | 795.4               | 821.47                  | 821.9               |
| 3p <sub>0</sub>        |                         | 796.3               |                         |                     |
| 3s                     |                         | 796.8               |                         |                     |
| ”                      |                         |                     |                         |                     |
| 4s                     |                         | 798.6               |                         |                     |
| <i>E</i> <sub>BE</sub> | 403 meV                 |                     | 380 meV                 |                     |

The lines labelled as fundamental correspond to the creation of a BE in its ground state. All the absorption measurements are performed at LHeT

<sup>a</sup> After [203], <sup>b</sup> [260], <sup>c</sup> After [261], <sup>d</sup> [97] PL

and the electron binding energies, and are 342 and 368 meV for the “C” and “P” centres, respectively. The hole binding energy of 342 meV of the “C” centre must be related to the donor level (a hole trap) at  $E_v + 0.38$  eV measured by DLTS [169]. The splitting under uniaxial stress of the *C*-line measured in absorption by Foy [66], and of the *P*-line measured in PL by Dörnen et al. [56] indicate the same *C*<sub>1h</sub> symmetry for the two corresponding centres. The centre giving the Si-G15 ESR spectrum, observed in electron-irradiated CZ silicon, first reported by Watkins [265], has spin  $S = 1/2$  and monoclinic I (*C*<sub>1h</sub>) symmetry, and it has been shown to be the same as the bare “C-centre” [256].

In a far-IR absorption study of the USTDs (see Table 6.31), the existence of a centre with an ionization energy of 34.82 meV (USTD11) has been reported in a C-rich CZ silicon sample by Hara [92]. This value is close to the ionization energy of the ID associated with the “P” centre (34.77 meV), containing C and O, but it is not known if the excitation conditions for the production of the far-IR ID spectrum were fulfilled in Hara’s study.

All the pseudo-donors do not have small ionization energies. In electron-irradiated n-type CZ silicon, the observation of an absorption line at 615.0 meV

( $4960\text{ cm}^{-1}$ ) at LHeT, after several hours of above-band-gap-light illumination, has been reported ([242] and references therein). Weak lines observed at energies near  $790\text{ meV}$  ( $\sim 6400\text{ cm}^{-1}$ ) have been associated with even-parity EM-like transitions related to the  $615\text{ meV}$ -line. The identification of a  $2s(E + T_2)$  transition at  $818\text{ meV}$ , assuming to simplify a  $T_d$  symmetry for the centre, allows one to estimate an ionization energy  $\sim 196\text{ meV}$  for this deep pseudo-donor, which has not yet been identified.

### 6.7.2 The (S,Cu) Centre in Silicon

In sulphur-doped silicon samples quenched from about  $1000^\circ\text{C}$  to RT, a series of PL lines, first reported by Brown and Hall [32], is observed in the  $800\text{--}980\text{ meV}$  range at low temperature. This is due to two metastable configurations, denoted  $S_A$  and  $S_B$ , of the same centre, assumed to consist of one (or more) S atom plus another impurity with nuclear spin  $I = 3/2$  (presumably Cu) [162]. For simplicity, this centre is denoted (S,Cu). In samples cooled from RT to LHeT under quasi-TEC, the  $S_A$  PL spectrum alone is first observed for low laser power illumination, but with increasing illumination times and laser power, the  $S_B$  spectrum starts appearing and its intensity increases at the expense of  $S_A$ . This indicates a transformation of the configuration of the (S,Cu) centre under illumination at LHeT [229]. Besides this metastability effect, each spectrum is characterized by two no-phonon lines separated by  $\sim 10\text{ meV}$ . The ones with the lowest energy, indexed 0, ( $S_A^0$ ,  $S_B^0$ ) are due to IBEs created in the triplet state and the others, indexed 1, ( $S_A^1$ ,  $S_B^1$ ) to IBEs created in the singlet state [229].

It appears that no absorption measurements of (S,Cu) in the near IR has been reported, but absorption measurements of the isoelectronic donor centres associated with  $S_A$  and  $S_B$  have been performed at lower energies under continuous photoexcitation with a Nd-YAG laser operated at  $1.06$  or  $1.32\mu\text{m}$  ( $1.17$  or  $0.939\text{ eV}$ ) by Beckett et al. [18]. At LHeT, the creation in the triplet state is predominant and the ground state for the EM spectra is therefore, the triplet states  $S_A^0$  and  $S_B^0$ . The photoinduced spectrum so obtained is displayed in Fig. 6.39.

The positions of the lines and the energy levels related to this (S,Cu) centre are given in Table 6.36.

The values of the hole binding energies of the (S,Cu) isoelectronic centre are  $137$  and  $292\text{ meV}$  for  $S_A$  and  $S_B$ , respectively. The ID ionization energies associated with this centre ( $65.28$  and  $66.21\text{ meV}$ ) are significantly larger than those of the pseudo-donor (C,O) complexes associated with lines  $C$  and  $P$ , and this has been attributed to the (S,Cu) centre for a central-cell potential which is also attractive for electrons, but to a lesser extent than for holes [18].

The triplet line at  $811.96\text{ meV}$  ( $6548.9\text{ cm}^{-1}$ ) of the  $S_B^0$  centre has been measured by PL at  $1.5\text{ K}$  in qmi  $^{28}\text{Si} : ^{\text{nat}}\text{S}$  and in qmi  $^{28}\text{Si} : ^{34}\text{S}$  samples [274]. As for absorption measurements in similar materials, the line becomes

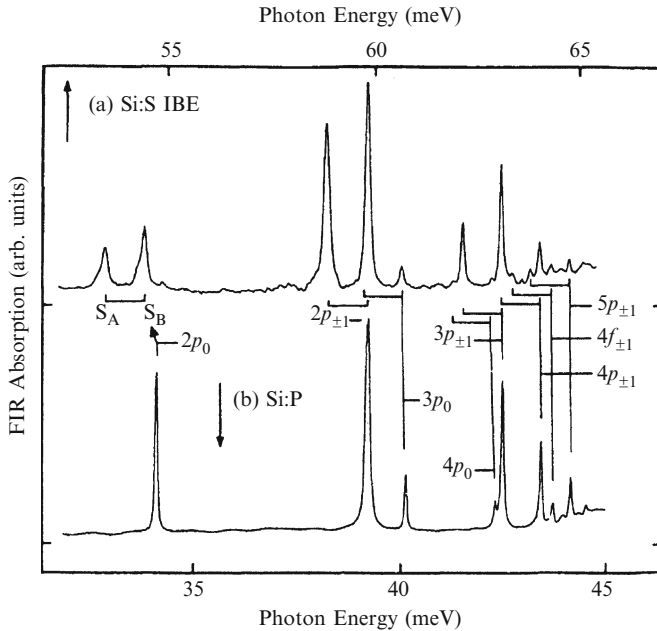


**Fig. 6.39.** (a) Absorption spectrum at LHeT between  $\sim 420$  and  $540\text{ cm}^{-1}$  of the  $S_A$  and  $S_B$  ID associated with the metastable (S,Cu) centre in silicon, obtained under near-band gap auxiliary illumination, compared to (b) the absorption of the P donor (*lower scale*). The top display consists of two spectra separated by about 1 meV, which arise from transitions from the  $S_A^0$  and  $S_B^0$  IBE ground states to EM excited state [18]. Copyright 1989 by the American Physical Society

very sharp. Besides the line shifts due to the shift of the energy gap in qmi materials, S- and Cu-related fine structures are observed showing that this centre contains at least three Cu atoms.

### 6.7.3 Pseudo-Donor BEs in Germanium

PL of excitons bound to neutral group-II acceptors in germanium has been reported by Nakata and Otsuka [179], Thewalt et al. [247], and references therein. Such excitons can be seen as positively ionized group-II acceptors ( $A^+$  ions) bound to an electron. These  $A^+$  ions, discussed in Sect. 7.5, are stable at very low temperature, and when they trap an electron, they can be considered as pseudo-donors. The far-IR absorption and magnetoabsorption at 1.6 and 4.2 K of these pseudo-donors, produced by the above-band-gap laser excitation of Be- and Zn-doped germanium samples, has for instance been reported by Natsaka and Otsuka [180], and references therein, [148], ([247], and references therein). This absorption is shown in Fig. 6.40.

**Table 6.36.** Energy levels (meV) of the  $S_A$  and  $S_B$  ID in silicon, deduced from the positions of the lines of the far IR absorption spectra and from those of the near IR PL lines (denoted \*) for the singlet and split 1s states

| Level        | $S_A$  |                    | $S_B$  |                    | EMT <sup>a</sup> |
|--------------|--------|--------------------|--------|--------------------|------------------|
|              | Energy | Position           | Energy | Position           |                  |
| Triplet      | 65.28  | 968.24*            | 66.21  | 811.96*            | 31.26            |
| Singlet      | 56.47  | 977.05*            | 56.26  | 821.91*            | "                |
| ?            | 45.52  | 988.0 ( $S_A^2$ )* | 44.37  | 833.8 ( $S_B^2$ )* | "                |
| Split 1s     | 22.8   | 1004.7*            | 29.9   | 848.3*             | "                |
| "            | 27.0   | 1006.5*            | 26.7   | 851.5*             | "                |
| $2p_0$       | 11.78  | 53.50              | 11.75  | 54.41              | 11.49            |
| $2p_{\pm 1}$ | 6.44   | 58.84              | 6.37   | 59.84              | 6.40             |
| $3p_0$       | 5.44   | 59.84              | 5.57   | 60.64              | 5.49             |
| $4p_0$       | 3.39   | 61.89              | 3.36   | 62.85              | 3.31             |
| $3p_{\pm 1}$ | 3.12   | 62.16              | 3.12   | 63.09              | 3.12             |
| $4p_{\pm 1}$ | 2.22   | 63.06              | 2.22   | 63.99              | 2.19             |
| $4f_{\pm 1}$ | 1.95   | 63.33              | 1.92   | 64.29              | 1.89             |
| $5p_{\pm 1}$ | 1.50   | 63.78              | 1.50   | 64.71              | 1.45             |
| $E_{IBE}$    | 202    |                    | 358    |                    |                  |

The energy levels are obtained for a  $3p_{\pm 1}$  binding energy of 3.12 meV. The uncertainty on the levels deduced from the absorption lines is  $\pm 0.17$  meV. The last row gives the IBE binding energy. All the values are in meV (after [18]), <sup>a</sup> [118])

The spectra show odd-parity transitions of EM donor spectra, but because of the splitting of the BE ground state, and also of the  $Be^0$  ground state (see Sect. 7.3.1.1), they include thermalized components. Taking 744.8 meV for  $E_g$  and estimated values of 734.8 and 737.2 meV (after [247]) for the ground state energies of  $Be^0X$  and  $Zn^0X$ , respectively, where X denotes an exciton, the dissociation energies of  $Be^0X$  and  $Zn^0X$  into an acceptor, an electron and a hole are found to be 9.9 and 7.5 meV respectively. A comparison with the binding energies of the extra hole to  $Be^0$  and  $Zn^0$  given in Sect. 7.5 (4.7 and 1.9 meV, respectively), yields ionization energies of 5.2 and 5.6 meV, respectively, for the pseudo-donor. The energies of the  $2P_{\pm}$  ( $2p_{\pm 1}$ ) transitions from the ground states of the  $Be^0X$  and  $Zn^0X$  pseudo-donors are 3.45 and 3.75 meV, respectively [247]. The binding energies of the  $2p_{\pm 1}$  states of these pseudo-donors are thus deduced to be 1.75 and 1.85 meV for Be and Zn, respectively. These values compare with the EM energy of 1.73 meV for the  $2p_{\pm 1}$  donor level in germanium, and they confirm the pseudo-donor behaviour of these centres.

## 6.8 Donors in III-V and II-VI Compounds

With the exception of GaAs, GaP, InP and InSb, the absorption studies on donors in compound semiconductors are much less documented than those in group-IV materials. This does not reflect a lack of interest for these materials, as they have been the subjects of many PL experiments, but rather

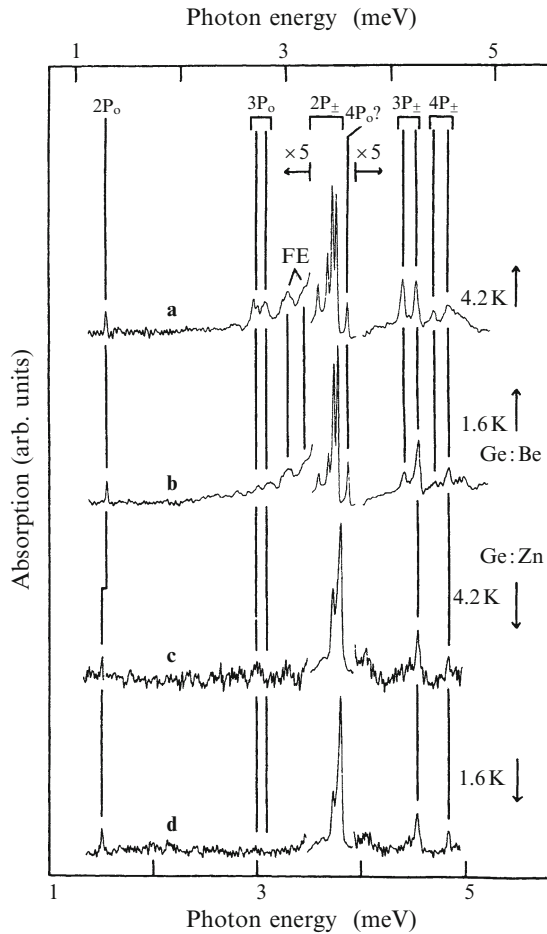


**Fig. 6.40.** Pseudo-donor absorption spectrum in the far IR of excitons bound to  $\text{Be}^0$  and  $\text{Zn}^0$  in germanium. The transition labels, at the top, are those of the shallow donor states associated with the excited states of the pseudo-donors. The components of the  $2P_{\pm}$  line in Ge:Be and Ge:Zn show thermalization between 1.6 and 4.2 K, indicating splitting of the BE ground states. The energy scales have been shifted so as to align the  $3P_{\pm}$  transitions of the Ge :  $\text{Be}^0$  and Ge :  $\text{Zn}^0$  spectra. The FE feature in (a) and (b) is due to the FE absorption. Reproduced from [247]. Copyright 1987, with permission from Elsevier

the difficulty to obtain good electronic absorption spectra in the vicinity of phonon absorption bands and also problems related to impurity complexing and interaction with native defects. Technologically, the study of the direct-band-gap compounds requires high-purity samples and besides GaAs and InP, they are hard to find in other semiconductors. Unless otherwise



specified, the compound semiconductors considered in this section have the sphalerite structure. From their spectroscopic behaviour, a distinction is made between the direct-band-gap and indirect-band-gap materials. Donor absorption and magnetoabsorption in a few direct-band-gap materials with small effective masses (GaAs, InP, InSb and CdTe) have been studied because of the high electron mobility or electro-optical interest of these materials. The donors in these semiconductors are nearly pure hydrogenic ones and their spectroscopy is presented in the following sub-section while the spectroscopy of shallow donors in indirect-band-gap materials, which is more intricate, is presented later.

### 6.8.1 Quasi-Hydrogenic Effective-Mass Donors

#### 6.8.1.1 Cubic Semiconductors

As mentioned above, the donor centres in the direct-gap cubic semiconductors with isotropic electron effective masses display a quasi-hydrogenic behaviour and are called quasi-hydrogenic donors (QHDs). To zeroth order, their ionization energies are given by the effective Rydberg  $R_{\infty}^* = R_{\infty} m_n / \epsilon_s^2$  and the theoretical donor spectrum by lines with energies  $E_n^*$  of a Lyman series equal to  $R_{\infty}^* (1 - 1/n^2)$ . The calculated energies of the first donor lines in InSb, GaAs, InP, ZnSe and CdTe are given in Table 5.10. Calculations taking into account wave-vector dependent dielectric functions and polaron effects have also been performed by Grinberg et al. [85] and for CdTe, the energy of the  $1s \rightarrow 2p$  transition obtained is larger than the experimental one.

High-resolution measurements of the discrete spectrum of donors in high-purity GaAs and InP have been performed by PTIS and in most cases, the spectra have been obtained under a magnetic field to reduce the spatial amplitude of the wave function, in order to limit the interaction between the electrons bound to neighbouring donors. With the application of a magnetic field, the FWHMs of the individual lines are drastically reduced and a comparison with the zero-field spectrum can be made in Fig. 6.41a, b.

The presence of several lines associated with the same Zeeman component indicates the presence in the sample of several QHDs with different central-cell corrections. Figure 6.42 shows a spectrum of a high-purity GaAs sample at a lower resolution, but in a broader spectral domain, where more components are observed.

These magneto-optical experiments, often performed with magnetic fields in the 5–20 T range, have been used to determine the effective masses and dielectric constants of the material, and a small dispersion of these values is observed. Table 6.37 gives the experimental energy positions of the  $2p$  lines for different QHDs in GaAs, InP and CdTe (PTIS measurements) and ZnSe (absorption measurements and two-electron PL) and the corresponding ionization energy. For GaAs, the comparison between the positions at zero magnetic

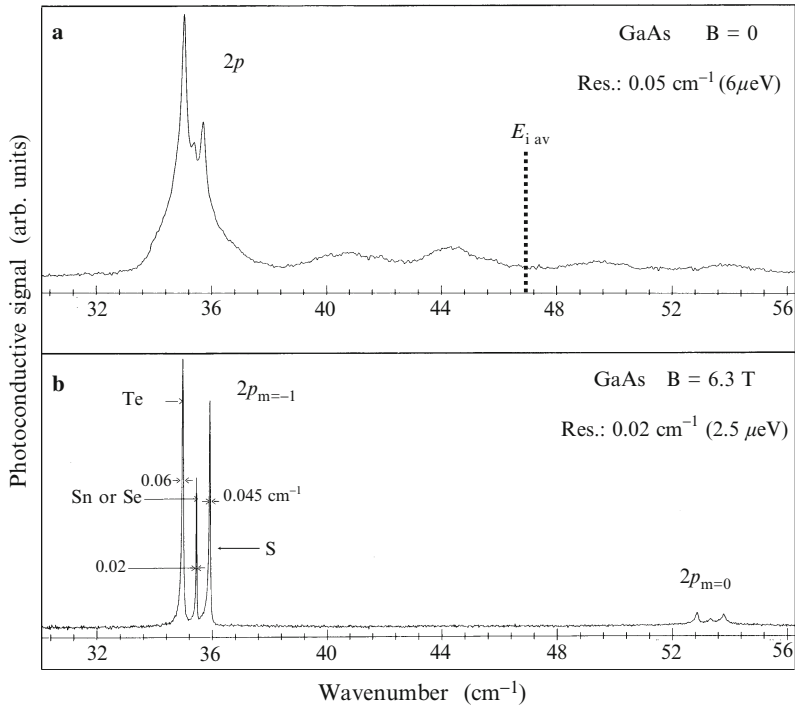


**Fig. 6.41.** (a) PTI spectrum at LHeT of a GaAs sample with  $N_D - N_A = 2 \times 10^{13}$  at cm⁻³ showing the  $1s \rightarrow 2p$  transition for three different impurities. The dotted bar indicates the average photoionization threshold at zero field. (b) PTI spectrum of the same sample under a magnetic field of 6.3 T showing the dominant  $1s \rightarrow 2p_{m=-1}$  component and the weak  $1s \rightarrow 2p_{m=0}$  component. The attributions to specific impurities and the FWHMs (cm⁻¹) are indicated (after [33])

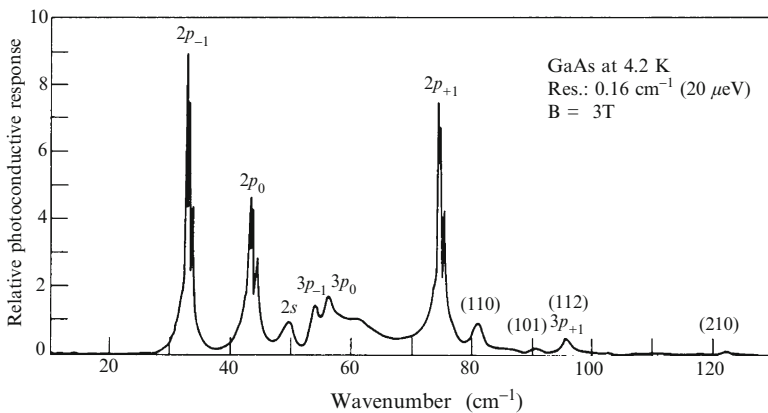


**Fig. 6.42.** PTI spectrum of a high-purity GaAs sample showing the full Zeeman splitting of the  $2p$  and  $3p$  lines and other transitions including a forbidden one ( $2s$ ). Some of the transitions are labelled along the high-field limit (after [236]). Copyright 1977, with permission from Elsevier)

**Table 6.37.** Peak positions (meV ( $\text{cm}^{-1}$  are given in parentheses)) of the  $2p$  line at LHeT for different chemical or unidentified QHDs in GaAs, InP, CdTe, and ZnSe. The experimental ionization energies of the last column are obtained by adding to the  $2p$  line positions the values of  $E_{2p}$  of Table 5.10

|                   |                     | B = 0<br>$2p$ line         | B = 6.32 T<br>$2p_{m=-1}$ line | $E_i$              |
|-------------------|---------------------|----------------------------|--------------------------------|--------------------|
| GaAs <sup>a</sup> | Te                  | 4.3458 (35.051)            | 4.3371 (34.981)                | 5.81               |
|                   | Si                  | 4.3728 (35.269)            | 4.3873 (35.386)                | 5.83               |
|                   | Sn or Se            | 4.3858 (35.374)            | 4.3986 (35.477)                | 5.85               |
|                   | S                   | 4.4269 (35.705)            | 4.4505 (35.896)                | 5.89               |
|                   | Ge                  | 4.5113 (36.386)            | 4.5688 (36.850)                | 5.97               |
| InP <sup>a</sup>  | P <sub>1</sub>      | 5.5630 (44.869)            | 5.1467 (41.511)                | 7.37               |
|                   | P <sub>2</sub> (Si) | 5.5847 (45.044)            | 5.2934 (42.694)                | 7.39               |
|                   | P <sub>3</sub>      | 5.6136 (45.277)            | 5.3235 (42.937)                | 7.42               |
|                   | P <sub>4</sub> (S)  | 5.6501 (45.571)            | 5.2375 (42.243)                | 7.46               |
|                   | P <sub>5</sub> (Ge) | 5.6978 (45.956)            | 5.3024 (42.767)                | 7.51               |
| CdTe <sup>b</sup> | A                   | 10.008 (80.72)             |                                | 13.28              |
|                   | C                   | 10.276 (82.88)             |                                | 13.56              |
|                   | D                   | ~10.35 (~83.5)             |                                | ~13.6              |
|                   | E                   | 10.834 (87.38)             |                                | 14.11              |
| ZnSe              | Al                  | 18.96 <sup>c</sup> (152.9) |                                | 25.39 <sup>c</sup> |
|                   |                     | 19.14 <sup>e</sup>         |                                |                    |
|                   | Cl                  | 19.64 <sup>c</sup> (158.4) |                                | 26.07 <sup>c</sup> |
|                   |                     | 19.66 <sup>e</sup>         |                                |                    |
|                   | Ga                  | 20.72 <sup>e</sup> (167.1) |                                | 27.15              |
|                   | In                  | 21.67 (174.8) <sup>c</sup> |                                | 28.10 <sup>c</sup> |
|                   |                     | 21.69 <sup>e</sup>         |                                |                    |
|                   | F                   | 22.14 <sup>d</sup> (178.6) |                                | 28.57 <sup>d</sup> |

<sup>a</sup> [235], <sup>b</sup> [228], <sup>c</sup> [181], <sup>d</sup> [25], <sup>e</sup> [164], two-electron PL

field and at 6.32 T for the  $2p_{m=-1}$  line shows a relatively small magnetic-field dependence of this component. For InP, the energies of the  $2p_{m=-1}$  components start decreasing with increasing values of  $\mathbf{B}$  down to a minimum at 2.5 T and then increase monotonously, the zero field values being reached for  $B \sim 10$  T [227]. This is in qualitative agreement with the calculations of [149]. For ZnSe, the differences between the values of  $E_i$  and those quoted by Merz et al. [164] come only from the value of  $E_{2p}$  taken in this reference as the values of the energy of the  $2p$  line obtained by absorption and by two-electron PL for different donors agree closely.

The possibility of two-photon absorption (TPA) due to non-linear effects has been mentioned in Sect. 4.1. The magnetic-field-tuned LHeT absorption by n-type GaAs of a laser line at  $20.2 \text{ cm}^{-1}$  (2.50 meV) has been reported by [28] for  $B = 1.15$  T and attributed to a two-photon  $1s \rightarrow 2s$  transition at  $40.4 \text{ cm}^{-1}$  (5.00 meV). The fact that the initial and final states of this transition have the same parity can be explained by assuming an odd-parity



produces a transition from a conducting to an insulating state due to the field-induced reduction of the spatial amplitude of the QHD wave functions. For InSb, the parameter  $\gamma_B = \hbar\omega_c/2R_{\infty d}^*$  is unity for  $B \sim 0.16$  T, and as the best magnetospectroscopic results for donors have been obtained for magnetic fields of the order of several T, the modelling of the interaction of the QHDs in InSb with a magnetic field, must be treated in the high-field limit (see Sect. 5.2.3). The  $(000) \rightarrow (0\bar{1}0)$  transitions of four residual QHDs, denoted A, B, C and D observed in high-purity InSb samples are shown in Fig. 4.10a, b. At magnetic fields in the 10 T range, the line positions depend on the chemical nature of the donor and the separation between the A and D components is  $\sim 1.8 \text{ cm}^{-1}$  or  $0.22 \text{ meV}$  at 13 T, but it decreases with the magnetic field. The average energy of the transition also decreases with the magnetic field and it is about  $0.6 \text{ meV}$  at 1 T; value extrapolated at zero magnetic field after the data of [125] is  $\sim 0.5 \text{ meV}$  ( $4 \text{ cm}^{-1}$  or  $120 \text{ GHz}$ ), close to the calculated value of Table 6.36 for the  $1s \rightarrow 2p$  transition. The attributions of A, B, C, and D to specific donor impurities is not yet solved: doping InSb with Sn produces a new line with an energy between those of B and C while Se and Te dopings produce lines at the position of B and C, respectively, and also new lines at energies below that of D. This and other tentative attributions are discussed in the paper by Kuchar et al. [146].

### 6.8.1.2 Non-Cubic Semiconductors

The LHeT absorption spectrum of QHDs in *w*-GaN samples shows for each donor a single line ascribed to  $1s \rightarrow 2p$  transitions. Such a line is shown at  $215 \text{ cm}^{-1}$  ( $26.7 \text{ meV}$ ) in Fig. 6.44. Similar lines have been reported at 23.30 and 25.95 meV [171]. The observation of a single transition implies that the anisotropy of the electron effective mass of *w*-GaN is small, and this assumption is validated by the results of [38]. A value of  $0.22m_e$  for  $m_{n\perp}$  has been derived from the Zeeman splitting measurements of [171], in excellent agreement with the CR value [5]. By taking a low-temperature isotropic dielectric constant  $\epsilon_s \sim 10$ , the above value of the electron effective mass yields a donor effective Rydberg value  $R_{\infty d}^*(w\text{-GaN}) \sim 29.9 \text{ meV}$ . The binding energy of a  $2p$  state in the quasi-hydrogenic approximation is  $0.25R_{\infty d}^*$ . By adding this energy ( $7.5 \text{ meV}$ ) to the positions of the  $2p$  lines at 23.3, 26.0, and  $26.7 \text{ meV}$ , one obtains the values of 30.8, 33.5, and  $34.2 \text{ meV}$ , respectively for  $E_{\text{io}}$ . These values are not too different from those obtained self-consistently (31.1, 33.8, and  $34.5 \text{ meV}$ ) by Moore et al. [171] by deriving first a value  $\epsilon_s = 9.8$  from the QHD with the  $2p$  line at  $23.30 \text{ meV}$ , assumed to yield an effective Rydberg value of  $31.07 \text{ meV}$ . If the dielectric constant  $\epsilon_s$  is taken as 9.5, the value of  $\epsilon_{s\perp}$  measured by Barker and Ilegems [17], the effective Rydberg for the  $\mathbf{E} \perp c$  experimental configuration is  $33.17 \text{ meV}$ .

HVPE GaN films are known from SIMS measurements to contain Si and O as dominant impurities, and a comparison with results obtained on Si-doped GaN [264] has led Moore et al. [171] to identify tentatively the  $31.1 \text{ meV}$  donor

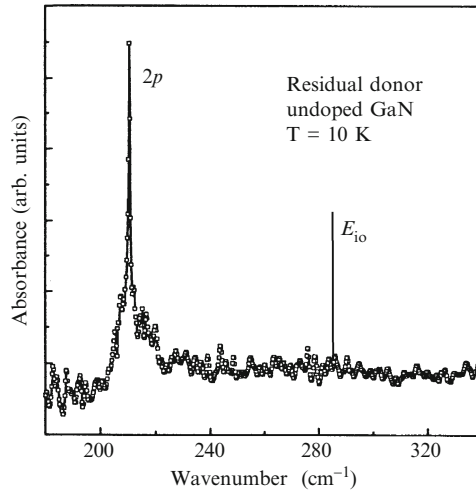


**Fig. 6.44.** Absorbance of an undoped GaN sample grown by hydride vapour phase epitaxy (HVPE) on a sapphire substrate between 22.3 and 42.2 meV. The FWHM of the  $2p$  line is  $2\text{ cm}^{-1}$  ( $\sim 0.25\text{ meV}$ ). The vertical bar indicates the ionization energy of 35.5 meV (after [165]). Copyright 1995, with permission from Elsevier

with Si. Calculation of the ionization energies of QHDs in  $c$ - and  $w$ -GaN including central-cell correction (see Table 5.11) predict that the shallowest donor is Si, followed with increasing energy by O and C. Considering their calculated ionization energies as quantitatively exact, Mireles and Uloa [167] have argued that the 31.1 meV donor should be O rather than Si and that the 34.6 meV donor could be C. However, from the previous comparisons for shallow donors in silicon and germanium we have learned that even when knowing the experimental ionization energy of a chemical donor, the agreement with the calculated ionization energy was largely qualitative. Thus, the Si attribution for the 31.1 meV donor remains plausible.

The choice of the values of  $m_{n//}$  and  $m_{n\perp}$  made by Mireles and Ulloa results in an energy position of the  $2p_0$  line slightly higher than that of the  $2p_{\pm 1}$  line. In the absence of Zeeman splitting, a line observed at 16.96 meV by Moore et al. [171] was tentatively attributed to a  $2p_0$  line associated with the line at 23.30 meV, the strongest of the whole spectrum, ascribed to the  $2p_{\pm 1}$  line of the 31.1 meV donor. With this attribution, the rather large positive  $2p_{\pm 1} - 2p_0$  difference between the energies of the two lines implies a value of  $\gamma < 1$ . The consequence of the non-parabolicity of the  $CB$  of  $w$ -GaN on the values of  $m_{n//}$  and  $m_{n\perp}$  has not been accurately evaluated, but the above attribution would require a value of  $m_{n\perp}$  significantly lower than that of  $m_{n//}$  and this seems unlikely, hence the attribution of the 16.96 meV line remains open.

An ionization energy of 19.5 meV for an unknown donor in CdSe has been determined from two-electron PL transitions [100]. As donors should

be considered as QHD in this material, this value should be representative of the donor ionization energies in *w*CdSe.

### 6.8.2 Semiconductors with CB Degeneracy

GaP is an indirect-band-gap cubic semiconductor with a *CB* minimum very close to the X point, resulting in a threefold degeneracy of the donor electron in *k*-space. As a consequence of the positive value of the antisymmetric part of the pseudo-potential, the apparent symmetry of the lowest *CB* depends on the donor site [172]. For O, S, Se, and Te donors on a P site, the lowest *CB* has  $X_1$  symmetry, and for Si, Ge, and Sn donors on a Ga site (in GaP, C is an acceptor on a P site), it has  $X_3$  symmetry (see Sect. 3.3.1). Consequently, the above threefold degeneracy of the ground-state electron corresponds to  $A_1 + E(\Gamma_1 + \Gamma_3)$  IRs of  $T_d$  for the P-site donors and to  $T_2(\Gamma_5)$  IR for the Ga-site donors. By analogy with the donors in silicon and germanium, one can expect a valley-orbit splitting of the  $A_1 + E$  degeneracy of the  $1s$  ground state of the group-VI donors, the  $1s(A_1)$  being the deeper. One outcome of this situation is that because of the different values of the electron effective masses at the  $X_1$  minimum with camel's back structure and the  $X_3$  minimum with ellipsoidal structure, the line spacings in the spectra for the donors on Ga sites is expected to be different from those in the spectra for the donors on P sites.

After several reports between 1965 and 1980, no new information has been published on the spectroscopy of donors in GaP. Odd-parity transitions from the ground to excited states associated with the lowest X band for the Si, S and Te donors have been reported in the 55–100 meV ( $\sim 440$ – $810\text{ cm}^{-1}$ ) spectral domain [10, 39, 196, 223]. The spectra are superimposed on the two-phonon spectrum of GaP and the FWHMs of the absorption lines at LHeT are  $\sim 0.6$  meV. LHeT photoconductivity measurements in the photoionization region of shallow impurities in GaP revealed dips due to electronic transitions accompanied by the emission of LA(X) and LO( $\Gamma$ ) phonons with energies of 404 and  $254\text{ cm}^{-1}$ , respectively, and they have contributed to the understanding of the donor spectra [222]. LHeT transmission spectra of GaP:Si samples at LHeT showing Si donor transitions are displayed in Fig. 6.45.

DAP spectra of GaP samples doped with Si from  $^{30}\text{Si}$ -enriched silica powder have produced evidence of a very small IS ( $-0.05$  meV or  $0.4\text{ cm}^{-1}$ ) of the ionization energy of  $\text{Si}_{\text{Ga}}$  when  $^{28}\text{Si}$  was replaced by  $^{30}\text{Si}$  [54]. Many fundamental results on the donor excited states in GaP have also been obtained through PL and excitation measurements, and they are also discussed here. Spectra of the O donor have been obtained in the 840–1,020 meV range ( $\sim 6670$ – $8225\text{ cm}^{-1}$ ) by PLE spectroscopy, measuring the intensity variation of the ZPL  $O^0$  line at 841 meV as a function of the energy of the photons producing PL [53]. This line is due to the radiative transition of an electron trapped in a shallow EM state, assumed to be  $1s(E)$  to the deep  $1s(A_1)$

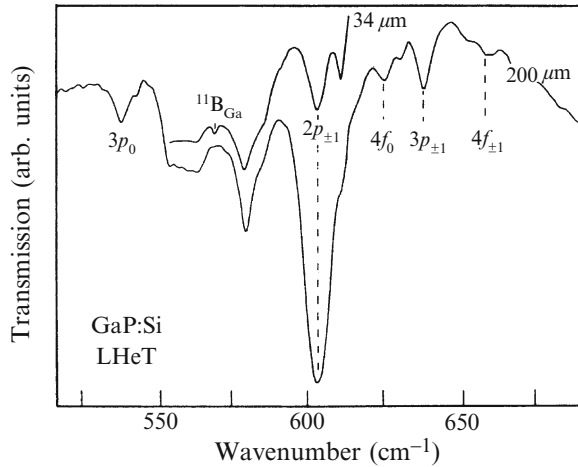


**Fig. 6.45.** Transmission spectra of two epitaxied GaP samples in the spectral range 64.7–85.3 meV (the thickness is indicated) superimposed on the two-phonon spectrum. Apart from the weak line between lines  $4f_0$  and  $3p_{\pm 1}$ , due to the mylar beam splitter of the FTS, a weak local vibrational mode of  $^{11}\text{B}_{\text{Ga}}$  is also observed (after [39]). Reproduced with permission from the Institute of Physics

ground state. This transition has the particularity to show an electronic O isotope effect of  $-0.67 \text{ meV}$  ( $-5.4 \text{ cm}^{-1}$ ) when  $^{16}\text{O}$  is replaced by  $^{18}\text{O}$ . The ionization energy of the deep  $\text{O}_{\text{P}}$  donor has been obtained experimentally from DAP spectra by Dean [51], Vink et al. [259] and it is 898.7 meV. The only transition observed by Raman scattering is the one between the  $1s(\text{A}_1)$  and  $1s(\text{E})$  states for S, Se and Te donors [160].

Internal donor absorption has also been observed in the 300–600 meV ( $2400\text{--}4800 \text{ cm}^{-1}$ ) spectral region ([195], and references therein). It is due to a transition from the ground state associated with the lowest energy X band to the  $2p_{\pm 1}$  excited state associated with the next X band at higher energy. Only one such transition has been observed for each of the Si, S and Te donors. For Si, the ground state is  $1s(\text{X}_3)$  and the final state  $2p_{\pm 1}(\text{X}_1)$  and the X bands are inverted for S and Te. These lines, denoted here  $2p'_{\pm 1}$ , have FWHMs  $\sim 20 \text{ meV}$  ( $\sim 160 \text{ cm}^{-1}$ ), mainly due to the decay of the excited electron into electron states of the lowest X band, and their positions are given in Table 6.38. The energy difference between the  $2p'_{\pm 1}$  line and the  $2p_{\pm 1}$  line associated with the lowest CB gives an estimation of the separation  $\Delta$  between the  $\text{X}_1$  and  $\text{X}_3$  CBs.

The number of donor transitions observed in GaP is limited and some attributions can differ, but line  $2p_{\pm 1}$  is observed for all the donors and its position is taken as a reference. The energies of these transitions are given in Table 6.38.



**Table 6.38.** LHeT positions (meV) of donor transitions observed in GaP samples, labelled by the final state of the transition

| Line                          | $1s(E)^f$          | $2s(A_1)$                  | $2s(E)$                    | $2p_0$                     | $3p_0$                     | $4p_0$                     | $2p_{\pm 1}$               | $4f_0$                     | $3p_{\pm 1}$     | $4p_{\pm 1}$     | $2p'_{\pm 1}^g$ |
|-------------------------------|--------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|------------------|------------------|-----------------|
| Si <sub>Ga</sub> <sup>a</sup> |                    |                            |                            | -                          | 66.86<br>(539.3)           |                            | 74.80<br>(603.3)           | 77.56<br>(625.6)           | 79.26<br>(639.3) | 81.74<br>(659.3) | 432             |
| SP <sup>b</sup>               | 53.4               |                            |                            | 71.5                       | 84.9                       | 89.4                       | 96.8                       |                            |                  |                  | 457             |
|                               |                    | 83.2 <sup>c</sup><br>(671) | 90.6 <sup>c</sup><br>(731) | 71.4 <sup>c</sup><br>(576) |                            | 89.4 <sup>c</sup><br>(721) | 96.7 <sup>c</sup><br>(780) |                            |                  |                  |                 |
| Se <sub>P</sub>               | 54.0               | 81.8 <sup>c</sup><br>(660) | 89.4 <sup>c</sup><br>(721) | 70.2 <sup>c</sup><br>(566) |                            | 87.5 <sup>c</sup><br>(706) | 95.0 <sup>c</sup><br>(766) |                            |                  |                  |                 |
| Te <sub>P</sub>               | 40.5               | 67.8 <sup>c</sup><br>(547) |                            | 56.3 <sup>d</sup><br>(449) | 55.7 <sup>c</sup><br>(449) | 71.5 <sup>c</sup><br>(578) | 73.9 <sup>c</sup><br>(597) | 82.6 <sup>d</sup><br>(666) |                  |                  | 441             |
| OP <sup>e</sup>               | 842.1 <sup>e</sup> |                            |                            | 864.8                      | 878.7                      | 884.4                      | 888.2                      |                            | 891.7            |                  |                 |

Some allowed and forbidden transitions are observed together with phonon emission (see text). For Si<sub>Ga</sub>, the ground state is  $1s(T_2)$ . For the other donors, it is  $1s(A_1)$ . When available, the values in  $\text{cm}^{-1}$  are indicated in parentheses

<sup>a</sup> [39], <sup>b</sup> [223], <sup>c</sup> [222], <sup>d</sup> [139] at 20 K, <sup>e</sup> [53], <sup>f</sup> [160] Raman scattering at 20 K, <sup>g</sup> [195]

**Table 6.39.** Comparison of the experimental spacings (meV) between line  $2p_{\pm 1}$  and other donor lines in GaP taken from Table 6.38

| Spacing                 | Si   | S    | Se   | Te   | O    |
|-------------------------|------|------|------|------|------|
| $2p_{\pm 1}-2p_0$       |      | 25.3 | 24.8 | 26.4 | 23.6 |
| $2p_{\pm 1}-3p_0$       | 7.94 | 11.9 |      | 11.1 | 9.5  |
| $2p_{\pm 1}-4p_0$       |      | 7.4  | 7.5  | 8.7  | 3.8  |
| $4f_0-2p_{\pm 1}$       | 2.76 |      |      |      |      |
| $3p_{\pm 1}-2p_{\pm 1}$ | 4.46 |      |      |      | 3.5  |
| $4p_{\pm 1}-2p_{\pm 1}$ | 6.94 |      |      |      |      |

In this table,  $2p_0(\text{Si})$  is missing as this line is expected at about 50 meV ( $400 \text{ cm}^{-1}$ ), a zone of strong lattice absorption.  $3s(E)(\text{S})$  is observed at  $772 \text{ cm}^{-1}$  (95.7 meV). Assuming that the identification is correct, a comparison of the spacings between the corresponding lines for different donors is given in Table 6.39.

The critical  $3p_{\pm 1}-2p_{\pm 1}$  spacing is expected to be independent of the nature of the chemical donor, but it differs significantly between Si<sub>Ga</sub> and OP. This reflects the fact that the  $CB$  minimum for the donors on P site is associated with the  $X_1$  camel's back structure. Variational calculations based on k.p perturbation theory have been performed for P-site donor and compared self-consistently with spectroscopic data [40]. The calculations are performed as a function of the ratio of a non-parabolicity parameter<sup>9</sup>  $Q$  to the separation  $\Delta$  between  $CB$ s  $X_1$  and  $X_3$ . The authors use an anisotropy parameter  $\mu$  equal

<sup>9</sup>  $Q$  is the same parameter as  $\Delta_0$  in expression (3.29).

to the inverse of the ratio  $\gamma$  of the transverse and longitudinal effective masses, but in order to obtain results that can be compared with the experimental data, they have to add a variational parameter  $\lambda$  describing the eccentricity of the wave functions, introduced in the coordinate vector  $\mathbf{r}$  defined as  $(x', y', z') = (x, y, \lambda^{1/2} z)$ . The energy level calculations have been performed with  $\mu = 4$  and the eigenvalues minimized independently as a function of parameter  $\lambda$ . The best agreement is obtained for *CB* minima at  $\pm 0.83 \mathbf{k}(\text{X})$  with a value of 3.2 meV of the camel's back energy  $\Delta E$ , close to the values reported in relation with Fig. 3.6. The binding energy of the  $2p_{\pm 1}$  level determined from this calculation using an effective Rydberg value of 28.5 meV is 10.54 meV. By adding this value to the positions of the  $2p_{\pm 1}$  lines of Table 6.38, the  $E_{\text{io}}$  values for the S, Se, Te, and O donors are determined to be 107.3,  $\sim 106$ , 103.1, and 898.7 meV, respectively, and for the O donor, this value is the same as the one obtained directly from the DAP spectra. The first energy levels calculated in this reference are given in Table 6.40.

Some two-electron PL lines have been observed at 1.6 K in GaP:S and GaP:Se samples, where the donor electron is left in an excited (usually even-parity) state [52]. Absorption dips due to transitions to even-parity states with phonon emission have also been reported for the S, Se, and Te donors by Scott [222] and they are included in Table 6.38. The experimental values of the energy levels of the corresponding states, not given in the original reference are for the S donor, 26.0, 17.1, 12.4 and 9.7 meV for  $2s(A_1)$ ,  $3s(A_1)$ ,  $3d_0(A_1)$ , and  $4s(A_1)$ , respectively [41].

The EM levels of the  $\text{Si}_{\text{Ga}}$  donor are associated with the  $\text{X}_3$  *CB* and there is no direct information on the electron effective masses of this band. To compare with their experimental results, the energy levels of the  $\text{Si}_{\text{Ga}}$  donor have been calculated by Carter et al. [39] using the numerical results of Faulkner [61] by assuming that the bound electron of this donor can be described by Hamiltonian (5.5) with a prolate effective mass. The idea is to find by interpolation the  $\gamma^{1/3}$  value for which the calculated ratio  $(2p_{\pm 1} - 3p_0) / (3p_{\pm 1} - 2p_{\pm 1})$  of the energy levels is the same as the experimental ratio for the energies of the corresponding lines. This allows an *a priori* determination of the effective Rydberg  $R_{\infty d}^*$ , and subsequently, the values of the energies. Combining this value of  $R_{\infty d}^*$  with the low-temperature value of the dielectric constant of

**Table 6.40.** Calculated energy levels (meV) for donors in GaP. The first row is for the donor on P site (S, Se, Te) associated with the *CB* with the camel's back structure

| Level                                | 1s    | 2s    | $2p_0$ | $3p_0$  | $4p_0$ | $4f_0$ | $2p_{\pm 1}$ | $3p_{\pm 1}$ | $4p_{\pm 1}$ | $4f_{\pm 1}$ |
|--------------------------------------|-------|-------|--------|---------|--------|--------|--------------|--------------|--------------|--------------|
| P-site <sup>a</sup>                  | 61.95 | 24.37 | 35.64  | 18.93   | 12.37  | 7.78   | [10.54]      | 7.39         | 5.01         | 3.41         |
| $\text{Si}_{\text{Ga}}$ <sup>b</sup> |       |       | 35.65  | [19.87] | 13.09  | 9.11   | [11.93]      | [7.47]       | 5.44         |              |
| $\text{Si}_{\text{Ga}}$ <sup>c</sup> | 69.92 | 27.13 | 35.67  | [19.89] | 13.30  | 9.70   | [11.95]      | [7.49]       | 5.52         | 4.48         |

<sup>a</sup> [40], <sup>b</sup> [39] with Faulkner's values ( $R_{\infty d}^* = 31.6$  meV), <sup>c</sup> Same as Carter et al. calculations with values of Table 5.2 ( $R_{\infty d}^* = 31.97$  meV)

GaP ( $\varepsilon_s = 11.02$ ) determined by Vink et al. [259] allows one to also obtain an estimation of the transverse effective mass  $m_t$ . The more recent data of [30] given in Table 5.2 have also been used for the calculation of the energy levels of  $\text{Si}_{\text{Ga}}$  and the results obtained are close to those of [39]. The calculated energy levels are given in Table 6.40, where they are compared with the results of [40], valid for the P-site donors. The optical ionization energy  $E_{\text{io}}$  ( $\text{Si}_{\text{Ga}}$ ) derived from these calculations and from the absorption data is 86.73 meV and it compares with the value of 85 meV given by Kopylov and Pikhtin [140].

With Faulkner's values (Table 5.1),  $m_t = 0.275m_e$  and  $\gamma^{1/3} = 0.325$  ( $\gamma = 0.0345$ ). With the values of Broeckx et al. (Table 5.2),  $m_t = 0.285m_e$  and the fit of the value (1.78) of the experimental ratio  $(2p_{\pm 1} - 3p_0) / (3p_{\pm 1} - 2p_{\pm 1})$  depends critically on the value of  $\gamma^{1/3}$ . This fit is obtained for  $\gamma^{1/3}$  between 0.3433 and 0.3434 ( $\gamma = 0.0405$ ).

Information on the Sn donor in GaP have been obtained from PL spectroscopy measurements of DAPs [55, 259]. The  $1s(\text{T}_2)$  ground state of Sn is split by spin-orbit interaction into  $1s(\text{T}_2, \Gamma_8)$  and  $1s(\text{T}_2, \Gamma_7)$  sublevels, in the same way as the  $1s(\text{T}_2)$  level of the Bi and Sb donors in silicon (see Table 6.5), but compared to Sb in silicon where it is 0.3 meV, this splitting amounts to 2.1 meV for Sn in GaP [55]. An ionization energy of 65.5 meV is given for  $\text{Sn}_{\text{Ga}}$  [55]. A value of 72 meV has also been quoted for this donor, but its origin is not clear. Spin-orbit splitting of the  $1s(\text{T}_2)$  ground state has also been detected and evaluated to be 0.5 meV ( $4 \text{ cm}^{-1}$ ) for the Si donor. This can be a supplementary cause of broadening of the Si absorption spectrum.

The absorption of Te and Se donors in AlSb has been measured by Ahlburn and Ramdas [4]. The Te spectrum is located in the 38–70 meV ( $306\text{--}565 \text{ cm}^{-1}$ ) spectral region, a very uncomfortable domain for the observation of an impurity spectrum as the strong absorption of the AlSb TO-phonon mode near  $320 \text{ cm}^{-1}$  is followed at higher energies by a relatively intense two-phonon spectrum. The Se spectrum is observed between 110 and 160 meV ( $\sim 890$  and  $1290 \text{ cm}^{-1}$ ). Recent studies of the shifts of the AlSb donor lines with hydrostatic pressure have been performed on the same samples [108]. As for GaP, the interpretation of the donor spectra in terms of EMT is far from obvious because of the camel's back structure of absolute CB minimum of AlSb. The lines of the two donors, whose positions are given in Table 6.41, were at first simply labelled by integers increasing with photon energy. Some of the initial attributions of Ahlburn and Ramdas for the donor lines have been modified in the light of calculations taking into account the camel's back structure of the CB minimum at  $\text{X}_1$  point.

On the basis of the scaling of the calculated values obtained for donors in GaP, the EM positions of the  $1s$ ,  $2p_0$  and  $2p_{\pm 1}$  donor levels in AlSb have been calculated to be 48.4, 22.2 and 3.2 meV, respectively, from the CB minimum [108]. One derives from them a  $2p_{\pm 1} - 2p_0$  spacing of 19.2 meV, in fair agreement with the experimental values of 25.2 and 21.6 meV for Te and Se, respectively, derived from Table 6.41. By adding to the position of the  $2p_{\pm 1}$

**Table 6.41.** Positions (meV) at LHeT of donor absorption lines in Te- and Se-doped AlSb samples with net doping concentrations between 1 and  $2 \times 10^{16}$  at  $\text{cm}^{-3}$  [4]

| Line <sup>a</sup> | Te attribution | Te <sup>a</sup>  | Se attribution | Se <sup>a</sup>   | Se <sup>b</sup> |
|-------------------|----------------|------------------|----------------|-------------------|-----------------|
| 1                 | $2p_0$         | $38.31 \pm 0.03$ | $2p_0$         | $117.13 \pm 0.05$ | 117             |
| 2                 |                | $57.96 \pm 0.04$ |                | $134.3 \pm 0.2$   |                 |
| 3                 |                | $59.2 \pm 0.1$   |                | $135.7 \pm 0.5$   |                 |
| 4                 |                | $59.7 \pm 0.1$   | $2p_{\pm 1}$   | $138.7 \pm 0.2$   | 139             |
| 5                 | $2p_{\pm 1}$   | $63.5 \pm 0.1$   | $3p_{\pm 1}$   | $142.4 \pm 0.3$   |                 |
| 6                 | $3p_{\pm 1}$   | $66.7 \pm 0.5$   |                | $146.3 \pm 0.5$   |                 |
| 7                 |                | $68.8 \pm 0.1$   |                |                   |                 |

<sup>a</sup> [4], <sup>b</sup> [108]

line the calculated value of the  $2p_{\pm 1}$  level, spectroscopic ionization energies  $E_{\text{io}}(\text{Te})$  and  $E_{\text{io}}(\text{Se})$  in AlSb of 67 and 142 meV, respectively are obtained. These values are comparable with ionization energies of 0.068 and 0.16 eV obtained through Hall effect measurements [257].

Other transitions have been observed in the Se and Te spectra at energies higher than those of the above-reported lines. They have been attributed to phonon-assisted donor transitions involving the emission of AlSb TO( $\Gamma$ ) and LO( $\Gamma$ ) phonons at 323 and 344  $\text{cm}^{-1}$ , respectively [4].

It has been mentioned at the end of Sect. 3.3.1 that for hydrostatic pressures  $\geq 4$  GPa, GaAs turned from a direct-band-gap semiconductor with  $CB$  minimum at the  $\Gamma$  point into an indirect-band-gap semiconductor with an absolute  $CB$  minimum at the X point. This has consequences on the absorption spectrum of the shallow donors in this material: discrete electronic absorption has been reported in GaAs at 487 (60.4 meV) and 405  $\text{cm}^{-1}$  (50.2 meV) for the  $\text{Si}_{\text{Ga}}$  and  $\text{Sn}_{\text{Ga}}$  donors, respectively under hydrostatic pressures of about 6 GPa, with a small pressure dependence of their positions ( $-0.5$  and  $+0.14$   $\text{meV GPa}^{-1}$  for the Si and Sn lines, respectively) [107]. This absorption is shown in Fig. 6.46 for GaAs:Sn.

The increase in energy of the positions of the lines for these two donors with respect to the positions of the lines associated with the  $\Gamma$  minimum of the  $CB$  under atmospheric pressure, whose positions are given in Table 6.37, reflects the effective mass difference. The fact that only one transition is observed for each donor has been related to the camel's back structure of the  $CB$  minimum at the X point for the cubic III-V semiconductors. The calculations of [139] for GaP have been adapted by Hsu et al. [107] to the situation for GaAs under pressure. They find that the ionization energies of the levels corresponding to the  $1s$  and  $2p_0$  EM states for silicon are 37.7 and 11.8 meV below the  $CB$  continuum while the  $2p_{\pm 1}$  and  $3p_0$  states lie several meV above the continuum. This means that states above  $2p_0$  are autoionizing states, and it can explain why only one line, attributed to  $2p_0$ , is observed under pressure. Assuming that the contribution of the donor central-cell is negligible for the

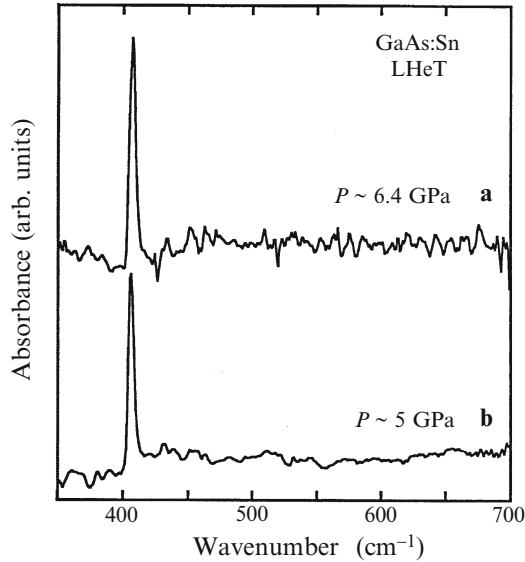


**Fig. 6.46.** Absorption spectra between 43.4 and 86.8 meV of two GaAs:Sn samples under hydrostatic pressures above the  $\Gamma/X$  crossover where the band gap of GaAs becomes indirect. (a):  $n = 2.3 \times 10^{16} \text{ cm}^{-3}$ , (b):  $n = 1.2 \times 10^{15} \text{ cm}^{-3}$ . The FWHM in (b) is  $4.7 \text{ cm}^{-1}$  or  $0.58 \text{ meV}$ . The final state of the transition giving the unique line observed is ascribed to  $2p_0$  (see text) (after [107])

$2p_0$  state, ionization energies of 73.7 and 61.7 meV are estimated for Si and Sn, respectively at the crossover pressure of 4 GPa in GaAs [107].

## 6.9 The $D^-$ Ion and Hopping Absorption

### 6.9.1 The Donor Equivalent of $H^-$ : the $D^-$ Ion

In weakly-compensated p- or n-type semiconductors held at LHeT, steady state illumination with RT background radiation can ionize the neutral shallow impurities. Some of the free carriers so created can recombine with neutral impurities to form  $D^-$  ions in n-type materials and  $A^+$  ions in p-type materials. The ionization energies of these centres are comparable to the EM ionization energy of the impurity centres scaled by the ratio (0.0554) of the ionization energy of  $H^-$  (0.754 eV) to the Rydberg constant. For donors in silicon, germanium, and gallium arsenide, such scaled values of  $E_i(D^-)$  are 1.7, 0.54, and 0.32 meV ( $\sim 14$ , 4.4, and  $2.6 \text{ cm}^{-1}$ ), respectively. The two electrons of these  $D^-$  states can be either antiparallel, giving a singlet state with zero spin, or parallel, giving a triplet state with spin one. It has been shown that the triplet state is not bound at zero magnetic field and that it has to be considered only in experiments under a magnetic field [150].

Determinations of  $E_i(P^-)$  singlet state in silicon were reported by several authors from absorption [71], photoconductivity [188] or phonon spectroscopy measurements [34]. The actual value for isolated centres is concentration-dependent and the most reliable one is that obtained for the smallest concentration. A value of  $E_i(P^-) \sim 2 \text{ meV}$  seems to be consistent with these measurements, while the predicted value scaled from the ionization energy of  $P^0$  is  $2.5 \text{ meV}$ . For germanium, photoconductivity measurements were performed at  $0.38 \text{ K}$  in the very far IR with a lamellar grating interferometer on germanium samples with a donor concentration of  $\sim 5 \times 10^{13} \text{ cm}^{-3}$ . They yielded values of  $E_i(D^-)$  of  $0.625$  and  $0.75 \text{ meV}$  for Sb and As, respectively, to be compared with predicted scaled values of  $0.57$  and  $0.78 \text{ meV}$ , respectively, for these two donors using the experimental ionization energies of the neutral state ([182], and references therein). Similar photoconductive measurements have also been performed in germanium and in silicon under uniaxial stresses and magnetic fields [182, 183].

The absorption or photoconductivity measurements on the  $D^-$  states associated with QHDs in III-V compounds are more difficult to perform because of the small values of the ionization energies, and experiments on GaAs have been performed in the presence of a magnetic field [178]. PL measurements at zero field performed between  $4.2$  and  $0.45 \text{ K}$  on a high-purity GaAs MBE sample under very low excitation conditions have revealed lines attributed to  $D^-A^0$  recombination at an energy higher than that of the  $D^0A^0$  DAP [94]. In this study, the identification of the residual acceptors, the observation of the corresponding  $eA^0$  PL lines, and a fit of the relative intensities of these lines as a function of the temperature of the He bath have allowed to obtain a value of the  $^1D^-$  singlet binding energy in GaAs of  $2.65 \text{ cm}^{-1}$  ( $0.329 \text{ meV}$ ), remarkably close to the estimation from the  $H^-$  scaling. Similar PL experiments with a magnetic field added have shown one additional line due to the  $^3D^-A^0$  recombination for each acceptor [93]. The increase of the energies of the  $^1D^-$  and  $^3D^-$  states with the magnetic field has been compared with existing calculations [150, 207]. For  $B \sim 2 \text{ T}$ , the measured values of  $E(^1D^-)$  and  $E(^3D^-)$  are about  $2.6$  and  $0.9 \text{ meV}$ , respectively.

### 6.9.2 Photon-Induced Hopping

In highly-doped compensated silicon and germanium, a theory of the absorption of electromagnetic radiation in the very far IR has been proposed by Blinowski and Mycielski [26]. This theory predicts low-temperature absorption (from  $\sim 1.5$  to  $12 \text{ meV}$  ( $800$  to  $100 \mu\text{m}$ ) in silicon and from  $0.4$  to  $2.5 \text{ meV}$  ( $2.5 \text{ cm}$  to  $500 \mu\text{m}$ ) in germanium) due to photon-induced hopping of a donor electron from a neutral to an ionized donor, with relatively large absorption cross-sections.

Evidence for this process was given by Milward and Neuringer [166], who reported an absorption between  $\sim 10$  and  $90 \text{ cm}^{-1}$  ( $\sim 1.2$  and  $11 \text{ meV}$ ) with a broad maximum in n-type silicon with neutral  $N_D^0$  in the  $10^{17}$ – $10^{18} \text{ cm}^{-3}$

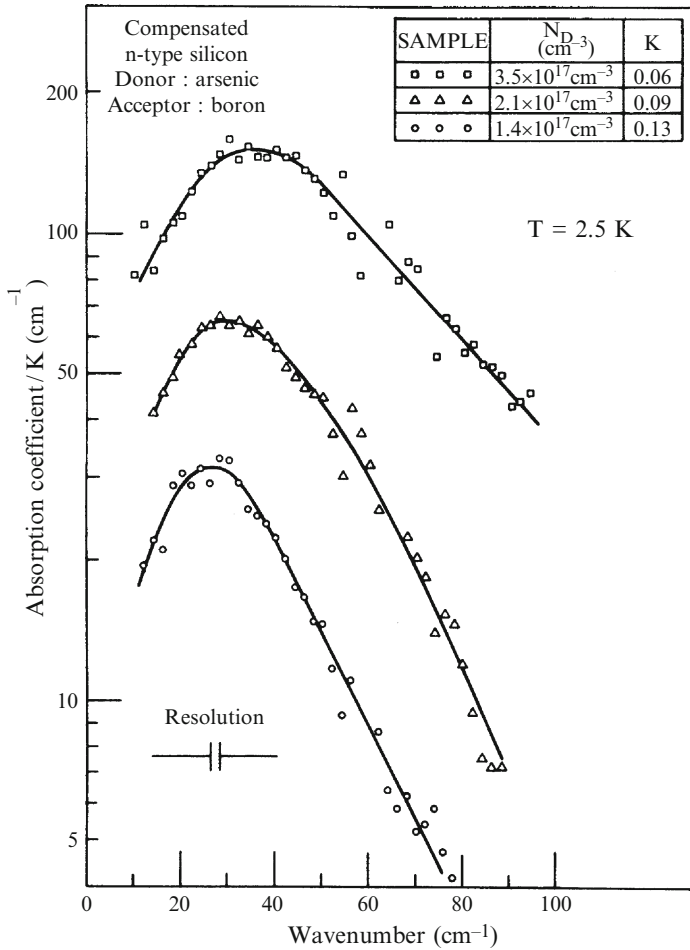


**Fig. 6.47.** Absorption between  $\sim 1.2$  and  $11.2$  meV of lightly-compensated n-type silicon samples due to electron hopping between  $D^0$  and  $D^+$ . The absorption is normalized by dividing by the compensation ratio  $K$  [166]. Copyright 1965 by the American Physical Society

range and compensation ratios between  $\sim 0.1$  and  $0.4$ . This absorption is shown in Fig. 6.47 for three As-doped samples with  $K \sim 0.1$ .

A similar absorption has been reported by Jang et al. [117] in p-type NTD germanium between  $\sim 4$  and  $40 \text{ cm}^{-1}$  ( $\sim 0.5$  and  $5 \text{ meV}$ ) and it is briefly presented here because photon-induced hopping is not discussed in Chap. 7. In this latter study, the compensation ratio was kept fixed at  $\sim 0.3$  and the position of the broad maximum shifted towards higher energies with the neutral acceptor concentration. Qualitatively, for the same neutral impurity concentration, the absorption coefficient in p-type germanium is larger than in

n-type silicon. These results are compared with calculations of the energy dependence of the process in p-type germanium and silicon [123], and the agreement is found to be only approximate.

## References

1. D. Åberg, M.K. Linnarson, B.G. Svensson, T. Hallberg, J.L. Lindström, J. Appl. Phys. **85**, 8054 (1999)
2. A. Adolf, D. Fortier, J.H. Albany, K. Suzuki, Phys. Rev. Lett. **41**, 1477 (1978)
3. R.L. Aggarwal, A.K. Ramdas, Phys. Rev. **140**, A1246 (1965)
4. B.T. Ahlborn, A.K. Ramdas, Phys. Rev. **167**, 717 (1968)
5. H.C. Alt, B.K. Meyer, D. Volm, A. Graber, M. Dreschler, D.M. Hoffmann, T. Detchprom, A. Amano, I. Akasaki, in *Defects in Semiconductors 18*, ed. by M. Suezawa, H. Katayama-Yoshida (Trans Tech, Switzerland, 1995); Mater. Sci. Forum **196–201**, 17
6. H.C.h. Alt, H.E. Wagner, W.v. Ammon, F. Bittersberger, A. Huber, L. Koester, Physica B **401**, 130 (2007)
7. C.A.J. Ammerlaan, in *Properties of Crystalline Silicon, EMIS Datareviews Series No 20*, ed. by R. Hull (INSPEC Publication, London, 1999), pp. 659–662
8. B.A. Andreev, T.M. Lifshits, High-Purity Subst. (Russian Journal) **5**, 7 (1990)
9. B.A. Andreev, E.B. Kozlov, T.M. Lifshits, in *Defects in Semiconductors 18*, ed. by M. Suezawa, H. Katayama-Yoshida (Trans Tech, Switzerland, (1995); Mater. Sci. Forum **196–201**, 121
10. T. Arai, N. Asanuma, K. Kudo, S. Umemoto, Jpn. J. Appl. Phys. **11**, 206 (1972)
11. M. Asche, O.G. Sarbei, Phys. Stat. Sol. B **103**, 11 (1981)
12. N. Baber, H.G. Grimmeiss, M. Kleverman, P. Omling, N. Zafar Iqbal, J. Appl. Phys. **62**, 2853 (1987)
13. R.J. Baker, Ph D thesis, University of Wollongong, New South Wales, Australia, 2000
14. R.J. Baker, P. Fisher, Solid State Commun. **99**, 679 (1996)
15. R.J. Baker, P. Fisher, R.E.M. Vickers, in *Shallow-level centers in semiconductors (Amsterdam, 17–19 July 1996)*, ed. by C.A.J Ammerlaan, B. Pajot (World Scientific, Singapore, 1997), pp. 483–488
16. M. Bara, M. Astier, B. Pajot, Can. J. Phys. **63**, 437 (1985)
17. A.S. Barker Jr, M. Ilegems, Phys. Rev. B **7**, 743 (1973)
18. D.J.S. Beckett, M.K. Nissen, M.L.W. Thewalt, Phys. Rev. B **40**, 9618 (1989)
19. H.H.P.Th. Beckman, T. Gregorkiewicz, I.F.A. Hidayat, C.A.J. Ammerlaan, P. Clauws, Phys. Rev. B **42**, 9802 (1990)
20. I.L. Beinikhes, Sh. M. Kogan, Sov. Phys. JETP **66**, 164 (1987)
21. I.L. Beinikhes, Sh. M. Kogan, in *Shallow Impurities in Semiconductors 1988*, ed. by B. Monemar (Linköping, Sweden, 1989), pp. 10–12; Inst. Phys. Conf. Ser. No 95, Bristol, pp. 161–166
22. K. Bergman, G. Grossmann, H.G. Grimmeiss, M. Stavola, Phys. Rev. Lett. **56**, 2827 (1986)
23. K. Bergman, G. Grossmann, H. G. Grimmeiss, M. Stavola, R.E. McMurray Jr, Phys. Rev. B **39**, 1104 (1989)
24. J.W. Birchard, J.C. Giles, Can. J. Phys. **40**, 1480 (1962)



25. P. Blanconnier, J.F. Hogrel, A.M. Jean-Louis, B. Sermage, J. Appl. Phys. **52**, 6895 (1981)
26. J. Blinowski, J. Mycielski, Phys. Rev. **136**, A266 (1964)
27. J. Bloem, C. Haas, P. Penning, J. Phys. Chem. Solids **12**, 22 (1959)
28. W. Böhm, E. Ettliger, W. Prettl, Phys. Rev. Lett. **47**, 1198 (1981)
29. J. Broeckx, P. Clauws, J. Vennik, J. Phys. C **13**, L141 (1980)
30. J. Broeckx, P. Clauws, J. Vennik, J. Phys. C **19**, 511 (1986)
31. K.L. Brower, Phys. Rev. B **26**, 6040 (1982)
32. T.G. Brown, D.C. Hall, Appl. Phys. Lett. **49**, 245 (1986)
33. H. Buijs, (1985) Photo thermal ionization spectroscopy for shallow donor impurity determination in GaAs. BOMEM application note no. 1
34. W. Burger, K. Lassmann, Phys. Rev. Lett. **53**, 2035 (1984)
35. N.R. Butler, P. Fisher, A.K. Ramdas, Phys. Rev. B **12**, 3200 (1975)
36. V.V. Buzdin, A.I. Demeshina, A. Kurskii Yu, V.N. Murzin, Sov. Phys. Semicond. **6**, 1792 (1975)
37. Y. Cai, T. Zhang, A.B. Anderson, J.C. Angus, L.N. Kostadinov, T.V. Albu, Diam. Relat. Mater. **15**, 1868 (2006)
38. W.E. Carlos, J.A. Freitas, M. Asif Khan, D.T. Olson, J.N. Kuznia, Phys. Rev. B **48**, 17878 (1993)
39. A.C. Carter, P.J. Dean, M.S. Skolnick, R.A. Stradling, J. Phys. C **10**, 5111 (1977)
40. Y.C. Chang, T.C. McGill, Solid State Commun. **33**, 1035 (1980)
41. Y.C. Chang, T.C. McGill, Phys. Rev. B **24**, 5779 (1981)
42. A. Chantre, S.J. Pearton, L.C. Kimerling, K.D. Cummings, W.C. Dautremont-Smith, Appl. Phys. Lett. **50**, 513 (1987)
43. C.Y. Cheung, R. Barrie, Can. J. Phys. **45**, 1421 (1967)
44. P. Clauws, in *Germanium-Based Technologies. From Materials to Devices*, ed. by C. Claves, E. Simoen (Elsevier, Amsterdam, 2007), Chap. 4
45. P. Clauws, Mater. Sci. Eng. B **36**, 213 (1996)
46. P. Clauws, J. Broeckx, E. Rotsaert, J. Vennik, Phys. Rev. B **38**, 12377 (1988)
47. P. Clauws, F. Callens, F. Maes, J. Vennik, E. Boesman, Phys. Rev. B **44**, 3665 (1991)
48. P. Clauws, J. Vennik, in *Defects in Semiconductors 15*, ed. by G. Ferenczi (Trans Tech, Switzerland, 1989); Mater. Sci. Forum **38–41**, 473
49. L.S. Darken, J. Appl. Phys. **65**, 1118 (1989)
50. G. Davies, E.C. Lightowers, R. Woolley, R.C. Newman, A.S. Oates, J. Phys. C **17**, L499 (1984)
51. P.J. Dean, in *Deep centers in semiconductors A state-of-the-art approach*, 2nd edn. 1992, Ed. by S.T. Pantelides (Gordon and Breach, 1986), pp. 215–377
52. P.J. Dean, D. Bimberg, F. Mansfield, Phys. Rev. B **15**, 3906 (1977)
53. P.J. Dean, C.H. Henry, Phys. Rev. **176**, 928 (1968)
54. P.J. Dean, C.J. Frosch, C.H. Henry, J. Appl. Phys. **39**, 5631 (1968)
55. P.J. Dean, R.A. Faulkner, S. Kimura, Phys. Rev. B **2**, 4062 (1970)
56. A. Dörnen, R. Sauer, J. Weber, in Proceedings of 13th International Conference on Defects in Semicond, ed. by L.C. Kimerling, J.M. Parsey Jr (The Metallurgical Society of AIME, Warrendale, 1984), pp. 653–660
57. G. Elliot, Nature (London) **180**, 1350 (1957)
58. V.V. Emtsev, G.A. Oganessian, K. Schmalz, Def. Dif. Forum **103–105**, 505 (1993)

59. H.Y. Fan, P. Fisher, J. Phys. Chem. Solids **8**, 270 (1959)
60. U. Fano, Phys. Rev. **124**, 1866 (1961)
61. R.A. Faulkner, Phys. Rev. **184**, 713 (1969)
62. G. Feher, Phys. Rev. **114**, 1219 (1959)
63. H. Feichtinger, J. Wlatl, A. Gachwandtner, Solid State Commun. **27**, 867 (1978)
64. R.A. Forman, Appl. Phys. Lett. **37**, 776 (1980)
65. R.J. Fox, IEEE Trans. Nucl. Sci. **13**, 367 (1966)
66. C. Foy, J. Phys. C **15**, 2059 (1982)
67. R.K. Franks, J.B. Robertson, Solid State Commun. **5**, 479 (1967)
68. C.S. Fuller, R.A. Logan, J. Appl. Phys. **28**, 1427 (1957)
69. A. Gali, J. Miro, P. Deák, C.P. Ewels, R. Jones, J. Phys Cond. Matter **8**, 7711 (1996)
70. E.M. Gershenzon, G.N. Gol'tsman, A.I. Elant'ev, Sov. Phys. JETP **45**, 555 (1977)
71. E.M. Gershenzon, G.N. Gol'tsman, A.P. Mel'nikov, Sov. Phys. JETP Lett. **14**, 185 (1971)
72. E.M. Gershenzon, G.N. Gol'tsman, N.G. Ptitsina, Sov. Phys. JETP **49**, 355 (1979)
73. E. Gheeraert, N. Casanova, S. Koizumi, T. Teraji, H. Kanda, Diam. Relat. Mater. **10**, 444 (2001)
74. E. Gheeraert, S. Koizumi, T. Teraji, H. Kanda, Solid State Commun. **113**, 577 (2000)
75. E. Gheeraert, B. Pajot, T. Teraji, S. Koizumi, (2002) Unpublished results
76. T.E. Gilmer, R.K. Franks, R.J. Bell, J. Phys. Chem. Solids **26**, 1195 (1965)
77. W. Götz, G. Pensl, W. Zulehner, Phys. Rev. B **46**, 4312 (1992)
78. T. Graf, M.S. Brandt, C.E. Nebel, M. Stutzmann, S. Koizumi, Phys. Stat. Sol. A **193**, 434 (2002)
79. T. Gregorkiewicz, H.H.P.Th. Beckman, C.A.J. Ammerlann, Phys. Rev. B **38**, 3998 (1988)
80. J.A. Griffin, J. Hartung, J. Weber, H. Navarro, L. Genzel, Appl. Phys. A **48**, 41 (1989)
81. H.G. Grimmeiss, E. Janzén, H. Ennen, O. Schirmer, J. Schneider, R. Wörner, C. Holm, E. Sirtl, P. Wagner, Phys. Rev. B **24**, 4571 (1981)
82. H.G. Grimmeiss, E. Janzén, K. Larsson, Phys. Rev. B **25**, 2627 (1982)
83. H.G. Grimmeiss, E. Janzén, in *Deep Centers in Semiconductors. A State-of-the Art Approach*, 2nd edn, ed. by S.T. Pantelides (Gordon and Breach, Switzerland, 1992), pp. 87–176
84. H.G. Grimmeiss, L. Montelius, K. Larsson, Phys. Rev. B **37**, 6916 (1988)
85. M. Grinberg, S. Legowski, H. Meczynska, Phys. Stat. Sol. B **130**, 325 (1985)
86. K. Haenen, M. Nesládek, L. De Schepper, R. Kravets, M. Vanecek, S. Koizumi, Diam. Relat. Mater. **13**, 2041 (2004)
87. R.N. Hall, *Interaction between quenched-in defects in high-purity germanium. Inst. Phys. Conf. Series, No 23* (The Institute of Physics, London, 1975), pp. 190–197
88. E.E. Haller, Phys. Rev. Lett. **40**, 584 (1978)
89. E.E. Haller, L.M. Falicov, Phys. Rev. Lett. **41**, 1192 (1978)
90. E.E. Haller, W.L. Hansen, F.S. Goulding, Adv. Phys. **30**, 93 (1981)
91. F.S. Ham, Phys. Rev. B **38**, 5474 (1988)

92. A. Hara, Jpn. J. Appl. Phys. **34**, 3418 (1995)
93. D.A. Harrison, J.A.H. Stotz, S.P. Watkins, M.L.W. Thewalt, D.J.S. Beckett, A.J. SpringThorpe, Phys. Rev. B **60**, 15527 (1999)
94. D.A. Harrison, S.P. Watkins, M.L.W. Thewalt, D.J.S. Beckett, A.J. SpringThorpe, Phys. Rev. Lett. **80**, 2461 (1998)
95. J. Hartung, J. Weber, Phys. Rev. B **48**, 14161 (1993)
96. H. Hatakeyama, M. Suezawa, J. Appl. Phys. **82**, 4945 (1997)
97. S. Hayama, G. Davies, J. Tan, J. Coutinho, R. Jones, K.M. Itoh, Phys. Rev. B **70**, 035202 (2004)
98. J.R. Haynes, J.A. Hornbeck, Phys. Rev. **100**, 606 (1955)
99. H. Heissenstein, H. Sadowski, R. Helbig, Physica B **324**, 49 (2002)
100. C.H. Henry, K. Nassau, J.W. Shiever, Phys. Rev. B **5**, 458 (1972)
101. M.O. Henry, E.C. Lightowers, J. Phys. C **10**, L601 (1977)
102. L.T. Ho, Def. Diff. Forum **221–223**, 41 (2003)
103. L.T. Ho, A.K. Ramdas, Phys. Rev. B **5**, 462 (1972)
104. J.J. Hopfield, D.G. Thomas, R.T. Lynch, Phys. Rev. Lett. **17**, 312 (1966)
105. H.H. Hrostowski, R.H. Kaiser, J. Phys. Chem. Solids **7**, 236 (1958)
106. H.H. Hrostowski, R.H. Kaiser, Phys. Rev. Lett. **1**, 199 (1958)
107. L. Hsu, S. Zehender, E. Bauser, E.E. Haller, Phys. Rev. B **55**, 10515 (1997)
108. L. Hsu, M.D. McCluskey, E.E. Haller, Phys. Rev. B **67**, 035209 (2003)
109. C.M. Hu, Y.X. Huang, H.J. Ye, S.C. Shen, M.W. Qi, Appl. Phys. Lett. **59**, 2260 (1991)
110. A. Imatake, J. Phys. Soc. Jpn. **35**, 164 (1973)
111. J. Isoya, M. Katagiri, T. Umeda, S. Koizumi, H. Kanda, N.T. Son, A. Henry, A. Gali, E. Janzén, Physica B **376–377**:358 (2006)
112. D. Israël, F. Callens, P. Clauws, P. Matthys, Solid State Commun. **82**, 215 (1992)
113. I.G. Ivanov, A. Henry, E. Janzén, Phys. Rev. B **71**, 241201 (2005)
114. I.G. Ivanov, B. Magnusson, E. Janzén, Phys. Rev. B **67**, 165212 (2003)
115. C. Jagannath, Z.W. Grabowski, A.K. Ramdas, Phys. Rev. B **23**, 2082 (1981)
116. K. Jain, S. Lai, M.V. Klein, Phys. Rev. B **13**, 5448 (1976)
117. H.F. Jang, G. Cripps, T. Timusk, Phys. Rev. B **41**, 5152 (1990)
118. E. Janzén, R. Stedman, G. Grossmann, H.G. Grimmeiss, Phys. Rev. B **29**, 1907 (1984)
119. E. Janzén, G. Grossmann, R. Stedman, H.G. Grimmeiss, Phys. Rev. B **31**, 8000 (1985)
120. N.M. Johnson, S.K. Hahn, Appl. Phys. Lett. **48**, 709 (1986)
121. C.E. Jones, D. Schafer, W. Scott, R.J. Hager, J. Appl. Phys. **52**, 5148 (1981)
122. B. Joós, E.E. Haller, L.M. Falicov, Phys. Rev. B **22**, 832 (1981)
123. E. Kaczmarek, Z. Gortel, Phys. Rev. B **10**, 2535 (1974)
124. W. Kaiser, H.L. Frisch, H. Reiss, Phys. Rev. **112**, 1546 (1958)
125. R. Kaplan, R.A. Cooke, R.A. Stradling, Solid State Commun. **26**, 741 (1978)
126. D. Karauskaj, J.A.H. Stotz, T. Meyer, M.L.W. Thewalt, M. Cardona, Phys. Rev. Lett. **90**, 186402 (2003)
127. J. Kato, K.M. Itoh, E.E. Haller, Physica B **302–303**, 1 (2001)
128. A. Klarenbosch, T.O. Klaassen, W.T. Wenckebach, C.T. Foxon, J. Appl. Phys. **67**, 6323 (1990)
129. W.H. Kleiner, W.E. Krag, Phys. Rev. Lett. **25**, 1490 (1970)
130. M. Kleverman, K. Bergman, H.G. Grimmeiss, Semicond. Sci. Tech. **1**, 49 (1986)

131. M. Kobayashi, S. Sawada, S. Narita, J. Phys. Soc. Jpn. **51**, 844 (1982)
132. Sh. M. Kogan, Sov. Phys. Semicond. **13**, 1131 (1980)
133. Sh. M. Kogan, R. Taskinboev, Sov. Phys. Semicond. **17**, 1007 (1983)
134. W. Kohn, Phys. Rev. **98**, 1856 (1955)
135. W. Kohn, in *Solid State Physics Advances in Research and Application*, vol. 5, ed. by F. Seitz, D. Turnbull (Academic, New York, (1957), pp. 257–320
136. W. Kohn, J.M. Luttinger, Phys. Rev. **98**, 915 (1955)
137. S. Koizumi, T. Teraji, H. Kanda, Diam. Relat. Mater. **9**, 935 (2000)
138. B.O. Kolbesen, Appl. Phys. Lett. **27**, 353 (1975)
139. A.A. Kopylov, A.N. Pikhtin, Sov. Phys. Semicond. **11**, 510 (1977)
140. A.A. Kopylov, A.N. Pikhtin, Solid State Commun **26**, 735 (1978)
141. W.E. Krag, W.H. Kleiner, H.J. Zeiger, Bull. Am. Phys. Soc. **15**, 279 (1970)
142. W.E. Krag, W.H. Kleiner, H.J. Zeiger, Phys. Rev. B **33**, 8304 (1986)
143. W.E. Krag, in *Proceedings of 10th International Conference On Physics of Semiconductor*, Cambridge, MA (USAEC Div. Technical Information, Washington DC, 1970), pp. 271–277
144. W.E. Krag, W.H. Kleiner, H.J. Zeiger, S. Fischler, J. Phys. Soc. Jpn. **21**(Suppl.) 230 (1966)
145. W.E. Krag, H.J. Zeiger, Phys. Rev. Lett. **8**, 485 (1962)
146. F. Kuchar, R. Kaplan, R.J. Wagner, R.A. Cookes, R.A. Stradling, P. Vogl, J. Phys. C **17**, 6403 (1984)
147. W. Kürner, R. Sauer, A. Dörnen, K. Thonke, Phys. Rev B **39**, 13327 (1989)
148. D. Labrie, M.L.W. Thewalt, B.P. Clayman, T. Timusk, Phys. Rev. B **32**, 5514 (1985)
149. D.M. Larsen, Phys. Rev. B **8**, 535 (1973)
150. D.M. Larsen, Phys. Rev. B **20**, 5217 (1979)
151. I. Latushko Ya, L.F. Makarenko, V.P. Markevich, L.I. Murin, Phys Stat. Sol. A **93**, K181 (1986)
152. A.L. Lin, J. Appl. Phys. **53**, 6989 (1982)
153. J.L. Lindström, T. Hallberg, (1996) in *Proceedings of NATO Advanced Workshop on the Early Stages of Oxygen Precipitation in Silicon. NATO ASI Series 3*, Vol. 17, ed. by R. Jones (Kluwer, Dordrecht, 1996), pp. 41–60
154. V.V. Litvinov, G.V. Pal'chik, V.I. Urenev, Sov. Phys. Semicond. **19**, 841 (1985)
155. S.P. Love, K. Muro, R.E. Peale, A.J. Sievers, W. Lo, Phys. Rev. B **36**, 2950 (1987)
156. G.W. Ludwig, Phys. Rev. **137**, A1520 (1965)
157. G.W. Ludwig, H.H. Woodbury, in *Solid State Physics Advances in Research and Application*, vol. 13, ed. by F. Seitz, D. Turnbull (Academic Press, New York, (1962), pp. 223–304
158. S.A. McQuaid, R.C. Newman, E.C. Lightowers, Semicond. Sci. Tech. **9**, 1736 (1994)
159. L.F. Makarenko, L.I. Murin, Sov. Phys. Semicond. **20**, 961 (1986)
160. D.D. Manchon Jr, P.J. Dean, in Proceedings of 10th International Conference on Physics of Semiconductors, Cambridge, MA (USAEC Div. Technical Information, Washington DC, 1970), pp. 760–766
161. A.V. Marinchenko, L.I. Khirunenko, V.I. Shakhovtsov, V.I. Yashnik, Sov. Phys. Semicond. **24**, 712 (1990)
162. P.W. Mason, H.J. Sun, B. Ittermann, S.S. Ostapenko, G.D. Watkins, L. Jeyanathan, M. Singh, G. Davies, E.C. Lightowers, Phys. Rev. B **58**, 7007 (1998)

163. A.J. Mayur, D.M. Sciacca, A.K. Ramdas, S. Rodriguez, *Phys. Rev. B* **48**, 10893 (1993)
164. J.L. Merz, H. Kukimoto, K. Nassau, J.W. Shiever, *Phys. Rev. B* **6**, 545 (1972)
165. B.K. Meyer, D. Volm, A. Graber, H.C. Alt, T. Detchprohm, A. Amano, I. Akasaki, *Solid State Commun.* **95**, 597 (1995)
166. R.C. Milward, L.J. Neuringer, *Phys. Rev. Lett.* **15**, 664 (1965)
167. F. Mireles, S.E. Ulloa, *Appl. Phys. Lett.* **74**, 248 (1999)
168. B. Monemar, U. Lindefelt, W.M. Chen, *Physica B + C* **146**, 256 (1987)
169. P.M. Mooney, L.J. Cheng, M. Süli, J.D. Gerson, J.W. Corbett, *Phys. Rev. B* **15**, 3836 (1977)
170. W.J. Moore, J.A. Freitas Jr, P.J. Lin-Chung, *Solid State Commun.* **93**, 389 (1995)
171. W.J. Moore, J.A. Freitas Jr, R.J. Molnar, *Phys. Rev. B* **56**, 12073 (1997)
172. T.N. Morgan, *Phys. Rev. Lett.* **21**, 819 (1968)
173. N.F. Mott, *Adv. Phys.* **21**, 785 (1972)
174. S.H. Muller, M. Sprenger, E.G. Sieverts, C.A.J. Ammerlaan, *Solid State Commun.* **25**, 987 (1978)
175. K. Murakami, H. Kuribayashi, K. Masuda, *Jpn. J. Appl. Phys.* **27**, L1414 (1988)
176. L.I. Murin, V.P. Markevich, J.L. Lindström, M. Kleverman, *Physica B* **340–342**, 1046 (2003)
177. T. Myazaki, H. Okushi, *Diam. Relat. Mater.* **10**, 449 (2001)
178. S.P. Najda, C.J. Armistead, C. Trager, R.A. Stradling, *Semicond. Sci. Tech.* **4**, 439 (1989)
179. H. Nakata, E. Otsuka, *Phys. Rev. B* **29**, 2347 (1984)
180. H. Nakata, E. Otsuka, *J. Phys. Soc. Jpn.* **55**, 391 (1986)
181. H. Nakata, K. Yamada, T. Ohyama, *Appl. Phys. Lett.* **74**, 3480 (1999)
182. S. Narita, *J. Phys. Soc. Jpn* **49**(Suppl. A), 173 (1980)
183. T. Narita, S. Shinbashi, M. Kobayashi, *J. Phys. Soc. Jpn.* **51**, 2186 (1982)
184. H. Navarro, J. Griffin, J. Weber, L. Genzel, *Solid State Commun.* **58**, 151 (1986)
185. H. Navarro, J. Griffin, E.E. Haller, R.E. McMurray Jr, *Solid State Commun.* **64**, 1297 (1987)
186. H. Navarro, E.E. Haller, F. Keilmann, *Phys. Rev. B* **37**, 10822 (1988)
187. R.C. Newman, J.H. Tucker, N.G. Semaltianos, E.C. Lightowlers, T. Gregorkiewicz, I.S. Zevenbergen, C.A.J. Ammerlaan, *Phys. Rev B* **54**, R6803 (1996)
188. P. Norton, *J. Appl. Phys.* **47**, 308 (1976)
189. J. Olajos, B. Bech Nielsen, M. Kleverman, P. Omling, P. Emanuelsson, H.G. Grimmeiss, *Appl. Phys. Lett.* **53**, 2507 (1988)
190. J. Olajos, M. Kleverman, H.G. Grimmeiss, *Phys. Rev. B* **38**, 10633 (1988)
191. J. Olajos, M. Kleverman, H.G. Grimmeiss, *Phys. Rev. B* **40**, 6196 (1989)
192. C.S. Olsen, J.W. Beeman, K.M. Itoh, J. Farmer, V.I. Ozhogin, E.E. Haller, *Solid State Commun.* **108**, 895 (1998)
193. H. Ono, *Appl. Phys. Express (Japan)* **1**, 025001 (2008)
194. A. Onton, *Phys. Rev. Lett.* **22**, 288 (1969)
195. A. Onton, *Phys. Rev. B* **4**, 4449 (1971)
196. A. Onton, R.C. Taylor, *Phys. Rev. B* **1**, 2587 (1970)
197. N. Orita, T. Nishimatsu, H. Katayama-Yoshida, *Jpn. J. Appl. Phys.* **46**, 315 (2007)

198. H. Overhof, M. Scheffler, C.M. Wienert, Phys. Rev. B **43**, 12494 (1991)
199. B. Pajot, Doctoral thesis, Faculté des Sciences de l'Université de Paris, 1969
200. B. Pajot, J. Kauppinen, R. Anttila, Solid State Commun. **31**, 759 (1979)
201. B. Pajot, B. Clerjaud, (to be published), *Optical Absorption of Impurities and Defects in Semiconducting Crystals - Deep Centres and Vibrational Absorption*, (Springer, Berlin Heidelberg New York, 2010)
202. B. Pajot, D. Débarre, in *Neutron-Transmutation-Doped Silicon*, ed. by J. Guldborg (Plenum, 1981), pp. 423–435
203. B. Pajot, J. von Bardeleben, in *Proceedings of 13th International Conference on Defects in Semiconductor*, ed. by L.C. Kimerling, J.M. Parsey Jr (The Metallurgical Society of AIME, Warrendale, 1985), pp. 685–691
204. B. Pajot, G. Grossmann, M. Astier, C. Naud, Solid State Commun. **54**, 57 (1985)
205. B. Pajot, A.M. Stoneham, J. Phys. C **20**, 5241 (1987)
206. B. Pajot, B. Clerjaud, M.D. McCluskey, Phys. Rev. B **69**, 085210 (2004)
207. T. Pang, S.G. Louie, Phys. Rev. Lett. **65**, 1635 (1990)
208. S.G. Pavlov, H.W. Hübers, P.M. Haas, J.N. Hovenier, T.O. Klaassen, R.Kh. Zhukavin, V.N. Shastin, D.A. Carder, B. Redlich, Phys. Rev. B **78**, 165201 (2008)
209. S.G. Pavlov, H.W. Hübers, H. Riemann, R.Kh. Zhukavin, E.E. Orlova, V.N. Shastin, J. Appl. Phys. **92**, 5632 (2002)
210. R.E. Peale, K. Muro, A.J. Sievers, F.J. Ham, Phys. Rev. B **37**, 10829 (1988)
211. R.E. Peale, K. Muro, A.J. Sievers, in *Shallow impurities in Semiconductors IV*, ed. by G. Davies (Trans Tech, Switzerland, (1991); Mater. Sci. Forum **65–66**, 151
212. G. Pensl, G. Roos, C. Holm, G. Sirtl, N.M. Johnson, Appl. Phys. Lett. **51**, 451 (1987)
213. G. Picus, E. Burstein, B. Henvis, J. Phys. Chem. Solids **1**, 75 (1956)
214. P.C.M. Planken, H.P.M. Pellemans, P.C. van Son, J.N. Hovenier, T.O. Klaassen, W.T.h. Wenckebach, P.W. Barmby, J.L. Dunn, C.A. Bates, C.T. Foxon, C.J.G.M. Langerak, Opt. Commun. **124**, 258 (1996)
215. M. Porrini, M.G. Pretto, R. Scala, A.V. Batunina, H.C. Alt, R. Wolf, Appl. Phys. A **81**, 1187 (2005)
216. R.E. Pritchard, M.J. Ashwin, J.H. Tucker, R.C. Newman, E.C. Lightowers, T. Gregorkiewicz, I.S. Zevenbergen, C.A.J. Ammerlaan, R. Falster, M.J. Binns, Semicond. Sci. Tech. **12**, 1404 (1997)
217. R.H. Reuszer, P. Fisher, An optical determination of the ground-state splitting of group V impurities in germanium. Phys. Rev. **135**, A1125 (1964)
218. E. Rotsaert, P. Clauws, Vennik, L. Van Goethem, Phys. **146B**, 75 (1987)
219. I. Sakaguchi, M. Nishitani-Gamo, Y. Kikuchi, E. Yasu, H. Haneda, T. Suzuki, T. Ando, Phys. Rev. B **60**, R2139 (1999)
220. O.F. Sankey, J.D. Dow, Solid State Commun. **51**, 705 (1984)
221. R. Sauer, J. Photolum. **12–13**, 495 (1976)
222. W. Scott, J. Appl. Phys. **50**, 472 (1979)
223. W. Scott, J.R. Onffroy, Phys. Rev. B **13**, 1664 (1976)
224. S.D. Secombe, D.M. Korn, Solid State Commun. **11**, 1539 (1972)
225. S.C. Shen, Z.Y. Yu, Y.X. Huang, Int. J. Infrared Millimeter Waves **11**, 595 (1990)
226. X.H. Shi, P.L. Liu, S.C. Shen, Appl. Phys. Lett. **69**, 3549 (1996a)

227. X.H. Shi, P.L. Liu, S.C. Shen, J.X. Chen, H.P. Xin, A.Z. Li, J. Appl. Phys. **80**, 4491 (1996b)
228. P.E. Simmonds, R.A. Stradling, J.R. Birch, C.C. Bradley, Phys. Stat. Sol. B **64**, 195 (1974)
229. M. Singh, E.C. Lightowers, G. Davies, Mater. Sci. Eng. B **4**, 303 (1989)
230. M.S. Skolnick, L. Eaves, R.A. Stradling, J.C. Portal, S. Askenazy, Solid State Commun. **15**, 1403 (1974)
231. A.G. Steele, L.C. Lenchyshyn, M.L.W. Thewalt, Appl. Phys. Lett. **56**, 148 (1990)
232. M. Steger, A. Yang, D. Karaiskaj, M.L.W. Thewalt, E.E. Haller, J.W. Ager III, M. Cardona, H. Riemann, N.V. Abrosimov, A.V. Gusev, A.D. Bulanov, A.K. Kaliteevskii, O.N. Godisov, P. Becker, H.J. Pohl, Phys. Rev. B **79**, 205210 (2009)
233. M. Steger, A. Yang, M.L.W. Thewalt, M. Cardona, H. Riemann, N.V. Abrosimov, M.F. Churbanov, A.V. Gusev, A.D. Bulanov, I.D. Kovalev, A.K. Kaliteevskii, O.N. Godisov, P. Becker, H.J. Pohl, E.E. Haller, J.W. Ager III, High-resolution absorption spectroscopy of the deep impurities S and Se in  $^{28}\text{Si}$  revealing the  $^{77}\text{Se}$  hyperfine splitting, Phys. Rev. B **80**, 115204 (2009)
234. H. Sternschulte, K. Thonke, R. Sauer, S. Koizumi, Phys. Rev. B **59**, 12924 (1998)
235. G.E. Stillman, S.S. Bose, M.H. Kim, B. Lee, T.S. Low, in *Handbook of Semiconductors*, vol. 3A, ed. by S. Mahayan (North Holland, Amsterdam, 1994), pp. 783–994
236. G.E. Stillman, C.M. Wolfe, J.O. Dimmock, in *Semiconductors and Semimetals*, vol. 12: Infrared detectors (II) Chap. 5. Willardson R K, Beer A C (Academic, New York, 1977)
237. A.M. Stoneham, *Theory of Defects in Solids*. (Oxford, Clarendon, 1975), p. 778
238. M. Suezawa, K. Sumino, H. Harada, T. Abe, Jpn. J. Appl. Phys. **25**, L859 (1986)
239. M. Suezawa, K. Sumino, H. Harada, T. Abe, Jpn. J. Appl. Phys. **27**, 62 (1988)
240. S. Sugano, Y. Tanabe, H. Kamimura, *Multiplets of Transition-Metal Ions in Crystals*. (Academic, New York, 1970)
241. W. Suttrop, G. Pensl, W.J. Choyke, R. Stein, S. Leibenzeder, J. Appl. Phys. **72**, 3708 (1992)
242. J.H. Svensson, B. Monemar, E. Janzén, Phys. Rev. Lett. **65**, 1796 (1990)
243. J.C. Swartz, D.H. Lemmon, R.N. Thomas, Solid State Commun. **36**, 331 (1980)
244. D. Thébault, J. Barrau, G. Armelles, N. Laurent, J.P. Noguier, Phys. Stat. Sol. B **125**, 357 (1984)
245. M.L.W. Thewalt, Can. J. Phys. **55**, 1463 (1977)
246. M.L.W. Thewalt, Solid State Commun. **133**, 715 (2005)
247. M.L.W. Thewalt, D. Labrie, I.J. Booth, B.P. Clayman, E.C. Lightowers, E.E. Haller, Physica **146B**, 47 (1987)
248. M.L.W. Thewalt, M. Steger, A. Yang, N. Stavrias, M. Cardona, H. Riemann, N.V. Abrosimov, M.F. Churbanov, A.V. Gusev, A.D. Bulanov, I.D. Kovalev, A.K. Kaliteevskii, O.N. Godisov, P. Becker, H.J. Pohl, J.W. Ager III, E.E. Haller, Physica B **401–402**, 587 (2007)
249. A. Thilderkvist, M. Kleverman, H.G. Grimmeiss, Phys. Rev. B **49**, 16338 (1994)
250. A. Thilderkvist, G. Grossmann, M. Kleverman, H.G. Grimmeiss, in *Defects in Semiconductors 17*, ed. by H. Heinrich, W. Jantsch (Trans Tech, Switzerland, 1994); Mater. Sci. Forum **143–147**, 165



251. A. Thilderkvist, G. Grossmann, M. Kleverman, H.G. Grimmeiss, in *Proceedings of 20th International Conference Physics of Semiconductor*, ed. by E.M. Anastassakis, J.D. Joannopoulos (World Scientific, Singapore, 1990), pp. 581–584
252. A. Thilderkvist, G. Grossmann, M. Kleverman, H.G. Grimmeiss, *Phys. Rev. B* **58**, 7723 (1998)
253. G.A. Thomas, M. Capizzi, F. DeRosa, R.N. Bhatt, T.M. Rice, *Phys. Rev. B* **23**, 5472 (1981)
254. V.D. Tkachev, A.V. Mudryi, in *Proc. Rad. Defects in Semicond.*, Dubrovnik 1975, Inst. Phys. Conf. Ser. No 31, ed. by N.B. Urli, J.W. Corbett (IOP, Bristol, 1977), pp. 231–243
255. V.D. Tkachev, L.F. Makarenko, V.P. Markevich, L.I. Murin, *Sov. Phys. Semicond.* **18**, 324 (1984)
256. J.M. Trombetta, G.D. Watkins, *Appl. Phys. Lett.* **51**, 1103 (1987)
257. W.J. Turner, W.E. Reese, *Phys. Rev.* **117**, 1003 (1960)
258. N.Q. Vinh, T. Gregorkiewicz, K. Thonke, *Phys. Rev. B* **65**, 033202 (2001)
259. A.T. Vink, R.L.A. van der Heyden, J.A.W. van der Does de Bye, *J. Lumin.* **8**, 105 (1973)
260. J. Wagner, A. Dörnen, R. Sauer, *Phys. Rev. B* **31**, 5561 (1985)
261. J. Wagner, K. Thonke, R. Sauer, *Phys. Rev. B* **29**, 7051 (1984)
262. P. Wagner, C. Holm, E. Sirtl, R. Oeder, W. Zulehner, in *Festkörperprobleme (Advances in Solid State Physics)*, vol. XXIV, ed. by P. Grosse (Vieweg, Braunschweig, 1984), pp. 191–228
263. P. Wagner, J. Hage, *Appl. Phys. A* **49**, 123 (1989)
264. Y.J. Wang, R. Kaplan, H.K. Ng, K. Doverspike, D.K. Gaskill, T. Ikeda, I. Akasaki, H. Amono, *J. Appl. Phys.* **79**, 8007 (1996)
265. G.D. Watkins, in *Radiation Damages in Semiconductors*, Paris-Royaumont 1964, ed. by P. Baruch (Dunod, Paris, 1964), pp. 97–113
266. G.D. Watkins, F.S. Ham, *Phys. Rev. B* **1**, 4071 (1970)
267. G.D. Watkins, M. Kleverman, A. Thilderkvist, H.G. Grimmeiss, *Phys. Rev. Lett.* **67**, 1149 (1991)
268. J.J. White, *Can. J. Phys.* **45**, 2797 (1967)
269. R.A. Wood, M.A. Khan, P.A. Wolff, R.L. Aggarwal, *Opt. Commun.* **21**, 154 (1977)
270. G.B. Wright, A. Mooradian, *Phys. Rev. Lett.* **18**, 608 (1967)
271. D. Wruck, P. Gaworzewski, *Phys. Stat. Sol. A* **56**, 557 (1979)
272. D. Wruck, F. Spiegelberg, *Phys. Stat. Sol. B* **133**, K39 (1986)
273. A. Yang, M. Steger, D. Karaiskaj, M.L.W. Thewalt, M. Cardona, K.M. Itoh, H. Riemann, N.V. Abrosimov, M.F. Churbanov, A.V. Gusev, A.D. Bulanov, I.D. Kovalev, A.K. Kaliteevskii, O.N. Godisov, P. Becker, H.J. Pohl, J.W. Ager III, E.E. Haller, *Phys. Rev. Lett.* **97**, 227401 (2006)
274. A. Yang, M. Steger, M.L.W. Thewalt, M. Cardona, H. Riemann, N.V. Abrosimov, M.F. Churbanov, A.V. Gusev, A.D. Bulanov, I.D. Kovalev, A.K. Kaliteevskii, O.N. Godisov, P. Becker, H.J. Pohl, J.W. Ager III, E.E. Haller, *Physica B* **401–402**, 593 (2007)
275. Z. Yu, Y.X. Huang, S.C. Shen, *Appl. Phys. Lett.* **55**, 2084 (1989)
276. A.V. Zastavnyi, V.M. Korol', A.N. Mikhaleva, V.D. Prozorovskii, *Sov. Phys. Semicond.* **13**, 580 (1979)
277. I.S. Zevenbergen, T. Gregorkiewicz, C.A.J. Ammerlaan, *Phys. Rev. B* **51**, 16746 (1995)



## EM Acceptor Spectra

---

### 7.1 Introduction

The first report of the absorption spectrum of acceptors in semiconductors is probably the paper by Burstein et al. [26], showing the LHeT transmission spectra of two p-type silicon samples. In one of these spectra, broad electronic lines, attributed to boron, could be seen at 0.034, 0.040 and 0.043 eV while in the other, from a nominally undoped sample, lines near 0.055 and 0.06 eV were observed, now known to be due to the aluminium acceptor. Since then, many acceptors have been identified in silicon and other semiconductor crystals and with the same technological incentive as for donors, their optical spectroscopy has been widely used to characterize them, evaluate their concentrations, provide physical insight into the *VB* structures of the crystals and more recently evaluate the effect of impurity isotope broadening in quasi-monoisotopic crystals.

Single substitutional acceptors at a given crystal site are atoms of the column of the periodic table preceding that of the atom they replace (e.g., group-III atoms in group-IV crystals). The position of the double acceptors in the periodic table is determined in a similar manner (e.g., group-II atoms in group-IV crystals). At a difference with donors, a few triple acceptors, like Cu in germanium, have been identified in semiconductors. Besides the well-defined isolated shallow acceptors, residual acceptor complexes involving C, O and H, some TMs and pseudo-acceptors (the counterpart of the pseudo-donors discussed in Sect. 6.6) have also produced EM acceptor spectra which are discussed in this chapter.

The electrical and optical activity of acceptors as a function of their charge state and of the electrical compensation of the semiconductor can be derived in the same way as what has been described for donors. Also, in all semiconductors and insulators, many of the spectroscopic properties of the hydrogen-like acceptors are determined by the energy structure of the *VB* maximum, located at  $\mathbf{k} = 0$ . There is no strict equivalent of the Fano resonances observed for donors in crystals with several equivalent *CB* minima in *k* space, but discrete

hole transitions accompanied by the emission of 1, 2, 3, ...,  $N$  zone-centre phonons superimposed on the photoionization spectrum have been observed in the acceptor spectra. Related oscillatory photoconductivity has been, for instance, reported in the p-type InSb by Engeler et al. [54] and in the p-type germanium by Benoit à la Guillaume and Cernogora [19].

In this chapter, the experimental results of the acceptor absorption spectra are presented. We follow the same sequence as in Chap. 6, beginning with acceptors in group-IV crystals and extending later to compound materials. For the donor spectra, a pseudo-atomic notation of the lines could be established relatively quickly. On the contrary, for the acceptor spectra, whose interpretation was essentially more difficult, notations varied from one material to the other, and I have taken some time, especially in the case of silicon, to try to establish a correlation between the lines and their spectroscopic attributions.

## 7.2 Group-III Acceptors in Group-IV Crystals

### 7.2.1 Silicon

We now have an acceptable insight into the acceptor absorption spectroscopy in silicon. It is based on high-quality experiments supplemented by the results of the acceptor level calculations presented in Sect. 5.3. The acceptor ground state is  $1\Gamma_8^+$  where the  $+$  superscript represents an even-parity state. This level is fourfold degenerate and can be split into two Kramers doublets by a uniaxial stress. In  $^{\text{nat}}\text{Si}$ , a small splitting of this ground state was observed by different techniques, the best evidence being given by high-resolution PL of the acceptor bound exciton (for a short summary, see [93]). These splittings for B, Al, Ga, and In in  $^{\text{nat}}\text{Si}$  are 5.3, 12, 12, and  $20\mu\text{eV}$  (0.043, 0.10, 0.10, and  $0.16\text{cm}^{-1}$ ), respectively, and they are too small to be detected by IR absorption spectroscopy because the FWHMs are larger than these values. Jahn-Teller effect was put forward to explain this splitting before the completion of the same high-resolution PL measurements with qmi  $^{28}\text{Si}$  samples. In these qmi samples, no splitting was detected, showing that it was actually due to the effect of the randomness of the  $^{\text{nat}}\text{Si}$  isotopic contribution [93]. The natural isotopic distribution would lower the symmetry at the acceptor site and produce the observed splitting, but up to now, no calculation to this effect has been published.

In the acceptor spectra, a distinction is made between the  $p_{3/2}$  spectrum due to transitions between the  $1\Gamma_8^+$  ground state and the excited states associated with the  $\Gamma_8^+$  VB (pseudo-angular momentum  $J = 3/2$ ) and the  $p_{1/2}$  spectrum, at higher energy, associated with the same ground state and excited states associated with the  $\Gamma_7^+$  VB (pseudo-angular momentum  $J = 1/2$ ). The ionization energy of the  $p_{3/2}$  spectra corresponds to the thermal ionization energy of the acceptors and it is lower than that of the  $p_{1/2}$  spectra.

### 7.2.1.1 The $p_{3/2}$ Spectra

Because of the large differences between the ionization energies of the group-III acceptors in silicon, their  $p_{3/2}$  spectra are observed between 30 and 230 meV, and the IR-allowed absorption transitions usually extend over  $\sim 15$  meV below the ionization energy of the acceptor. Presently, over 40 lines have been observed in the B absorption spectrum and about 30 in the Al, Ga and In spectra. In the early times, the attribution of their final states to specific levels was not possible in the absence of accurate calculation of the energy levels, and the observed acceptor lines in silicon were labelled by integers increasing with their energy positions [41]. Further spectra showed that some lines had been overlooked and rather than modifying the labelling, letters were added to the number with eventual changes. This led to some inconsistencies (4A line, observed before line 4B in boron, is at a higher energy, while the order is reversed for gallium). To avoid the extra letters, Lewis et al. [108] relabelled *ab initio* the boron transitions they observed, being aware that with the improvement of the measurement techniques, this labelling was provisional for the lines near from the continuum. The correspondence between the different numberings (Numberings 1, 2, 3, and 4 of Table 7.1) is given for the comparison of the spectra from different origins.

A boron spectrum in  $^{\text{nat}}\text{Si}$  is displayed in Fig. 7.1a, where lines 1, 2, and 4, 5 are truncated, and Fig. 7.1b shows these lines on extended horizontal and vertical scales [82]. A comparison with the OSs of Table 5.22 indicates that the final states of lines 1, 2, 3, 4, 5 and 6 are the  $1\Gamma_8$ ,  $2\Gamma_8$ ,  $3\Gamma_8$ ,  $1\Gamma_6$ ,  $1\Gamma_7$ , and  $4\Gamma_8$  states, respectively (level ordering of Binggeli and Baldereschi [21]).

The less intense h-e boron lines are displayed in Fig. 7.2 and it also allows one to follow the numbering used in Fig. 7.1a. In the spectrum of Fig. 7.2, the sharpest boron lines, like line 7, have FWHMs  $\sim 0.2 \text{ cm}^{-1}$  ( $\sim 25 \mu\text{eV}$ ), taking into account the instrumental resolution.

The positions of the first absorption lines observed for group-III acceptors are given in Table 7.2. In this table, the lines are labelled using numbering 4 of Table 7.1. The correspondence between the numbers and the final states of the transitions is based on the calculated level ordering given by Binggeli and Baldereschi [21] and on the OSs of the transitions. For lines at higher energies, because of the crowding of the transitions, there cannot be a one-to-one correspondence between the indexed lines and the transitions. As for the donor centres, the choice of the calculated energy of a reference acceptor level, associated with a well-identified transition allows determination of semi-experimental spectroscopic values of the ionization energies and also of the binding energies of the excited states of the transitions observed with respect to the VB. For boron, it has been argued that because of the different scalings between the calculated energies and the line spacings, a selected fitting of several calculated energies to the corresponding experimental transitions was preferable [108]. By construction, this method gives a perfect agreement between the calculated and semi-experimental values for the lines used for

**Table 7.1.** Position (meV) at LHeT and correspondence between the different numberings (Number) of the first boron lines in <sup>nat</sup>Si obtained from different experiments

| Ramdas and<br>Rodriguez [143] |          | Fischer and Rome [59] |          | Lewis et al. [108] |          | Pajot,<br>unpublished |                      |
|-------------------------------|----------|-----------------------|----------|--------------------|----------|-----------------------|----------------------|
| Number.                       | Position | Number.               | Position | Number.            | Position | Number.               | Position             |
| 1                             |          | 2                     |          | 3                  |          | 4                     |                      |
| 1                             | 30.38    | 1                     | 30.37    | 1                  | 30.371   | 1                     | 30.369               |
| 2                             | 34.53    | 2                     | 34.49    | 2                  | 34.510   | 2                     | 34.505               |
| 3                             | 38.35    | 3                     | 38.35    | 3                  | 38.378   | 3                     | 38.374               |
| 4                             | 39.6     | 4                     | 39.59    | 4                  | 39.67    | 4                     | 39.601               |
| 4B                            | 39.68    | 4B                    | 39.67    | 5                  |          | 5                     | 39.679               |
| 4A                            | 39.92    | 4A                    | 39.91    | 6                  | 39.93    | 6                     | 39.913               |
| 5                             | 41.52    | 5                     | 41.47    | 7                  | 41.474   | 7                     | 41.473               |
|                               |          | 6A                    | 41.91    | 8                  | 41.913   | 8                     | 41.913               |
|                               |          | 6B                    | 42.06    | 9                  | 42.060   | 9                     | 42.047               |
| 6                             | 42.19    | 6                     | 42.16    | 10                 | 42.168   | 10                    | 42.166               |
|                               |          | 7                     | 42.41    | 11 <sup>†</sup>    | 42.423   | 11                    | 42.409               |
| 7                             | 42.79    | 8                     | 42.74    | 12                 | 42.716   | 12                    | 42.7166 <sup>a</sup> |
|                               |          |                       |          | 13                 | 42.761   | 13                    | 42.7480 <sup>a</sup> |
|                               |          | 8A                    | 42.92    | 14                 | 42.922   | 14                    | 42.936               |
|                               |          | 9A                    | 43.16    | 15                 | 43.169   | 15                    | 43.166               |
| 8                             | 43.27    | 9                     | 43.24    | 16                 | 43.282   | 16                    | 43.277               |
|                               |          |                       |          |                    |          | 17                    | 43.305 <sup>a</sup>  |
|                               |          |                       |          | 17 <sup>‡</sup>    | 43.378   |                       |                      |
|                               |          |                       |          | 18                 | 43.454   |                       |                      |
|                               |          | 10A                   | 43.49    | 19                 | 43.522   | 18                    | 43.479               |
|                               |          | 10B                   | (43.64)  | 20                 | 43.616   | 19                    | 43.613               |
|                               |          | 10                    | 43.71    | 21                 | 43.729   | 20                    | 43.72                |
|                               |          | 10C                   | 43.78    | 22                 | 43.793   | 21                    | 43.800               |
| 9                             | 43.86    |                       |          | 23                 | 43.865   | 22                    | 43.867               |
|                               |          | 10D                   | 43.95    | 24                 | 43.965   | 23                    | 43.959               |
|                               |          |                       |          |                    |          | 24                    | 44.10                |
|                               |          | 11B                   | (44.20)  |                    |          | 25                    | 44.167               |
|                               |          |                       |          |                    |          | 26                    | 44.24                |
|                               |          | 11                    | 44.27    |                    |          | 27                    | 44.260               |
| 10                            | 44.32    |                       |          |                    |          | 28                    | 44.344               |
|                               |          |                       |          | 25                 | 44.408   | 29                    | 44.442               |

Unless otherwise specified, the lines of the acceptor spectra in silicon are labelled later using numbering 4. As other weak or blended lines have been observed or separated in qmi silicon, modifications to numbering 4 is expected in the range of line 20 and above when considering the qmi spectra

<sup>a</sup> Steger and Thewalt, private communication, <sup>‡</sup> Blended with  $3p_{\pm}$  (P), <sup>§</sup>  $4p_{\pm}$  (P)

the fit, but a better agreement is not a goal in itself and differences can lead to central-cell corrections. It is true, especially for acceptors that the semi-experimental energy values depend on the choice of the reference transition, but by choosing reference lines with sufficiently EM-like excited states, the

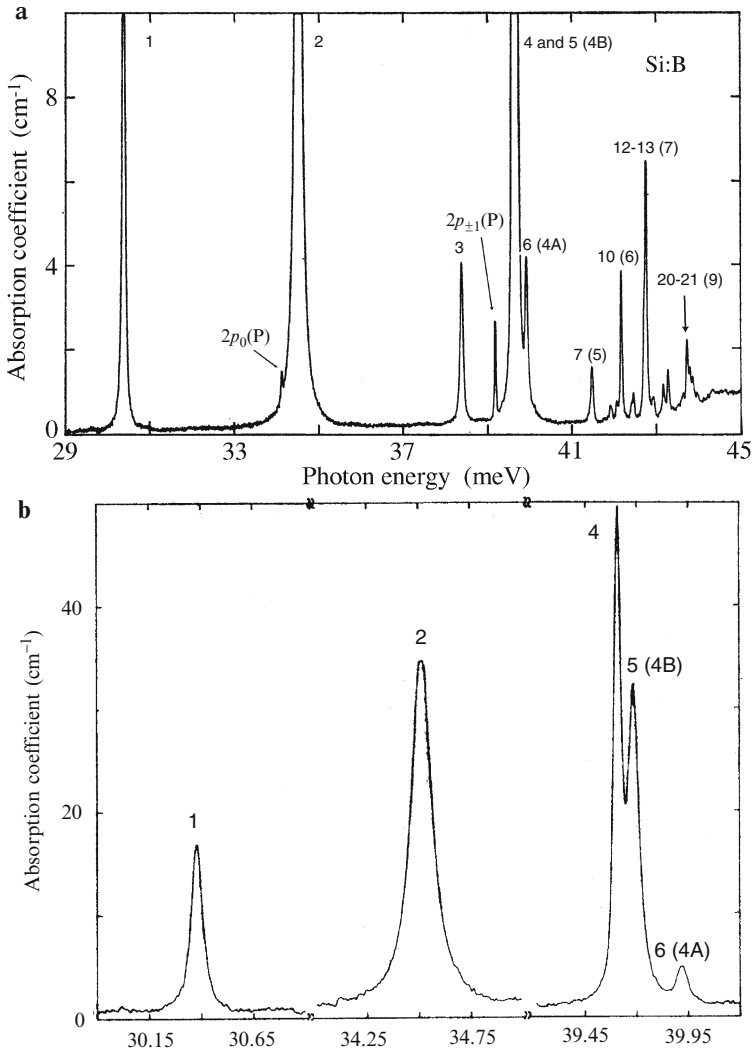


**Fig. 7.1.** (a) Absorption spectrum at LHeT of  $p_{3/2}(B)$  between  $234$  and  $363\text{ cm}^{-1}$  in a  $^{\text{nat}}\text{Si}$  sample with  $[B] = 8.5 \times 10^{14}\text{ cm}^{-3}$ . P donor lines are also observed because band-gap radiation reaches the sample. (b) Lines 1, 2 and 4, 5, 6 of B on an expanded scale in the same sample with a reduced thickness [82]. Numbering 1 is given in parentheses. For the attributions, see Table 7.2. Copyright 1981 by the American Physical Society

energy dispersion is small: while it is  $0.52\text{ meV}$  for lines 1–5, it reduces to  $0.15\text{ meV}$  for lines 6–15. Line 14, observed in the four acceptor spectra, is reasonably sharp and its excited state has been identified as  $8\Gamma_8^-$  by Binggeli and Baldereschi [21], with a calculated energy of  $2.67\text{ meV}$ , and as  $9\Gamma_8^-$  by

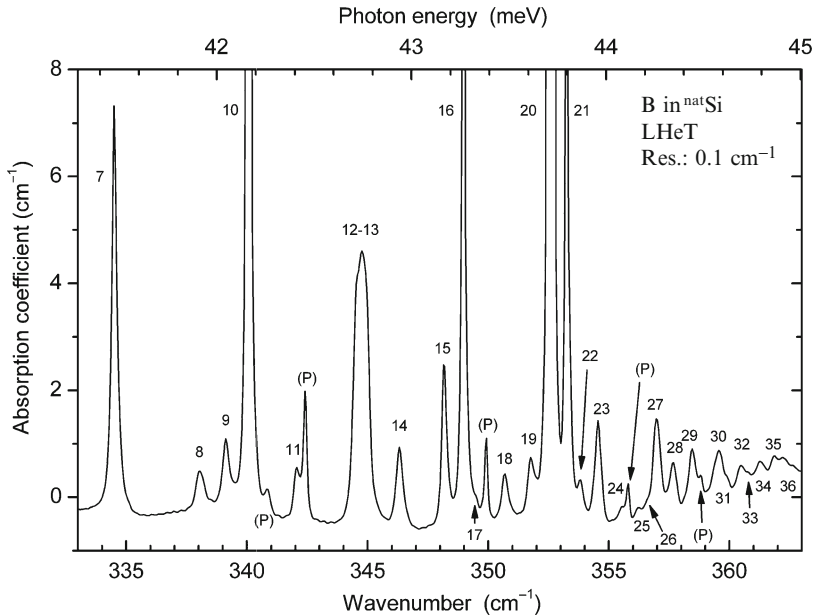


**Fig. 7.2.** Part of the  $p_{3/2}(\text{B})$  absorption spectrum at LHeT in a  $^{\text{nat}}\text{Si}$  FZ sample with  $[\text{B}] \sim 10^{15} \text{ cm}^{-3}$  at a resolution of  $0.1 \text{ cm}^{-1}$  ( $12.4 \mu\text{eV}$ ). P lines are also observed because of the band-gap illumination of the sample

Beinikhes et al. [18], with a calculated energy of 2.71 meV. The average calculated value of the energy of the excited state of line 14 (2.69 meV) is added to its measured position to obtain the optical ionization energy  $E_{\text{io}}$  of the group-III acceptors in silicon. The excited state of line 11, identified as  $7\Gamma_8^-$ , has been used before as the reference level to obtain  $E_{\text{io}}$  [132], but in most boron spectra, this line is rather close to the  $3p_{\pm 1}(\text{P})$  line of residual P while line 14 is well isolated and more intense.

The positions of higher energy lines 31, 32, 33, 34, 35, and 36 of the boron spectrum of Fig. 7.2 are 44.62, 44.70, 44.73, 44.80, 44.87, and 44.91 meV (359.9, 360.5, 360.8, 361.3, 361.9, and 362.2  $\text{cm}^{-1}$ ), respectively.

By comparison, the value of  $E_{\text{io}}$  for boron obtained by Lewis et al. [108] with a curve-fitting method is  $\sim 45.6 \text{ meV}$ , depending slightly on the origin of the calculated values. The values of  $E_{\text{io}}$  of Table 7.2 obtained from the method indicated in the title are close to those given by Ramdas and Rodriguez [143] (45.71, 70.18, 74.05, and 156.90 meV for B, Al, Ga, and In, respectively), except for  $E_{\text{io}}(\text{Al})$  because of the resonant broadening of line 4 (Al) used as a reference by these authors. The values of Fischer and Rome [59], determined empirically from a value of  $E_{\text{io}}(\text{B})$ , are  $\sim 1.3 \text{ meV}$  lower.

The Tl spectrum in silicon at LHeT shows only four resolved lines or features at 1877, 1907, 1948, and 1968  $\text{cm}^{-1}$  (232.7, 236.4, 241.5, and 244.0 meV) attributed to lines 1, 2, (4,5,6) and probably (7,8,9), respectively, of the Tl acceptor spectrum, and a shoulder at 1937  $\text{cm}^{-1}$  (240 meV) attributed to line

**Table 7.2.** Positions (meV (cm<sup>-1</sup> in parentheses)) at LHeT of lines of the  $p_{3/2}$  spectrum of group-III acceptors in <sup>nat</sup>Si

| Line | Attribution                   | B <sup>a</sup>                  | Al <sup>b</sup>               | Ga <sup>c</sup>    | In <sup>b</sup>      |
|------|-------------------------------|---------------------------------|-------------------------------|--------------------|----------------------|
| 1    | 1Γ <sub>8</sub> <sup>-</sup>  | 30.3694<br>(244.946)            | 54.910<br>(442.88)            | 58.24              | 142.020<br>(1145.47) |
| 2    | 2Γ <sub>8</sub> <sup>-</sup>  | 34.5042<br>(278.295)            | 58.534<br>(472.10)            | ~61.7 <sup>†</sup> | 145.792<br>(1175.89) |
| 3    | 3Γ <sub>8</sub> <sup>-</sup>  | 38.3770<br>(309.531)            |                               | 67.13              | 149.784<br>(1208.09) |
| 4    | 1Γ <sub>6</sub> <sup>-</sup>  | 39.5973<br>(319.374)            | 64.09<br>(516.9) <sup>†</sup> | 67.97              | 150.813<br>(1216.39) |
| 5    | 1Γ <sub>7</sub> <sup>-</sup>  | 39.6789<br>(320.032)            | 64.997<br>(524.24)            | 68.26              | 151.088<br>(1218.61) |
| 6    | 4Γ <sub>8</sub> <sup>-</sup>  | 39.9118<br>(321.910)            | 65.187<br>(525.77)            | 68.44              | 151.16<br>(1219.2)   |
| 7    | 5Γ <sub>8</sub> <sup>-</sup>  | 41.4748<br>(334.517)            | 66.351<br>(535.16)            | 69.95              | 152.786<br>(1232.30) |
| 8    | 2Γ <sub>6</sub> <sup>-</sup>  | ±41.9119<br>(338.042)           |                               |                    |                      |
| 9    | 6Γ <sub>8</sub> <sup>-</sup>  | ±42.0494<br>(339.151)           | 66.75<br>(538.4)              | [70.40]            | 153.29<br>(1236.44)  |
| 10   | 2Γ <sub>7</sub> <sup>-</sup>  | 42.1602<br>(340.045)            | 66.82<br>(538.9)              | 70.51              | 153.390<br>(1237.17) |
| 11   | 7Γ <sub>8</sub> <sup>-</sup>  | 42.409<br>(342.05)              | 67.095<br>(541.16)            | 70.79              | 153.647<br>(1239.25) |
| 12   | 3Γ <sub>6</sub> <sup>-</sup>  | 42.7180<br>(344.544)            | 67.400<br>(543.62)            | 71.13              | 153.987<br>(1241.99) |
| 13   | 3Γ <sub>7</sub> <sup>-</sup>  | 42.7540<br>(344.834)            | 67.475<br>(544.22)            |                    |                      |
| 14   | 8Γ <sub>8</sub> <sup>-</sup>  | 42.9361<br>(346.303)            | 67.67<br>(545.8)              | 71.35              | 154.210<br>(1243.79) |
| 15   | 4Γ <sub>6</sub> <sup>-</sup>  | 43.1677<br>(348.171)            | 67.83<br>(547.1)              | [71.53]            | 154.43<br>(1245.6)   |
| 16   | 4Γ <sub>7</sub> <sup>-</sup>  | 43.2683<br>(348.982)            | 67.911<br>(547.74)            | 71.62              | 154.50<br>(1246.0)   |
| 17   | 10Γ <sub>8</sub> <sup>-</sup> | 43.305<br>(349.28) <sup>b</sup> |                               |                    |                      |
| 18   | 11Γ <sub>8</sub> <sup>-</sup> | 43.4799<br>(350.689)            | 68.139<br>(549.58)            | 71.85              | 154.715<br>(1247.86) |
| 19   | 5Γ <sub>6</sub> <sup>-</sup>  | 43.6116<br>(351.751)            | 68.354<br>(551.31)            |                    | 154.87<br>(1249.1)   |
| 20   | 5Γ <sub>7</sub> <sup>-</sup>  | 43.7160<br>(352.593)            | 68.437<br>(551.98)            | 72.07              | 154.938<br>(1249.66) |
| 21   | 6Γ <sub>6</sub> <sup>-</sup>  | 43.7985<br>(353.259)            | 68.519<br>(552.64)            | [72.13]            | 155.02<br>(1250.3)   |
| 22   | 6Γ <sub>7</sub> <sup>-</sup>  | ±43.8714<br>(353.847)           | 68.603<br>(553.32)            |                    | 155.10<br>(1251.0)   |

(continued)

**Table 7.2.** (continued)

| Line     | Attribution       | B <sup>a</sup>                  | Al <sup>b</sup>    | Ga <sup>c</sup> | In <sup>b</sup>      |
|----------|-------------------|---------------------------------|--------------------|-----------------|----------------------|
| 23       | $7\Gamma_7^-$     | 43.9616<br>(354.574)            | 68.727<br>(554.32) | 72.31           | 155.192<br>(1251.71) |
| 24       | $17\Gamma_8^-$    | 44.0868<br>(355.584)            | 68.84<br>(555.2)   | [72.44]         | 155.332<br>(1252.84) |
| 25       | $8\Gamma_6^{-*}$  | 44.167<br>(356.23) <sup>b</sup> | 68.90<br>(555.7)   | [72.52]         | 155.44<br>(1253.7)   |
| 26       | $18\Gamma_8^{-*}$ | 44.24<br>(356.8) <sup>‡b</sup>  | 72.62              | 72.62           | 155.49<br>(1254.1)   |
| 27       | $9\Gamma_7^-$     | 44.2692<br>(357.055)            | 68.986<br>(556.41) |                 |                      |
| 28       | $10\Gamma_6^-$    | 44.3444<br>(357.662)            | 69.096<br>(557.30) |                 | 155.57<br>(1254.8)   |
| 29       |                   | 44.4446<br>(358.470)            | 69.212<br>(558.23) |                 | 155.69<br>(1255.7)   |
| 30       |                   | 44.56<br>(359.4) <sup>b</sup>   |                    |                 | 155.79<br>(1256.5)   |
| $E_{io}$ | $1\Gamma_8^+$     | 45.63                           | 70.36              | 74.04           | 156.90               |

The attributions of the final states of the transitions are those of [161] except those with an asterisk. They are derived from the energy levels of the last two columns of Table 5.15 [21]. The accuracy of the positions for Ga is  $\pm 0.02$  meV and  $\pm 0.05$  for the values in brackets. The optical ionization energy  $E_{io}$  is obtained by adding 2.69 meV to the position of line 14

<sup>a</sup> [161], <sup>b</sup> Pajot, unpublished, <sup>c</sup> [59], <sup>±</sup> Reduced accuracy, <sup>†</sup> Phonon broadened, <sup>‡</sup> Not resolved from 27

3 [153]. When adding to the energy of line 2 (Tl) 11.1 meV, the energy separation of lines 2(B) or 2(In) from the VB, an ionization energy  $E_{io}$  (Tl) of 247.5 meV is obtained, close to that of 246 meV given in the original reference.

In the boron absorption spectrum, a line at 22.77 meV has been reported for [B]  $\approx 10^{17}$  cm<sup>-3</sup> and it has been attributed to a parity-forbidden transition between the  $1\Gamma_8^+$  state and the  $1\Gamma_7^+$  state associated with the  $\Gamma_7^+$  VB (Chandrasekhar et al. [32]). This transition, which represents the boron spin-orbit splitting  $\Delta_{so}^B$  in silicon (see Fig. 5.2), is Raman-allowed and it has been observed by Raman scattering [190]. The energies of some even- and odd-parity acceptor states in silicon have been determined from the two-hole bound exciton (BE) PL spectra [111, 171]. Knowing  $E_{io}$ , the shift  $E$  between the energy of the principal BE (PBE) line leaving the acceptor in its ground state  $1\Gamma_8^+$  and that of the BE leaving the acceptor in an excited state is the equivalent of a transition energy between the two states. In silicon, the most intense two-hole BE PL lines are the TO-phonon-assisted lines. Most of these lines correspond to even-parity excited states, but a few odd-parity states are also considered: for boron,  $E(1\Gamma_8^-)$  and  $E(2\Gamma_8^-)$  obtained from these experiments are 30.42 and 34.54 meV, respectively [171], and they compare



**Table 7.3.** Comparison between the calculated energies (meV) of even-parity acceptor levels in silicon and the experimental ones deduced from absorption, PL and Raman scattering experiments

| Level <sup>a</sup> | B                  |                                      | Al                 |                   | Ga                 |                   | In                 |                      |
|--------------------|--------------------|--------------------------------------|--------------------|-------------------|--------------------|-------------------|--------------------|----------------------|
|                    | calc. <sup>a</sup> | Exp. <sup>b</sup>                    | calc. <sup>b</sup> | Exp. <sup>b</sup> | calc. <sup>b</sup> | exp. <sup>b</sup> | calc. <sup>b</sup> | Exp. <sup>b</sup>    |
| $1\Gamma_7^+$      | 21.94              | 22.86 <sup>c</sup>                   | 56.72 <sup>a</sup> | $\sim 55^d$       |                    | $\sim 60^d$       |                    | 152.7 <sup>d,e</sup> |
| $2\Gamma_8^+(0)$   | 13.34              | $13.44 \pm 0.1$<br>13.3 <sup>f</sup> | 17.22 <sup>a</sup> |                   | 16.94              |                   | 20.65              | $19.22 \pm 0.5$      |
| $3\Gamma_8^+(2)$   | 6.35               | $6.38 \pm 0.1$                       | 7.14               | $6.11 \pm 0.3$    | 7.34               | $6.58 \pm 0.15$   | 8.26               | $8.12 \pm 0.3$       |
| $4\Gamma_8^+(2)?$  | 3.75               | $3.85 \pm 0.15$                      | 4.06               | $3.78 \pm 0.15$   | 4.14               | $4.02 \pm 0.15$   | 4.52               | $4.48 \pm 0.3$       |
| $5\Gamma_8^+(2)?$  | 2.7 <sup>b</sup>   | $2.7 \pm 0.2$                        | 2.6                | $2.6 \pm 0.2$     | 2.62               | $2.78 \pm 0.2$    | 2.82               | $2.59 \pm 0.3$       |

<sup>a</sup> [24], <sup>b</sup> [111], <sup>c</sup> After [32], <sup>d</sup> After [152], <sup>e</sup> After [154], <sup>f</sup> [164]

with the energies of lines 1 and 2 of Table 7.2. A Fano resonance due to an even-parity state has also been observed by Suezawa et al. [164]. The relevant energies of the first even-parity states of B, Al, Ga and In in silicon with respect to the  $VB$  obtained from such experiments and from calculations are given in Table 7.3.

In P-compensated In-doped silicon, an absorption line at  $1213\text{ cm}^{-1}$  ( $150.4\text{ meV}$ ) is observed at LHeT under TEC [135]. The vanishing of this line<sup>1</sup> when the compensating donor is neutralized suggests that it could be a parity-forbidden transition. Its excited-state binding energy of  $6.5\text{ meV}$  makes the attribution to a  $2\Gamma_7^+$  level plausible.

The acceptor spin-orbit splitting  $\Delta_{\text{so}}^A = 1\Gamma_8^+ - 1\Gamma_7^+$  is  $22.77$ ,  $\sim 15$ ,  $\sim 14$ , and  $4.1\text{ meV}$  for B, Al, Ga, and In, respectively and this decrease has been discussed by Schroth et al. [152]. One consequence of the moderate splitting for In is that transitions from the  $1\Gamma_7^+$  state could be observed for this acceptor at moderate temperatures ( $\sim 30\text{--}40\text{ K}$ ) about  $4\text{ meV}$  below the  $p_{3/2}$  spectrum of In.

The line widths of some acceptor lines in silicon show an anomalous broadening due to resonant interaction with phonons. This is the case for line 2(Ga), whose severe broadening is due to the interaction with the  $O(\Gamma)$  phonon at  $65.0\text{ meV}$  at LHeT. This effect, which is very strong, as can be judged from Fig. 7.3, has been discussed by Chandrasekhar et al. [32].

The  $p_{3/2}$  spectrum of Al in silicon in the  $60\text{ meV}$  spectral region also shows evidence of the interaction of electronic transitions with the  $O(\Gamma)$  phonon of the silicon lattice, as seen in Fig. 7.4, where part of the broadening of lines 2 and 4, and the absence of line 3, are due to this interaction. The absorption profiles of lines 1 and 2 of the  $p_{3/2}$  Al spectrum seem to depend on the

<sup>1</sup> This line was reported at  $150.38 \pm 0.06\text{ meV}$  as an elbow of line 4(In) in Onton's thesis [131].

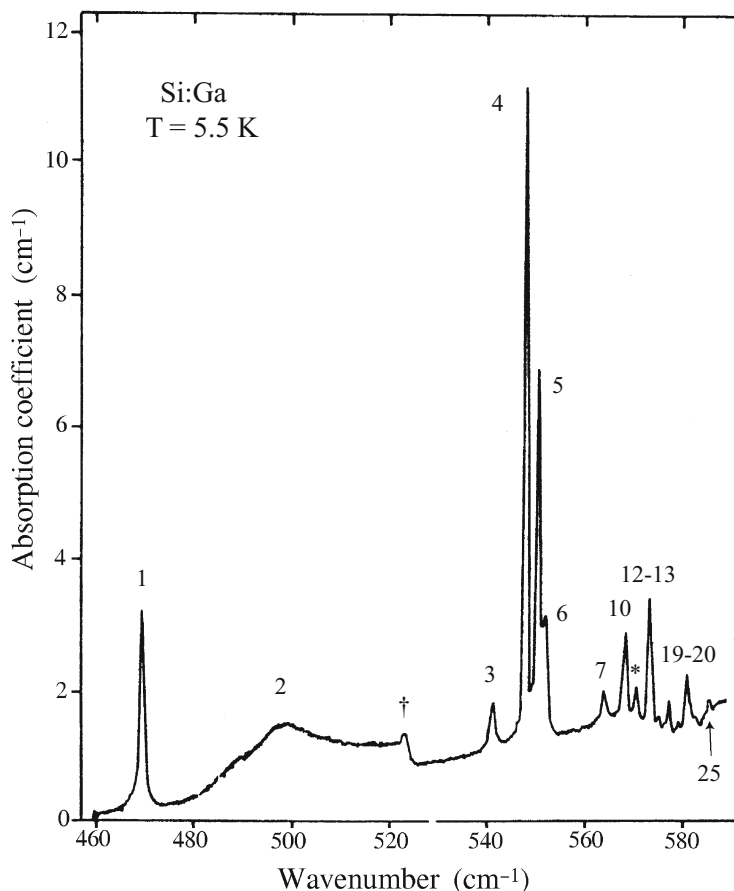


**Fig. 7.3.** Absorption spectrum of  $p_{3/2}(\text{Ga})$  between 57 and 73 meV in a  $^{\text{nat}}\text{Si}$  sample with  $[\text{Ga}] \sim 1 \times 10^{15} \text{ cm}^{-3}$ . It shows the anomalous broadening of line 2 by interaction with the  $\text{O}(\Gamma)$  phonon. The dagger denotes a component of line 2 split by the interaction and very close to the energy of the  $\text{O}(\Gamma)$  phonon of silicon (after [59])

illumination conditions of the sample and this effect has not been elucidated. This resonant interaction also has some influence on the positions of the lines.

The FWHMs of lines 1 and 2 of the  $\text{Al}$  spectrum of Fig. 7.4 are  $\sim 0.14$  and  $0.21 \text{ meV}$  ( $\sim 1.1$  and  $1.7 \text{ cm}^{-1}$ ), respectively, compared to  $\sim 0.06 \text{ meV}$  ( $\sim 0.5 \text{ cm}^{-1}$ ) for the sharpest line of this spectrum. By comparison with the Ga and In spectra, the complete spectrum of indium in silicon, without any resonant broadening is shown in Fig. 7.5. In this spectrum, as in the  $\text{Al}$  spectrum, some of the highest-energy transitions are identified as unresolved doublets or shoulders. The lines of the  $\text{Al}$  and Ga spectra are superimposed on the 2-phonon spectrum of silicon and the In spectrum on the 3-phonon spectrum,

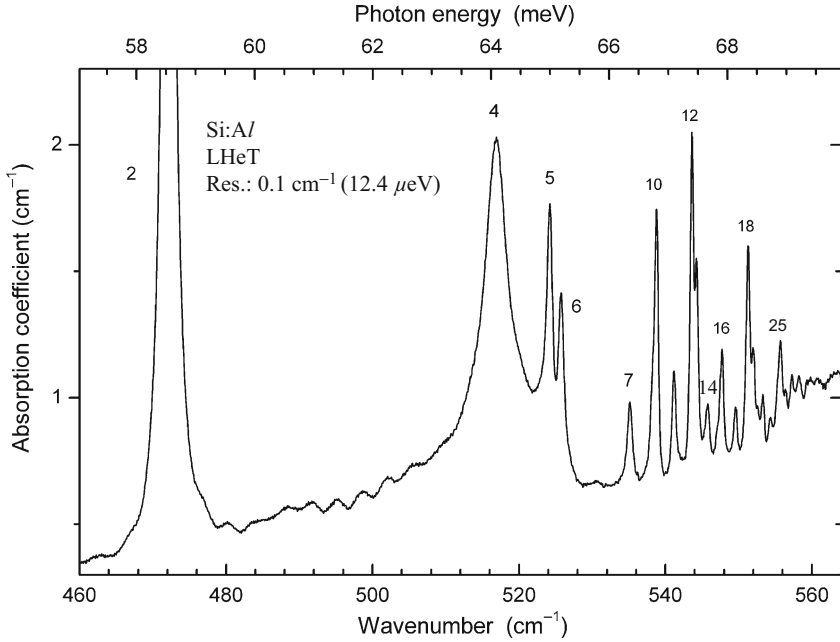


**Fig. 7.4.** Part of the absorption spectrum of  $p_{3/2}(\text{Al})$  in a FZ  $^{\text{nat}}\text{Si}$  sample with  $[\text{Al}] \sim 10^{15} \text{ cm}^{-3}$ . The peak absorption coefficients of lines 1 (not shown) and 2 are  $2.8$  and  $\sim 6 \text{ cm}^{-1}$ , respectively, and line 3 is absent

and this contributes to a general broadening of the electronic lines. This is why some lines observed in the boron spectrum are not observed in the other acceptor spectra, making line numbering and attributions a delicate task. For instance, line 8(B) does not seem to have an equivalent in the other acceptor spectra and the peak attributed to line 13 in the In spectrum should correspond to the 12–13 doublet in the boron spectrum.

On an expanded scale, the In lines of Fig. 7.5 show a low-frequency asymmetry indicating a possible residual inhomogeneous Stark effect, so that better spectra could in principle be obtained.

Table 7.4 gives a comparison of the measured spacings, between line 14 and the other lines of the boron, aluminium, gallium, and indium spectra, and the corresponding spacings, derived from calculations based on the attributions of Table 7.2. The choice of the correspondence has been made by considering first the similarity between the spacings and subsequently, the calculated OSs.

In Table 7.4, the differences between the experimental values for Al and Ga for the first lines compared to B and In can be attributed to the above-mentioned phonon resonances. There are also non-negligible differences between the measured and calculated spacings as well as between the calculated spacings for the deepest levels. As already mentioned, it is possible to use a self-consistent method to obtain experimental acceptor energy levels in

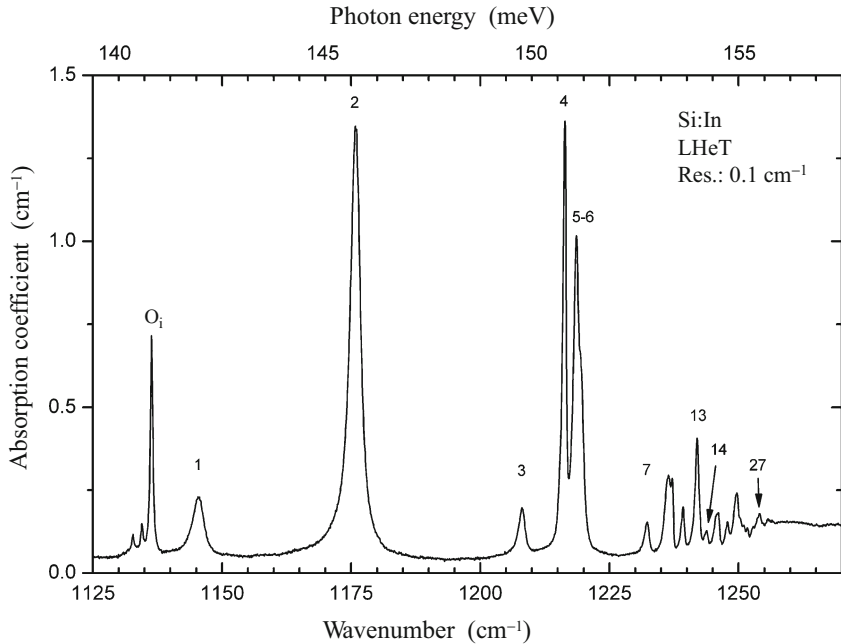


**Fig. 7.5.** Absorption spectrum obtained under band-gap light illumination of  $p_{3/2}(\text{In})$  in a FZ  $^{\text{nat}}\text{Si}$  sample. The estimated value of  $[\text{In}]$  is  $4 \times 10^{15} \text{ cm}^{-3}$ . The vibrational absorption of residual  $\text{O}_i$  is observed near  $1136 \text{ cm}^{-1}$

agreement with the calculated ones [108], but the physical meaning of such an agreement seems limited as the differences between the calculated and experimental levels are more fundamental. Even without resonant interaction with phonons, the widths of the acceptor lines are not uniform. FWHMs of some of the lines of the B and In spectra in  $^{\text{nat}}\text{Si}$  are given in Table 7.5.

Recent measurements on high-purity  $^{\text{nat}}\text{Si}$  show that for boron, the FWHMs decrease to  $\sim 0.2 \text{ cm}^{-1}$  ( $25 \mu\text{eV}$ ) for some of the higher energy lines. For Al and In, the FWHMs also show some decrease with increasing line energies. Part of this broadening results from some kind of inhomogeneous broadening due to isotopic disorder.

Absorption experiments have been performed with qmi silicon B-doped samples. They show a small increase of the line positions with the Si isotope mass, already observed for the P donor lines, which is due to the increase of  $E_g$  with the Si isotope mass. For line 1 ( $1\Gamma_8^-$ ), the estimated shift between qmi  $^{28}\text{Si}$  and  $^{30}\text{Si}$  is  $+0.26 \text{ cm}^{-1}$  ( $+33 \mu\text{eV}$ ), and it reaches  $+0.38 \text{ cm}^{-1}$  ( $+47 \mu\text{eV}$ ) for line 13 ( $3\Gamma_7^-$ ). The corresponding IS for  $E_{i0}(\text{B})$ , is about  $+0.41 \text{ cm}^{-1}$  or  $+51 \mu\text{eV}$  [161]. These measurements also show that while no sharpening with respect to the FWHMs in natural silicon is observed for some lines like 1, 5, 7, and 8, the FWHMs of other lines can be reduced by an order of magnitude in qmi silicon. With this reduction of the FWHM, a splitting due to the presence

**Table 7.4.** Comparison of the measured separations (meV) between line 14 and other lines of Table 7.2 with spacings derived from the calculations by (a) Beinhikes et al. [18] and (b) [21]. The energy level of line 14 is taken as 2.69 meV

| Separ. | B     | Al    | Ga    | In    | Spacing <sup>a</sup>         | Calc. <sup>a</sup> | Spacing <sup>b</sup>         | Calc. <sup>b</sup> |
|--------|-------|-------|-------|-------|------------------------------|--------------------|------------------------------|--------------------|
| 14-1   | 12.57 | 12.76 | 13.11 | 12.19 | $9\Gamma_8^- - 1\Gamma_8^-$  | 13.08              | $8\Gamma_8^- - 1\Gamma_8^-$  | 13.07              |
| 14-2   | 8.43  | 9.14  | ~9.7  | 8.41  | $9\Gamma_8^- - 2\Gamma_8^-$  | 8.78               | $8\Gamma_8^- - 2\Gamma_8^-$  | 8.98               |
| 14-3   | 4.56  |       | 4.22  | 4.43  | $9\Gamma_8^- - 3\Gamma_8^-$  | 4.54               | $8\Gamma_8^- - 3\Gamma_8^-$  | 4.77               |
| 14-4   | 3.34  | 3.58  | 3.38  | 3.40  | $9\Gamma_8^- - 1\Gamma_7^-$  | 3.53               | $8\Gamma_8^- - 1\Gamma_6^-$  | 3.42               |
| 14-5   | 3.26  | 2.67  | 3.08  | 3.12  | $9\Gamma_8^- - 1\Gamma_6^-$  | 3.48               | $8\Gamma_8^- - 1\Gamma_7^-$  | 3.38               |
| 14-6   | 3.02  | 2.48  | 2.91  | 3.05  | $9\Gamma_8^- - 4\Gamma_8^-$  | 3.25               | $8\Gamma_8^- - 4\Gamma_8^-$  | 3.29               |
| 14-7   | 1.46  | 1.32  | 1.40  | 1.42  | $9\Gamma_8^- - 5\Gamma_8^-$  | 1.54               | $8\Gamma_8^- - 5\Gamma_8^-$  | 1.54               |
| 14-8   | 1.02  |       |       |       | $9\Gamma_8^- - 6\Gamma_8^-$  | 1.14               | $8\Gamma_8^- - 2\Gamma_6^-$  | 1.11               |
| 14-9   | 0.89  | 0.92  | 0.95  | 0.91  | $9\Gamma_8^- - 2\Gamma_6^-$  | 1.11               | $8\Gamma_8^- - 6\Gamma_8^-$  | 0.97               |
| 14-10  | 0.77  | 0.85  | 0.84  | 0.82  | $9\Gamma_8^- - 2\Gamma_7^-$  | 0.92               | $8\Gamma_8^- - 2\Gamma_7^-$  | 0.82               |
| 14-11  | 0.53  | 0.57  | 0.56  | 0.56  | $9\Gamma_8^- - 7\Gamma_8^-$  | 0.63               | $8\Gamma_8^- - 7\Gamma_8^-$  | 0.56               |
| 14-12  | 0.22  | 0.27  | 0.22  | 0.22  | $9\Gamma_8^- - 3\Gamma_6^-$  | 0.27               | $8\Gamma_8^- - 3\Gamma_6^-$  | 0.24               |
| 14-13  | 0.19  | 0.19  |       |       | $9\Gamma_8^- - 4\Gamma_7^-$  | 0.18               | $8\Gamma_8^- - 3\Gamma_7^-$  | 0.16               |
| 15-14  | 0.23  | 0.16  | 0.18  | 0.22  | $10\Gamma_8^- - 9\Gamma_8^-$ | 0.09               | $4\Gamma_6^- - 8\Gamma_8^-$  | 0.26               |
|        |       |       |       |       | $5\Gamma_7^- - 9\Gamma_8^-$  | 0.20               |                              |                    |
| 16-14  | 0.34  | 0.24  | 0.27  | 0.29  | $11\Gamma_8^- - 9\Gamma_8^-$ | 0.26               | $4\Gamma_7^- - 8\Gamma_8^-$  | 0.34               |
|        |       |       |       |       | $5\Gamma_6^- - 9\Gamma_8^-$  | 0.29               |                              |                    |
| 17-14  | 0.37  |       |       |       |                              |                    | $10\Gamma_8^- - 8\Gamma_8^-$ | 0.40               |
| 18-14  | 0.54  | 0.47  | 0.50  | 0.51  | $13\Gamma_8^- - 9\Gamma_8^-$ | 0.53               | $11\Gamma_8^- - 8\Gamma_8^-$ | 0.56               |
| 19-14  | 0.68  | 0.68  |       | 0.66  | $6\Gamma_6^- - 9\Gamma_8^-$  | 0.63               | $5\Gamma_6^- - 8\Gamma_8^-$  | 0.69               |
|        |       |       |       |       | $6\Gamma_7^- - 9\Gamma_8^-$  | 0.66               |                              |                    |
| 20-14  | 0.78  | 0.77  | 0.72  | 0.73  | $14\Gamma_8^- - 9\Gamma_8^-$ | 0.75               | $12\Gamma_8^- - 8\Gamma_8^-$ | 0.79               |
|        |       |       |       |       | $7\Gamma_6^- - 9\Gamma_8^-$  | 0.78               |                              |                    |
| 21-14  | 0.87  | 0.85  | 0.78  | 0.81  | $15\Gamma_8^- - 9\Gamma_8^-$ | 0.82               | $13\Gamma_8^- - 8\Gamma_8^-$ | 0.83               |
|        |       |       |       |       |                              |                    | $5\Gamma_7^- - 8\Gamma_8^-$  | "                  |
| 22-14  | 0.93  | 0.93  |       | 0.89  |                              |                    | $6\Gamma_6^- - 8\Gamma_8^-$  | 0.94               |
| 23-14  | 1.02  | 1.06  | 0.96  | 0.98  | $8\Gamma_7^- - 9\Gamma_8^-$  | 1.02               | $6\Gamma_7^- - 8\Gamma_8^-$  | 0.98               |
| 24-14  | 1.16  | 1.17  | 1.09  | 1.11  | $16\Gamma_8^- - 9\Gamma_8^-$ | 1.09               | $7\Gamma_6^- - 8\Gamma_8^-$  | 1.07               |
|        |       |       |       |       | $9\Gamma_7^- - 9\Gamma_8^-$  | 1.15               | $15\Gamma_8^- - 8\Gamma_8^-$ | 1.09               |
|        |       |       |       |       |                              |                    | $7\Gamma_7^- - 8\Gamma_8^-$  | 1.09               |
| 25-14  | 1.23  | 1.23  | 1.17  | 1.23  | $17\Gamma_8^- - 9\Gamma_8^-$ | 1.17               | $16\Gamma_8^- - 8\Gamma_8^-$ | 1.17               |
|        |       |       |       |       |                              |                    | $17\Gamma_8^- - 8\Gamma_8^-$ | 1.20               |
| 26-14  | 1.30  |       | 1.27  | 1.28  | $18\Gamma_8^- - 9\Gamma_8^-$ | 1.26               | $18\Gamma_8^- - 8\Gamma_8^-$ | 1.28               |
| 27-14  | 1.32  | 1.32  |       |       | $19\Gamma_8^- - 9\Gamma_8^-$ | 1.35               | $19\Gamma_8^- - 8\Gamma_8^-$ | 1.34               |
| 28-14  | 1.41  | 1.43  |       | 1.36  |                              |                    | $20\Gamma_8^- - 8\Gamma_8^-$ | 1.37               |
| 29-14  | 1.51  | 1.54  |       | 1.48  |                              |                    | $9\Gamma_7^- - 8\Gamma_8^-$  | 1.41               |
| 30-14  | 1.62  |       |       | 1.58  |                              |                    | $10\Gamma_6^- - 8\Gamma_8^-$ | 1.51               |

of the  $^{11}\text{B}$  and  $^{10}\text{B}$  isotopes is observed [93], as in Fig. 7.6 for a qmi  $^{28}\text{Si}$  sample, allowing a direct chemical identification of the spectrum. The boron IS, which is independent of the transitions, is  $0.154\text{ cm}^{-1}$  ( $19.1\text{ }\mu\text{eV}$ ) for the whole boron spectrum [161].

**Table 7.5.** Intrinsic FWHM ( $\mu\text{eV}$  ( $\text{cm}^{-1}$  in parentheses)) at LHeT of some of the B lines ([82], Steger and Thewalt, private communication, Pajot, unpublished) and In lines (Pajot, unpublished) in  $^{\text{nat}}\text{Si}$ . The lines are identified with numbering 4 of Table 7.1 with numbering 1 in parentheses. The second row refers to the attributions of [21] for the final state

| Line | 1             | 2             | 3             | 4                            | 5(4B)         | 6(4A)         | 7(5)                        | 11                          | 15            | 16            |
|------|---------------|---------------|---------------|------------------------------|---------------|---------------|-----------------------------|-----------------------------|---------------|---------------|
|      | $1\Gamma_8^-$ | $2\Gamma_8^-$ | $3\Gamma_8^-$ | $1\Gamma_6^-$                | $1\Gamma_7^-$ | $4\Gamma_8^-$ | $5\Gamma_8^-$               | $7\Gamma_8^-$               | $4\Gamma_6^-$ | $4\Gamma_7^-$ |
| B    | 59<br>(0.48)  | 105<br>(0.85) | 63<br>(0.51)  | 37<br>(0.30)                 | 61<br>(0.49)  | 66<br>(0.53)  | $\sim 25$<br>( $\sim 0.2$ ) |                             | 36<br>(0.29)  | 32<br>(0.26)  |
| In   | 310<br>(2.5)  | 285<br>(2.3)  | 210<br>(1.7)  | $\sim 110$<br>( $\sim 0.9$ ) |               |               |                             | $\sim 86$<br>( $\sim 0.7$ ) |               |               |

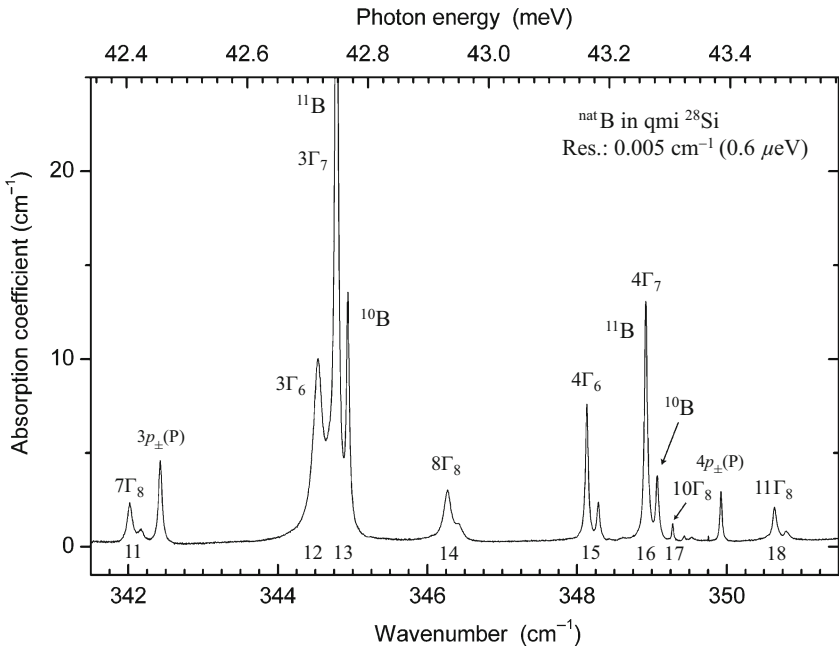


**Fig. 7.6.** Part of the  $p_{3/2}$  absorption spectrum of  $^{\text{nat}}\text{B}$  at 1.8 K in a qmi  $^{28}\text{Si}$  sample showing a B isotope effect (the  $^{11}\text{B}/^{10}\text{B}$  natural abundance has a ratio of 4). The  $^{10}\text{B}$  component of  $3\Gamma_6$  is masked by  $3\Gamma_7$ . Transition  $10\Gamma_8$  is clearly observed in this spectrum (Steger and Thewalt, private communication). The line labels below the spectrum are those of Table 7.2

In this figure, a weak transition is observed on the h-e side of line 16 ( $4\Gamma_7$  in the notations of [21] used for the attributions of the lines of this figure). This weak transition due to  $10\Gamma_8$  is the weak h-e shoulder 17 of line 16 of Fig. 7.2. Considering the numbering 4, the FWHMs of the  $^{11}\text{B}$  component of lines 13, 15, 21, and 23 measured in this qmi  $^{28}\text{Si}$  sample are 0.041, 0.043,

0.024, and  $0.025\text{ cm}^{-1}$  (5.1, 5.3, 3.0, and  $3.1\text{ }\mu\text{eV}$ ), respectively [161]. In the qmi  $^{28}\text{Si}$  spectrum, other lines too weak or too close from stronger ones, not observed in the  $^{\text{nat}}\text{Si}$  sample studied in this work, are also observed, so that numbering 4 of Table 7.1 has to be reconsidered after proper identification of all the boron transitions. An extensive list of the positions of the  $^{11}\text{B}$  lines in qmi  $^{28}\text{Si}$ ,  $^{29}\text{Si}$ , and  $^{30}\text{Si}$  is given by Steger et al. [161]. An estimation of the positions of the  $^{10}\text{B}$  components can be deduced by adding the B IS to the positions of the  $^{11}\text{B}$  components.

Calibration factors relating the integrated intensity absorptions ( $\text{cm}^{-2}$ ) of  $p_{3/2}$  boron lines in silicon at LHeT and the boron concentration ( $\text{cm}^{-3}$ ) have been obtained by Porrini et al. [142]. For the 1(B), 2(B) and 4–5(B) lines in silicon, they are 6.8, 1.5, and  $1.7 \times 10^{13}\text{ cm}^{-1}$ , respectively. NTD of In-doped FZ silicon has been used to determine a spectroscopic calibration coefficient of indium in silicon [134]. The calibration factors at LHeT for lines 1(In) and 2(In) are found to be  $5.6 \times 10^{15}$  and  $8 \times 10^{14}\text{ cm}^{-1}$ , respectively<sup>2</sup> (unless otherwise specified, the spectroscopic quantity considered is the integrated intensity). LHeT calibration factors for 2(B), 2(Al), 2(In), and 2(Tl) have been given by Jones et al. [85]; they are  $1.5 \times 10^{13}$ ,  $5 \times 10^{13}$ ,  $2 \times 10^{15}$ , and  $1.2 \times 10^{16}\text{ cm}^{-1}$ , respectively, and the difference between the values of the calibration factor of 2(In) in the two references is discussed by Tardella and Pajot [167]. The possibility of absorption spectroscopy for the measurement of residual impurities and of compensation in high-purity silicon is illustrated in Fig. 7.7 (see also [102]).

The  $\text{B}^0$  concentration under equilibrium deduced from spectrum (a) of Fig. 7.7 is  $\sim 7 \times 10^{11}\text{ cm}^{-3}$ , and it corresponds to a RT resistivity of about  $18\text{ k}\Omega\text{ cm}$  (a value of  $495\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  is taken for the RT hole mobility [162]) and the estimated  $[\text{B}^-]$  from spectrum (b) is  $\sim 1.4 \times 10^{12}\text{ cm}^{-3}$ . As already mentioned for donors, PTIS is much more sensitive than absorption spectroscopy, however, because of the principles of this method, compensation effects are not so clearly dealt with by PTIS, and the lines of the compensating species neutralized by band-gap illumination appear as negative peaks in the PTI spectra.

A model of the spectral dependence of the photoionization spectrum of group-III acceptors in silicon has been presented by Edwards and Fowler [52]. This model uses hydrogenic continuum states and hydrogenic ground-state wave functions scaled to account for central-cell corrections, and it provides a good description of the energy dependence of the cross-sections, as can be seen from Fig. 7.8.

These results show that the increase of the shift of the maximum absorption correlates with the difference between  $E_i$  and the EM ionization energy. These maximums for B, Al, Ga, and In are approximately located at 50, 80, 100, and  $310\text{ meV}$  ( $400$ ,  $650$ ,  $800$ , and  $2500\text{ cm}^{-1}$ ). Near LHeT, the optical

<sup>2</sup> In the original publication, the calibration factor of  $1.1 \times 10^{14}\text{ cm}^{-1}$  for line 1 is an error.

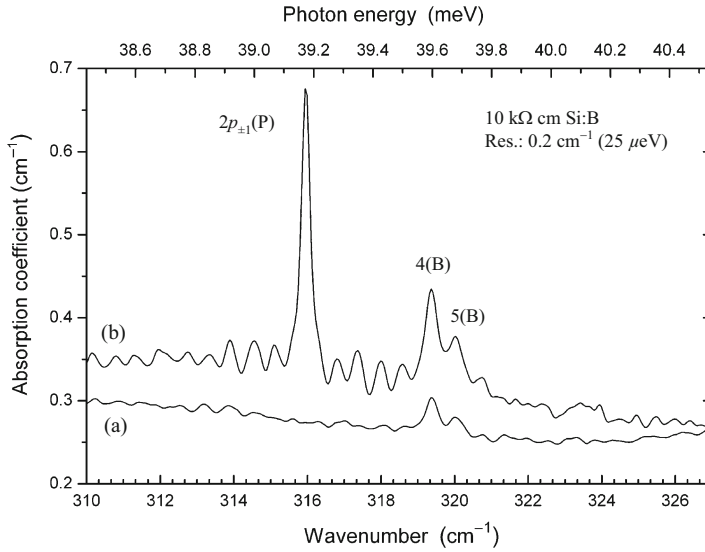


**Fig. 7.7.** Absorption coefficient at LHeT of a FZ p-type  $^{\text{nat}}\text{Si}$  sample with a nominal RT resistivity of  $10 \text{ k}\Omega \text{ cm}$  (a) under TEC and (b) under band-gap light illumination. The sample thickness is  $7.6 \text{ mm}$

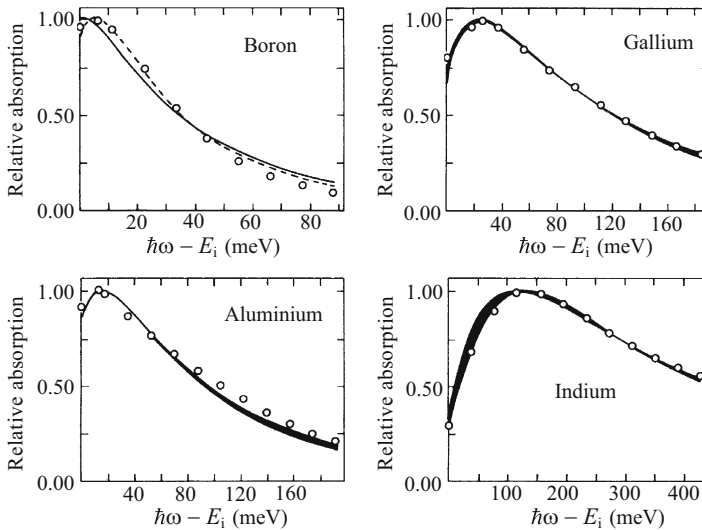


**Fig. 7.8.** Comparison of the calculated spectral dependence of the photoionization absorption for group-III acceptors in silicon (solid and dashed curves) with experiment (open circles).  $E_i$  is the ionization energy of the acceptor. The widths of the solid lines correspond to the use of different basic assumptions in the calculation (after [52]). The solid and dashed curves for boron correspond to different values of a mass parameter. The experimental results for B, Al, and Ga are from [27], and those for In from [116]. Copyright 1977 by the American Physical Society



cross-section  $\sigma_M$  at this maximum, expressed in units of  $10^{-16} \text{ cm}^2$ , is  $\sim 10$ , 4, 2.5, and 0.45 for B, Al, Ga, and In, respectively, [62, 151]. For indium, a higher value of  $\sigma_M$  (1.55) at LNT has been reported by Parker et al. [136], based on corrections to the determination of [In] from the Hall-effect measurements.

In the 1980s, EM acceptor spectra related to group-III elements, but with ionization energies somewhat smaller than those of the isolated acceptors, were reported [85]. An estimation of the concentration of the corresponding centres compared to that of the isolated acceptors varied from  $10^{-2}$  to  $10^{-5}$ . These so-called acceptor- $X$  centres received special attention from the manufacturers of extrinsic photoconductive detectors based on group-III acceptors, especially In, because these new centres produced unwanted photoconductivity at energies lower than the normal low-frequency cut-off for these detectors. The low-frequency lines of the acceptor- $X$  spectra are given in Table 7.6. For these spectra, the reference line 14 used for the isolated acceptors cannot be observed and  $E_{i0}$  is obtained by adding the value calculated by Beinikhes et al. [18] for the  $2\Gamma_8^-$  state (11.5 meV) to the position of line 2. This produces a slight increase of the value of  $E_{i0}$  with respect to the other procedures.

The results of piezospectroscopic measurements on the Al- $X$  spectrum are consistent with a trigonal  $\langle 111 \rangle$  oriented centre [33]. Early measurements of the  $X$ -centre concentration showed no dependence on the concentration of interstitial oxygen, but a linear dependence on  $[C_s]$  which led to their attribution to (C, acceptor) pairs [85]. However, subsequent measurements on NTD Ga-doped FZ silicon with undetectable  $[C_s]$  showed the presence of Ga- $X$  centres after annealing at 450–550°C [145] so that the atomic structure of these centres is still an open problem. Calibration factors for lines 1(B- $X$ ), 2(Al- $X$ ), 2(Ga- $X$ ), and 2(In- $X$ ) given by Jones et al. [85] are 1.1, 2.5, 2.5, and  $28 \times 10^{13} \text{ cm}^{-1}$ , respectively.

In B- and Al-doped FZ silicon samples subjected to NTD, two new EM acceptor spectra are observed after annealing at 500–600°C, besides the above-discussed B- $X$  and Al- $X$  spectra [179]. These spectra, called B<sub>NTD</sub> and Al<sub>NTD</sub>, are similar to those of the isolated acceptors, but their ionization energies are 28.24 and 43.25 meV for B<sub>NTD</sub> and Al<sub>NTD</sub>, respectively. The ionization energy of B<sub>NTD</sub> is smaller than the EM energy calculated for acceptors in silicon (31.6 meV) by Baldereschi and Lipari [13]. Such centres have also been

**Table 7.6.** Positions (meV ( $\text{cm}^{-1}$  in parentheses)) at LHeT of the first acceptor  $X$  lines in silicon [85]. The value of  $E_{i0}$  for these centres is obtained by adding 6.2 meV to the position of line 4. The value of  $E_{i0}$  for the isolated acceptor is given in brackets for comparison

| Line    | 1          | 2           | 3           | 4           | $E_{i0}$      |
|---------|------------|-------------|-------------|-------------|---------------|
| B- $X$  | 22.8 (184) | 27.3 (220)  | 31.0 (250)  | 32.4 (261)  | 38.6 [45.7]   |
| Al- $X$ | 41.9 (338) | 46.1 (372)  | 50.1 (404)  | 51.3 (414)  | 57.5 [70.4]   |
| Ga- $X$ | 43.0 (347) | 47.2 (381)  |             | 52.4 (423)  | 58.6 [74.1]   |
| In- $X$ | 99.1 (799) | 103.0 (831) | 107.0 (863) | 108.2 (873) | 114.4 [157.0] |

found on the donor side (see Sect. 6.4.3) and this has been attributed to a repulsive core for electrons. Here, the explanation would be for a repulsive core for holes. The  $B_{\text{NTD}}$  and  $Al_{\text{NTD}}$  spectra anneal above  $700^\circ\text{C}$  and the piezospectroscopic measurements reveal an unexpected cubic symmetry [179].

### 7.2.1.2 The $p_{1/2}$ Spectra

For an acceptor in a group-IV semiconductor, the  $p_{1/2}$  spectrum consists of transitions from the  $1\Gamma_8^+$  state to  $n\Gamma_6^-$  ( $\ell = 1$ ) odd-parity states associated with the  $\Gamma_7^+$  VB (see Fig. 5.2 and Table 5.19), and it was first reported for boron in a combined Zeeman study by Zwerdling et al. [193]. A maximum of four lines, denoted  $2p'$ ,  $3p'$ ,  $4p'$ , and  $5p'$ , which can be labelled  $2\Gamma_6^-$ ,  $3\Gamma_6^-$ ,  $4\Gamma_6^-$ , and  $\Gamma_6^-$  has been observed for the  $p_{1/2}$  spectra of the different group-III acceptors and they are shown for the Al acceptor in Fig. 7.9.

The positions of the  $np'$  lines observed for different group-III acceptors are given in Table 7.7.

The limit of these  $np'$  lines for large values of  $n$  is the ionization energy  $E_{\text{io}}^*$  with respect to the  $\Gamma_7^+$  VB. It must be borne in mind that in expression (5.21) for  $E_{n,\ell}$ , the contribution of the  $n^{-k}$  terms with  $k > 2$  is very small. Thus, a good approximation of  $E_{\text{io}}^*$  is obtained by linear extrapolation of the experimental values  $E_{np'}$  as a function of  $n^{-2}$ , and when applied to the Al spectrum, it gives a value of 113.0 meV for  $E_{\text{io}}^*(\text{Al})$ . The values of the first  $np'$  levels have been calculated using expressions similar to (5.21), with

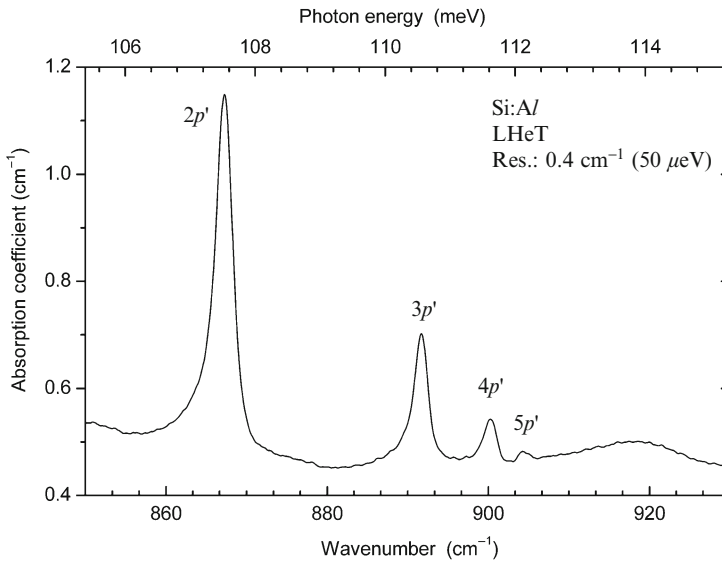


**Fig. 7.9.** Absorption spectrum of  $p_{1/2}(\text{Al})$  in a FZ silicon sample with  $[\text{Al}] \sim 10^{15} \text{ cm}^{-3}$ . The FWHM of  $3p'$  is  $2.0 \text{ cm}^{-1}$  ( $0.25 \text{ meV}$ )

**Table 7.7.** Transition energies  $E'_{np}$  (meV ( $\text{cm}^{-1}$  in parentheses)) of the lines of the  $p_{1/2}$  spectrum of group-III acceptor in silicon at LHeT

|                 | $E_{2p'}$        | $E_{3p'}$        | $E_{4p'}$        | $E_{5p'}$      |
|-----------------|------------------|------------------|------------------|----------------|
| B <sup>a</sup>  | 82.901 (668.64)  | 85.914 (692.94)  | 87.011 (701.79)  |                |
| Al <sup>b</sup> | 107.528 (867.27) | 110.555 (891.69) | 111.619 (900.27) | 112.11 (904.2) |
| Ga <sup>c</sup> | 111.24 (897.2)   | 114.25 (921.5)   | 115.30 (930.0)   | 115.8 (934)    |
| In <sup>c</sup> | 194.08 (1565.4)  | 197.11 (1589.8)  | 198.18 (1594.4)  |                |

<sup>a</sup> [192], <sup>b</sup> Pajot, unpublished, <sup>c</sup> [59]

**Table 7.8.** Values of the separation  $E^*_{io}$  (meV) between the  $1\Gamma_8^+$  ground state of group-III acceptors and the  $\Gamma_7^+$  VB in silicon. The last column gives an average value of the silicon so splitting  $\Delta_{so}$  (meV) deduced from the data for each acceptor

|    | Ref. 1 <sup>a</sup> | Ref. 2 <sup>b</sup> | Ref. 3 <sup>c</sup> | Ref. 4 <sup>d</sup> | $\Delta_{so}$ (see text) |
|----|---------------------|---------------------|---------------------|---------------------|--------------------------|
| B  | 88.2                | 88.39               | 88.45               |                     | 42.71                    |
| Al | 113.0               | 113.04              |                     | 112.97, 113.0*      | 42.61                    |
| Ga |                     | 116.73              |                     |                     | 42.64                    |
| In |                     | 199.58              |                     |                     | 42.63                    |

<sup>a</sup> [193], <sup>b</sup> [59], same VB parameters as (a), <sup>c</sup> [192], <sup>d</sup> Pajot, unpublished, \* Linear extrapolation (see text)

appropriate VB parameters [192, 193] or more sophisticated methods also requiring the same VB parameters [24]. Thus, a “preliminary” value of the VB s-o splitting  $\Delta_{so}$  is needed for this calculation. However, this value is not critical as it intervenes in a small corrective term (in the first measurements of the  $p_{1/2}$  spectra of B and Al by Zwerdling et al. [193], an estimate of 0.05 eV was used for  $\Delta_{so}$ ). The first  $np'$  levels in silicon calculated by Buczko and Bassani are given in Table 5.19 and from the calculated OSs, the level considered in this table for the accurate determination of  $\Delta_{so} = E^*_{io} - E_{io}$  is the  $\ell = 1$  level corresponding to  $\Gamma_6$  symmetry. Values of  $E^*_{io}$  for different acceptors are summarized in Table 7.8. For Ref. 3 and Ref. 4, they are obtained by adding the calculated value of the  $3\Gamma_6^-(1)$  energy level given in Table 5.19 (2.41 meV) to the experimental value of  $E_{3p'}$  of the appropriate reference.

The main aim of this comparison is to show that there is a good agreement between the values of  $E^*_{io}$  obtained by the different groups. When subtracting from the average values of  $E^*_{io}$  of Table 7.8, the values of  $E_{io}$  of Table 7.2, the values of  $\Delta_{so}$  of the last column of Table 7.8 are obtained. From these results, an average value of  $(42.65 \pm 0.06)$  meV is obtained for  $\Delta_{so}$  in silicon, in good agreement with that proposed  $(42.62 \pm 0.01)$  meV by Yu et al. [192]. The difference with the accepted value of 44 meV deserves some comments. For the values given by Zwerdling et al. [193] and Fischer and Rome [59], it is derived from the underestimation of the ionization energies  $E_{io}$  of the acceptors in these references. The value of  $\Delta_{so}$  determined from the electroreflectance measurements by [10] is  $(44 \pm 10)$  meV. Values of  $\Delta_{so}$  near 44 meV have also been

obtained from electroabsorption experiments at 50 K by Evangelisti et al. [55] and from modulated absorption at 1.8 K [130], slightly above the silicon band gap. These measurements are based on the observation of phonon-assisted exciton absorptions at the  $\Gamma_8^+$  and  $\Gamma_7^+$  VB maxima. In these determinations, a possible difference between the exciton binding energies at these two maxima is not taken into account.

Finally, it can be pointed out from the origin of the  $np'$  levels that their energies with respect to the  $\Gamma_7^+$  VB maximum show a pronounced acceptor EM-like behaviour. This can be appreciated from the energy differences between these lines and some lines of the  $p_{3/2}$  spectrum whose energies can be assumed to be acceptor-independent. For instance, the energy differences between the  $3p'$  line and the reference  $p_{3/2}$  line 14 of Table 7.2 are 42.98, 42.89, 42.90, and 42.90 meV for B, Al, Ga, and In, respectively.

For  $2p'(\text{B})$ , an integrated calibration factor of  $\sim 1.7 \times 10^{14} \text{ cm}^{-1}$  at LHeT is given by Jones et al. [85]. As for  $2p'(\text{Al})$  shown in Fig. 7.9, this line is asymmetric, and its FWHM at LHeT is  $\sim 6 \text{ cm}^{-1}$  ( $\sim 0.7 \text{ meV}$ ) for [B] up to  $\sim 10^{17} \text{ cm}^{-3}$ . The linear coefficient between the peak absorption coefficient of the line near LHeT and [B] is given<sup>3</sup> as  $2.58 \times 10^{15} \text{ cm}^{-2}$  [158].

### 7.2.2 Germanium

In germanium, the value of the VB s-o splitting ( $\sim 0.3 \text{ eV}$ ) is significantly larger than the ionization energy of the shallow acceptors, and the  $p_{1/2}$  spectra should be observed near 0.3 eV, but no report of such spectra has apparently been published. An exhaustive study of the group-III acceptor spectra in germanium was published in 1965 by Jones and Fisher [84], with the lines denoted in alphabetical order from the h-e side. The line shapes in these early spectra were determined mainly by spectral resolution, and the spectra obtained later at higher resolution using PTIS and band-gap pumping revealed more acceptor lines. New empirical labels were, therefore, added to the old ones with eventual differences, as primed or double-primed *A* lines. As for the acceptor spectra in silicon, labelling of lines can be done using integers increasing with energies. However, in the different presentations of the experimental results, the notation with letters is traditionally used and has been retained here. A LHeT absorption spectrum of boron in germanium is displayed in Fig. 7.10. Despite the low resolution, it has the advantage of showing lines like *G* and *E*, not usually seen in the more recent PTIS spectra.

In the boron spectrum of Fig. 7.10, as well as in the thallium spectrum displayed in the same reference, the intensity of line *C* is larger than that of line *D* while in other spectra, the inverse is observed systematically. Calculations also predict this latter intensity ordering, however, the reason for this difference is not explained. Table 7.9 gives the positions of the group-III acceptor lines in germanium with attributions taken from the calculations of

<sup>3</sup> In the original reference, it is misprinted as  $2.575 \times 10^5$ .

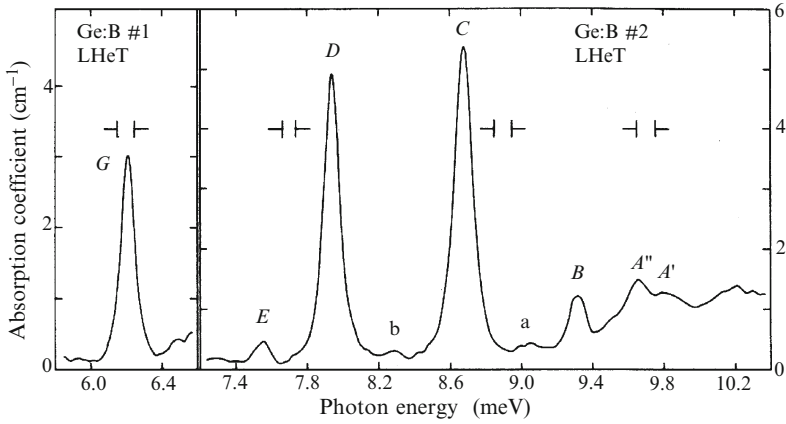


**Fig. 7.10.** Absorption spectrum of boron in germanium at LHeT between  $\sim 47$  and  $53 \text{ cm}^{-1}$  (line *G*) and  $\sim 58$  and  $84 \text{ cm}^{-1}$ . [B] in sample #1 is  $\sim 2 \times 10^{14} \text{ cm}^{-3}$  and  $\sim 8 \times 10^{14} \text{ cm}^{-3}$  in sample #2. The resolution is indicated by the vertical bars (after [157]). Copyright 1973 by the American Physical Society

Kurskii [104]. For the  $A_i$  and  $I_i$  lines, the notations used are those of Darken [46]. Some of the attributions are not easy to make because of the closeness between some of the calculated levels. As we shall see later, most of these absorption lines correspond to transitions between the  $1\Gamma_8^+$  ground state and the odd-parity states, with a few attributed to the even-parity excited states.

The choice of the calculated value of the  $4\Gamma_8^-$  excited state of line *B* to determine  $E_{i0}$  is deliberate and the apparent accuracy does not truly reflect the physical accuracy: if the energy calculated for the  $2\Gamma_8^-$  state by Kurskii (2.8673 meV) is added to the position of line *D*, the  $E_{i0}$  values for B, Al, Ga, In and Tl are 10.813, 11.144, 11.307, 11.953 and 13.42 meV, respectively. All these values of  $E_{i0}$  are marginally different from those of Table 6 of [143], and they show the EM character of the odd-parity excited states of the group-III acceptors in germanium. This is further demonstrated in the comparison of the energy spacings between the acceptor lines given in Table 7.10.

A high-resolution overall spectrum of Al in  $^{\text{nat}}\text{Ge}$  is shown in Fig. 7.11, and the weak line of highest energy is  $I_1$  (Al) of Table 7.9 at  $87.62 \text{ cm}^{-1}$ . The strongest lines of Fig. 7.11 are truncated, but the relative intensities of the *B* and *G* lines are found to be acceptor-dependent. The calculated ratio of the OSs of the *B* ( $4\Gamma_8^-$  final state) transition to the *G* ( $1\Gamma_8^-$  final state) one for isocoric Ga in germanium (Table 5.23) is  $\sim 2.5$ , and it seems to be comparable to the experimental intensity ratio for Al.

The above spectrum provides an upper limit for the FMHM of  $\sim 0.1 \text{ cm}^{-1}$  ( $\sim 12 \mu\text{eV}$ ) for the sharpest lines (see Fig. 8.26). The absorption of Al in a  $^{\text{nat}}\text{Ge}$  sample with  $p = 3 \times 10^{11} \text{ cm}^{-3}$  has also been measured at LHeT at a resolution of  $0.01 \text{ cm}^{-1}$  ( $1.24 \mu\text{eV}$ ) by Andreev et al. [6] and the FWHM of *C* (Al) was found to be the narrowest of the spectrum, with a value of

**Table 7.9.** Positions (meV (cm<sup>-1</sup> in parentheses when available)) of the group-III acceptor lines in germanium.  $E_{io}$  is obtained by adding 1.4786 meV to the position of line  $4\Gamma_8^-$  (line  $B$ ). The attributions are based on the calculations of Kurskii [104] and correspond to the excited state of the transition

| Label       | Attribution                    | B <sup>a</sup>                  | Al <sup>f</sup>                | Ga <sup>a</sup>                 | In <sup>a</sup>     | Tl <sup>b</sup>   |
|-------------|--------------------------------|---------------------------------|--------------------------------|---------------------------------|---------------------|-------------------|
| $G$         | $1\Gamma_8^-$                  | 6.2150<br>(50.127) <sup>c</sup> | 6.5849<br>(53.111)             | 6.7199<br>(54.200) <sup>c</sup> | 7.39 <sup>d</sup>   | 8.91              |
| $E$         | $2\Gamma_8^+$                  | 7.55 <sup>b</sup>               |                                | 8.02 <sup>d</sup>               | 8.42 <sup>d</sup>   | 9.86 <sup>b</sup> |
| $D$         | $2\Gamma_8^-$                  | 7.9457<br>(64.086) <sup>c</sup> | 8.2834<br>(66.810)             | 8.440<br>(68.07)                | 9.086<br>(73.28)    | 10.552            |
| $C$         | $1\Gamma_7^- + 3\Gamma_8^{+e}$ | 8.6939<br>(70.121) <sup>c</sup> | 9.0356<br>(72.877)             | 9.188<br>(74.11)                |                     | 11.30             |
| $C^{*f}$    | $3\Gamma_8^-$                  |                                 | 9.0475<br>(72.973)             |                                 |                     |                   |
| $a$         | $4\Gamma_8^+$                  | 9.06 <sup>d</sup>               |                                |                                 | 10.20 <sup>d</sup>  | 11.65             |
| $B$         | $4\Gamma_8^-$                  | 9.3262<br>(75.221)              | 9.6648<br>(77.952)             | 9.8238<br>(79.234)              | 10.4705<br>(84.450) | 11.93             |
| $A_4 (A'')$ | $5\Gamma_8^-$                  | 9.580<br>(77.27)                | 9.9269<br>(80.066)             | 10.080<br>(81.30)               | 10.730<br>(86.54)   |                   |
| $A_3 (A')$  | $2\Gamma_7^- + 6\Gamma_8^-$    | 9.661<br>(77.92)                | 10.0025<br>(80.676)            | 10.159<br>(81.84)               | 10.805<br>(87.15)   | 12.29             |
| $A_2 (A)$   | $3\Gamma_7^-$                  | 9.789<br>(78.95)                | 10.1338<br>(81.735)            | 10.288<br>(82.98)               | 10.938<br>(88.22)   | 12.42             |
| $A_1$       | $7\Gamma_8^-$                  | 9.869<br>(79.60)                | 10.2112<br>(82.359)            | 10.368<br>(83.62)               | 11.012<br>(88.82)   |                   |
| $I_8$       | $8\Gamma_8^-$                  | 9.999<br>(80.65)                | 10.333<br>(83.34) <sup>a</sup> | 10.495<br>(84.65)               | 11.140<br>(89.85)   |                   |

|                 |                              |                   |                                |                   |                   |
|-----------------|------------------------------|-------------------|--------------------------------|-------------------|-------------------|
| $I_7$           | $2\Gamma_6^- + 9\Gamma_8^-$  | 10.053<br>(81.08) | 10.3392<br>(83.875)            | 10.550<br>(85.09) | 11.201<br>(90.34) |
| $I_6$           | $5\Gamma_7^- + 12\Gamma_8^-$ | 10.144<br>(81.82) | 10.487<br>(84.58) <sup>a</sup> | 10.647<br>(85.87) | 11.297<br>(91.12) |
| $I_5$           | $3\Gamma_6^-$                | 10.190<br>(82.19) | 10.531<br>(84.94) <sup>a</sup> | 10.692<br>(86.24) | 11.338<br>(91.45) |
| $I_4$           | $6\Gamma_7^-$                | 10.267<br>(82.81) | 10.607<br>(85.55) <sup>a</sup> | 10.767<br>(86.84) | 11.415<br>(92.07) |
| $I_3$           | $8\Gamma_7^- + 18\Gamma_8^-$ | 10.332<br>(83.33) | 10.675<br>(86.10) <sup>a</sup> | 10.836<br>(87.40) | 11.477<br>(92.57) |
| $I_2$           |                              | 10.399<br>(83.87) | 10.740<br>(86.62) <sup>a</sup> | —                 | 11.573<br>(93.34) |
| $I_1$           |                              | 10.530<br>(84.93) | 10.863<br>(87.62) <sup>a</sup> | 11.030<br>(88.96) | 11.678<br>(94.19) |
| $E_{\text{to}}$ |                              | 10.805            | 11.142                         | 11.301            | 11.947            |

<sup>a</sup> [46], <sup>b</sup> [157], <sup>c</sup> [7], <sup>d</sup> [84], <sup>e</sup> [181], <sup>f</sup> [6]

**Table 7.10.** Energy spacings (meV) between line *B* ( $4\Gamma_8^-$  excited state) and other lines of the group-III acceptor spectra in germanium derived from Table 7.9, compared with the calculated spacings. The final state of the second line is indicated in the “Attribution” column

|                        | B     | Al    | Ga    | In    | Tl   | Attribution                      | EM <sup>a</sup> | EM <sup>b</sup>   |
|------------------------|-------|-------|-------|-------|------|----------------------------------|-----------------|-------------------|
| <i>B–G</i>             | 3.111 | 3.080 | 3.104 | 3.08  | 3.02 | $1\Gamma_8^-$                    | 3.071           | 3.104             |
| <i>B–E</i>             | 1.78  |       | 1.80  | 2.05  | 2.07 | $2\Gamma_8^+$                    | 1.66            | 1.81 <sup>c</sup> |
| <i>B–D</i>             | 1.381 | 1.381 | 1.384 | 1.385 | 1.38 | $2\Gamma_8^-$                    | 1.388           | 1.398             |
| <i>B–C</i>             | 0.632 | 0.629 | 0.636 | 0.635 | 0.63 | $1\Gamma_7^-$                    | 0.665           | 0.648             |
| <i>B–C*</i>            |       | 0.617 |       |       |      | $3\Gamma_8^-$                    | 0.612           | 0.626             |
| <i>A<sub>4</sub>–B</i> | 0.254 | 0.262 | 0.256 | 0.260 |      | $5\Gamma_8^-$                    | 0.266           | 0.267             |
| <i>A<sub>3</sub>–B</i> | 0.335 | 0.338 | 0.335 | 0.335 | 0.37 | $2\Gamma_7^-$ and $6\Gamma_8^-$  | 0.324           | 0.335             |
|                        |       |       |       |       |      |                                  |                 | 0.337             |
| <i>A<sub>2</sub>–B</i> | 0.463 | 0.468 | 0.464 | 0.468 | 0.50 | $3\Gamma_7^-$                    | 0.465           | 0.456             |
| <i>A<sub>1</sub>–B</i> | 0.543 | 0.546 | 0.544 | 0.542 |      | $7\Gamma_8^-$                    | 0.549           | 0.557             |
| <i>I<sub>8</sub>–B</i> | 0.673 | 0.668 | 0.671 | 0.670 |      | $8\Gamma_8^-$                    | 0.681           | 0.700             |
| <i>I<sub>7</sub>–B</i> | 0.727 | 0.727 | 0.726 | 0.731 |      | $2\Gamma_6^-$ and $9\Gamma_8^-$  | 0.738           | 0.721             |
| <i>I<sub>6</sub>–B</i> | 0.818 | 0.822 | 0.823 | 0.827 |      | $5\Gamma_7^-$ and $12\Gamma_8^-$ | 0.817           |                   |
|                        |       |       |       |       |      |                                  | 0.836           |                   |
| <i>I<sub>5</sub>–B</i> | 0.864 | 0.866 | 0.868 | 0.868 |      | $3\Gamma_6^-$                    | 0.864           |                   |
| <i>I<sub>4</sub>–B</i> | 0.941 | 0.942 | 0.943 | 0.945 |      | $6\Gamma_7^-$                    | 0.945           |                   |
| <i>I<sub>3</sub>–B</i> | 1.006 | 1.010 | 1.012 | 1.007 |      | $8\Gamma_7^-$ and $18\Gamma_8^-$ | 1.013           |                   |
|                        |       |       |       |       |      |                                  | 1.015           |                   |
| <i>I<sub>2</sub>–B</i> | 1.073 | 1.075 | –     | 1.103 |      |                                  |                 |                   |
| <i>I<sub>2</sub>–B</i> | 1.204 | 1.198 | 1.206 | 1.208 |      |                                  |                 |                   |

<sup>a</sup> Kurskii [104], <sup>b</sup> [39], <sup>c</sup> The value chosen for the  $2\Gamma_8^+$  level is the one for isocoric Ga of Table 5.17

$0.038\text{ cm}^{-1}$  ( $4.7\mu\text{eV}$ ). For line *D*(Ga), a FWHM value of  $\sim 40\mu\text{eV}$  ( $0.3\text{ cm}^{-1}$ ) at LHeT has been extrapolated from compensation measurements in germanium samples containing controlled mixtures of  $^{70}\text{Ge}$  and  $^{74}\text{Ge}$  [81].

Calibration of the integrated absorption of lines *D* and *C* of the group-III acceptors and of  $\text{Cu}^0$  spectra in germanium have been reported by Rotsaert et al. [146]. These calibration factors are given in Table 7.11.

This table shows a tendency of the OSs of the transitions to decrease when the ionization energy of the acceptor increases.

### 7.2.2.1 Single Acceptor Complexes

Besides the isolated group-III acceptors, the spectra of several complexes with single-acceptor behaviour have been observed in germanium. They are generally produced by high-temperature annealing followed by quenching at RT. One category is the H-related complexes found in germanium crystals grown under a hydrogen atmosphere in graphite or silica crucibles, ascribed to acceptor centres denoted *A*(H,C) or *A*(H,Si), respectively [66]. They have been



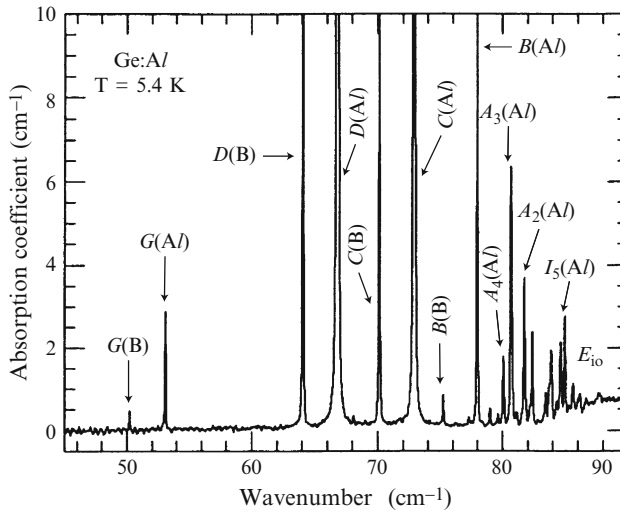


**Fig. 7.11.** Absorption spectrum between  $\sim 5.9$  and  $11.2$  meV of Al in a  $^{\text{nat}}\text{Ge}$  sample ( $p = 8.5 \times 10^{13} \text{ cm}^{-3}$ ) contaminated with B. The resolution is  $\sim 0.04 \text{ cm}^{-1}$  or  $5 \mu\text{eV}$ . The notations correspond to the Label column of Table 7.9 and the bar indicates the ionization energy  $E_{\text{io}}$  of the Al acceptor (after [12]). Copyright 1997, with permission from World Scientific Publishing Co. Pte. Ltd, Singapore

**Table 7.11.** Calibration factors (in  $\text{cm}^{-1}$ ) of the integrated absorption of the  $D$  and  $C$  lines of the group-III acceptors and of  $\text{Cu}^0$  in germanium. For their positions, see Tables 7.9 and 7.15 (after [146])

|                       | B                    | Al                   | Ga                   | In                   | $\text{Cu}^0$        |
|-----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| Line                  |                      |                      |                      |                      |                      |
| $D (2\Gamma_8^-)$     | $4.9 \times 10^{12}$ | $6.9 \times 10^{12}$ | $7.2 \times 10^{12}$ | $8.8 \times 10^{12}$ | $2.5 \times 10^{14}$ |
| $C (3\Gamma_8^-)$     | $6.4 \times 10^{12}$ | $1.0 \times 10^{13}$ | $9.3 \times 10^{12}$ | $1.3 \times 10^{13}$ | $5.0 \times 10^{14}$ |
| $E_{\text{io}}$ (meV) | 10.81                | 11.14                | 11.30                | 11.95                | 43.20                |

identified by Kahn et al. [88] as static trigonal centres with  $C_{3v}$  symmetry and they are stable up to  $\sim 200^\circ\text{C}$ . The ground state spectrum of these acceptors, observed at the lowest temperature compatible with PTIS measurements, is indexed 2 and the thermalized spectrum indexed 1 in Table 7.12, where the positions of the first lines of these spectra are given.

Other H-related complexes with Be and Zn double acceptors and with Cu have also been identified and they are discussed in Sect. 7.3.1.1 where the neutral multi-charged acceptors in germanium are presented.

Another rather large category of acceptors is produced when germanium samples containing group-I or TM elements are annealed at temperatures above  $\sim 850^\circ\text{C}$  and quenched to RT. From the temperature dependence of the Hall effect, centres produced by this method were labelled as  $\text{SA}_1$  and  $\text{SA}_2$ ,

**Table 7.12.** Positions (meV) at LHeT of the first lines of the  $A(\text{H,C})$  and  $A(\text{H,Si})$  spectra in germanium.  $E_{\text{io}}$  is obtained by adding 2.87 meV to the position of line  $D$  [66]

|                    | $D$  | $C$   | $B$   | $A_4$ | $A_3$ | $A_2$ | $A_1$ | $E_{\text{io}}$ |
|--------------------|------|-------|-------|-------|-------|-------|-------|-----------------|
| $A(\text{H,C})_1$  | 7.42 | 8.17  |       |       |       |       |       | 10.29           |
| $A(\text{H,C})_2$  | 9.39 | 10.14 | 10.77 | 11.04 | 11.13 | 11.24 | 11.32 | 12.26           |
| $A(\text{H,Si})_1$ | 7.71 | 8.44  |       |       |       |       |       | 10.58           |
| $A(\text{H,Si})_2$ | 8.78 | 9.53  | 10.17 | 10.41 | 10.50 | 10.64 | 10.71 | 11.65           |

with ionization energies of 8.4 and 12 meV, respectively.  $\text{SA}_1$  was found to be stable up to  $\sim 350^\circ\text{C}$  and  $\text{SA}_2$  up to  $\sim 450^\circ\text{C}$  [91]. In the  $45\text{--}75\text{ cm}^{-1}$  (5.6–9.3 meV) region, two EM acceptor spectra labelled  $\text{SA}'_1$  and  $\text{SA}''_1$  separated by  $6.44\text{ cm}^{-1}$  (0.80 meV) were observed by PTIS at LHeT in quenched germanium samples in the same domain of stability as  $\text{SA}_1$  [90]. Their attribution to different acceptors with ionization energies of 8.69 and 9.48 meV for  $\text{SA}'_1$  and  $\text{SA}''_1$ , respectively, seemed more likely than an attribution to the spectra arising from the same acceptor with the ground state split into two sublevels. New EM spectra, with ground-state binding energies of 13.89 meV ( $\text{SA}'_2$ ) and 14.42 meV ( $\text{SA}''_2$ ), were tentatively attributed to the same  $\text{SA}_2$  acceptor with a split ground state, while a third spectrum, with a ground state binding energy of 17.89 meV was attributed to acceptor  $\text{SA}_3$  [23]. Fast-diffusing TM contaminants were suspected to be involved in these quenched-in acceptors, and this was confirmed indirectly as other similar spectra were observed in quenched-in Ni-diffused or Cu-contaminated germanium samples [23]. In some quenched-in samples, new acceptor spectra  $\text{SA}'_1(\text{s})$  and  $\text{SA}''_1(\text{s})$  with a small upward shift from  $\text{SA}'_1$  and  $\text{SA}''_1$ , associated presumably to a  $\text{SA}_1(\text{s})$  acceptor, were also reported in the same study. The vanishing of the  $\text{SA}'_1(\text{s})$  and  $\text{SA}''_1(\text{s})$  spectra for temperatures  $\sim 450\text{--}500^\circ\text{C}$  indicated a higher stability of the  $\text{SA}_1(\text{s})$  acceptor compared to  $\text{SA}_1$ .

The spectroscopy of these quenched-in centres was revisited by Hattori and co-workers, who performed measurements as a function of temperature [69], magnetic field [70], presence of additional impurities [71], and uniaxial stress [72, 73]. In a first paper [69], it was established that the  $\text{SA}'_1$  and  $\text{SA}''_1$  spectra were associated with the split ground state of only the  $\text{SA}_1$  acceptor. They used labels different from those above for the spectra and the correspondences can be found in Table 7.13, with the binding energies of the ground state of each spectrum.

In germanium samples diffused with TMs or Cu-contaminated,  $\text{SA}_1$ -like acceptor spectra were also observed [23, 71]. These acceptors are also characterized by a split ground state. The ionization energies of their ground and thermalized states are given below, with  $\text{SA}_1$  for comparison:

In the Ni-diffused samples, two other spectra apparently related to  $\text{SA}_{1\text{Ni}}$ , with ionization energies of 9.37 and 9.62 meV, were reported [23]. It must be noted that the closeness of the ground state energies of the above-mentioned  $\text{SA}'_1(\text{s})$

**Table 7.13.** Groundstate (GS) energies (meV) of the EM spectra associated with the different quenched-in acceptors in germanium

|                             |                   |                    |                 |                   |                    |                 |       |
|-----------------------------|-------------------|--------------------|-----------------|-------------------|--------------------|-----------------|-------|
| Spectrum label <sup>a</sup> | SA <sub>1</sub> ' | SA <sub>1</sub> '' |                 | SA <sub>2</sub> ' | SA <sub>2</sub> '' | SA <sub>3</sub> |       |
| Spectrum label <sup>b</sup> | SA <sub>1a</sub>  | SA <sub>1b</sub>   | A               | SA <sub>2</sub> 1 | SA <sub>2</sub> 2  | 3               | 4     |
| Acceptor label              | SA <sub>1</sub>   | A                  | SA <sub>2</sub> | SA <sub>3</sub>   |                    |                 |       |
| GS energy <sup>b</sup>      | 8.69              | 9.48               | 11.89           | 13.89             | 14.42              | 17.89           | 25.75 |

<sup>a</sup> [23, 90], <sup>b</sup> [69]

|                 | SA <sub>1</sub> | SA <sub>1Ni</sub> | SA <sub>1Cu</sub> | SA <sub>1Ag</sub> | SA <sub>1Au</sub> |
|-----------------|-----------------|-------------------|-------------------|-------------------|-------------------|
| $E_{ig}$ (meV)  | 9.49            | 9.21              | 10.06             | 9.57              | 9.58              |
| $E_{ith}$ (meV) | 8.72            | 9.02              | 9.76              | 8.88              | 9.09              |

and SA<sub>1</sub>''(s) spectra (8.86 and 9.59 meV, respectively) with the energies of the ground-state sublevels of SA<sub>1Ag</sub> make the identification between the two spectra very likely. Other Cu-related spectra connected with acceptor A of Table 7.13 have been reported by Hattori et al. [74].

The piezospectroscopic measurements performed on some of the quenched-in centres [72, 73] suggest that the SA<sub>1</sub> acceptor series are constructed from a pair of substitutional and interstitial atoms on a  $\langle 111 \rangle$  axis, with an additional TM atom for the SA<sub>1TM</sub> centres, but the conclusions remain vague in the absence of other kind of measurements where spin properties could be measured.

### 7.2.3 Diamond and SiC

There is only one known acceptor in diamond, responsible for the p-type conductivity of the IIb diamonds. For some time, it was assumed that this acceptor was aluminium [49], but it has been suggested [43] and finally shown conclusively [38] that boron was indeed responsible for the p-type conductivity and the spectroscopic properties of type IIb blue diamonds. Natural IIb diamonds had been identified *ca.* 1954 (see Sect. 2.11), and synthetic IIb diamonds were obtained at the beginning of the 1960s [80]. Boron is commonly introduced as a dopant in synthetic diamonds and its ionization energy  $E_i$  is 370 meV [177]. The discrete acceptor spectrum of B extends approximately 70 meV below  $E_i$  and is superimposed on the two- and three-phonon spectra of C<sub>diam.</sub> Boron acceptor absorption lines are observed at 305, 347 and 363 meV ( $\sim 2780$ , 2800, and 2930 cm<sup>-1</sup>) at RT, giving phonon-assisted transitions near 464 and 504 meV (see [140], and references therein).

In silicon, the electronic spectra arising from the  $1\Gamma_8^+$  ground state to the excited states associated with the  $\Gamma_8$  and  $\Gamma_7$  VBs (the so-called  $p_{3/2}$  and  $p_{1/2}$  spectra) are well separated and clearly distinguished, but no acceptor transitions from the  $1\Gamma_7^+$  state has been reported in silicon. In diamond, the position of the  $1\Gamma_7^+$  state has been measured by Raman scattering and it is

distant from the  $1\Gamma_8^+$  ground state (the boron s-o splitting  $\Delta_{so}^B$ , denoted also  $\Delta'$ ) by only 2.00 meV ( $16.1\text{ cm}^{-1}$ ) [96]. Thus, transitions from the  $1\Gamma_7^+$  state can be observed in diamond at moderate temperatures. High-resolution Raman scattering measurements have shown that the  $1\Gamma_8^+ \rightarrow 1\Gamma_7^+$  transition is indeed a doublet separated by 0.100 meV ( $0.81\text{ cm}^{-1}$ ) and this effect is attributed to a JT splitting of the  $1\Gamma_8^+$  ground state into a Kramers doublet [95].

The two lowest-energy electronic lines of the B acceptor at 290 and 304 meV are resonant with a two-phonon combination and they are broad (FWHMs  $\sim 6\text{ meV}$ ). Compared to the B lines in silicon, the other B lines reported in  $C_{\text{diam}}$  at LHeT are significantly broader, with line widths varying from  $\sim 0.6$  to  $5.5\text{ meV}$  ( $\sim 5$  to  $44\text{ cm}^{-1}$ ), and there is a huge difference between the intensities of the strongest and faintest lines. Figure 7.12 shows the compared absorptions at LHeT of a pure IIa diamond and of a IIb semi-conducting diamond. The absorption of the IIa diamond is only due to the two- and three-phonon absorption while B contributes to the absorption of IIb diamond. The three most intense lines of the B spectrum, truncated in the global spectrum, are lines 13, 14 and 15 of the inset of Fig. 7.12 at 346.6, 347.21, and 349.29 meV ( $2795.5$ ,  $2800.4$ , and  $2817.2\text{ cm}^{-1}$ ), respectively. Also observed is the already-mentioned broad B line at 304 meV superimposed on

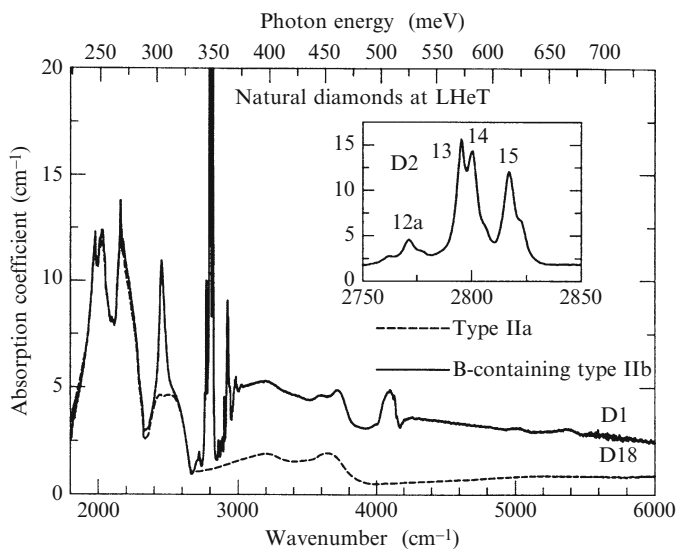


**Fig. 7.12.** Absorption spectrum of a natural type IIb diamond showing the acceptor B lines. The dashed spectrum is that of a high-purity type IIa diamond. The low-energy features are 2-phonon absorptions of  $C_{\text{diam}}$ . The strong B lines in the range  $2750\text{--}2850\text{ cm}^{-1}$  are shown in the inset for a natural type IIb diamond with a smaller B concentration. The resolution is  $1\text{ cm}^{-1}$  or  $0.124\text{ meV}$  (after [96]). The numbering of the lines of the inset corresponds to that of Table 7.12. Copyright 1998 by the American Physical Society

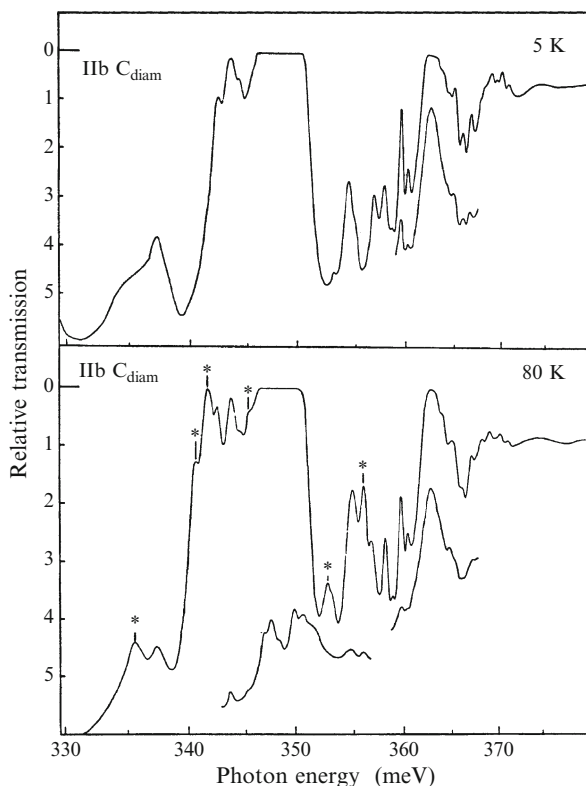


**Fig. 7.13.** Transmission between  $2660$  and  $3065\text{ cm}^{-1}$  of a high-quality natural IIb diamond (spectral resolution  $\sim 0.2\text{ meV}$  or  $1.6\text{ cm}^{-1}$ ). The asterisks indicate absorption peaks only observed at  $80\text{ K}$ . The inset at  $\sim 350$  and near  $363\text{ meV}$  in the  $80\text{ K}$  spectrum illustrates features in spectral regions of high absorption (after [42]). All the features are due to the boron acceptor. Note the inverted transmission scale. Copyright 1968 by the American Physical Society

a two-phonon combination of  $C_{\text{diam}}$ . The photoionization spectrum of B in diamond extends in the red region of the visible spectrum, and it is the absence of this contribution in the visible spectrum transmitted or refracted by the IIb diamonds which is considered responsible for their characteristic blue colour.

Spectra allowing observation of weaker B lines in natural IIb diamond at  $5$  and  $80\text{ K}$  are displayed in Fig. 7.13 (the acceptor was not specifically identified as B at the time when these spectra were obtained). In this figure, the lines denoted by an asterisk are due to transitions from the  $1\Gamma_7^+$  level, split from the  $1\Gamma_8^+$  ground state level by  $\sim 2\text{ meV}$  (see also Fig. 5 of [96]).

A continuous absorption spectrum extending from about  $1000\text{ cm}^{-1}$  to the  $C_{\text{diam}}$  Raman frequency ( $1332\text{ cm}^{-1}$ ) with a peak at  $1290\text{ cm}^{-1}$  ( $160\text{ meV}$ ) is also observed in B-containing diamond at RT. This spectrum shows structures

at lower temperature, which have been attributed to a first-order phonon spectrum of  $C_{\text{diam}}$  activated by the presence of substitutional B [96]. The photoionization spectrum of B extends over 370 meV and its continuity is broken by structures with Fano resonances [47]. These structures have also been interpreted as a combination of B transitions, with the activated first-order phonon spectrum [96].

As in silicon, the B lines are denoted by integers increasing with energy.<sup>4</sup> In connection with an experimental study of the effect of the Stark effect on the acceptor levels in diamond, an energy level diagram of these states is given by [4]. There has, however, been no calculation of the EM acceptor levels in diamond similar to those performed for silicon and germanium, making the identification of the observed lines difficult. The positions of some of these lines are given in Table 7.14 and compared with those measured in qmi  $^{13}\text{C}$  diamond. It is seen that, at a difference with  $\Delta'$ , the B lines in qmi  $^{13}\text{C}_{\text{dia}}$  are shifted upwards by different amounts with respect to  $^{\text{nat}}C_{\text{diam}}$  ( $^{12}\text{C}_{0.989}$   $^{13}\text{C}_{0.011}$ ), in agreement with the shift of the band gap. These ISs have been discussed by Cardona [28] in terms of the re-normalization of the energy gap of diamond by electron-phonon interaction. (In silicon, a qualitatively similar shift, but with smaller (+35  $\mu\text{eV}$ ) has been mentioned for line 1(B) between qmi  $^{28}\text{Si}$  and  $^{30}\text{Si}$ .)

In Fig. 7.13, new electronic lines are observed in the 80 K spectrum. They are due to transitions from the  $1\Gamma_7^+$  state, which is populated at this temperature, to odd-parity levels associated with the  $\Gamma_8^+ VB$ . It is possible to identify pairs of lines (one appearing at 5 and 80 K and the other only at

**Table 7.14.** Positions (meV ( $\text{cm}^{-1}$  in parentheses)) at LHeT of some electronic lines of B in  $^{\text{nat}}C_{\text{diam}}$  and in qmi  $^{13}\text{C}_{\text{diam}}$  including the most intense ones (after [96]).  $\Delta'$  is the boron acceptor s-o splitting

| Line      | $^{\text{nat}}C_{\text{diam}}$ | qmi $^{13}\text{C}_{\text{diam}}$ | $^{13}\text{C}_{\text{diam}} - ^{\text{nat}}C_{\text{diam}}$ |
|-----------|--------------------------------|-----------------------------------|--------------------------------------------------------------|
| $\Delta'$ | 2.07 (16.7)                    | 2.01 (16.2)                       | -0.06                                                        |
| 11        | 337.38 (2721.2)                | 337.76 (2724.2)                   | 0.38                                                         |
| 12a       | 343.60 (2771.3)                | 344.65 (2779.8)                   | 1.05                                                         |
| 13        | 346.60 (2795.5)                | 347.81 (2805.3)                   | 1.21                                                         |
| 14        | 347.21 (2800.4)                | 348.37 (2809.8)                   | 1.16                                                         |
| 15        | 349.29 (2817.2)                | 350.54 (2827.3)                   | 1.25                                                         |
| 17        | 354.1 <sup>a</sup>             |                                   |                                                              |
| 18        | 356.7 <sup>a</sup>             |                                   |                                                              |
| 19        | 357.9 <sup>a</sup>             |                                   |                                                              |
| 20        | 359.56 (2900.0)                | 360.96 (2911.3)                   | 1.40                                                         |
| 22        | 362.64 (2924.9)                | 364.10 (2936.7)                   | 1.46                                                         |

<sup>a</sup> [73]

<sup>4</sup> In the paper by Collins and Lightowlers (1968), phonon-assisted transitions in the 490–550 meV range have also been noted from the low-energy side by letters in alphabetical order.

80 K) and all these pairs exhibit a separation close to 2 meV, the value of the separation of the  $1\Gamma_8^+$  and  $1\Gamma_7^+$  acceptor levels.

A good linear correlation was found between the integrated absorption of the strongest RT line centred at 347 meV and the neutral acceptor concentration obtained from Hall effect measurements of five natural IIb diamonds [43]. This was later converted into a RT calibration factor of this band of  $\sim 1 \times 10^{14} \text{ cm}^{-1}$ , assumed to be valid for B concentrations up to a few  $10^{18} \text{ cm}^{-3}$ . For larger B concentrations going up to  $\sim 1 \times 10^{20} \text{ cm}^{-3}$ , a calibration factor of about one order of magnitude larger was obtained by correlation with SIMS measurements on CVD diamonds [64]. These calibration factors are discussed in the review by Thonke [177].

A  $p_{1/2}$  spectrum, similar to the one observed in silicon, should be observed at energies a few meV above the ionization energy. However, such a spectrum has not been clearly identified.

An ESR spectrum denoted C-NL1 corresponding to  $J = 3/2$  has been detected in IIb diamond at 1.4 K under a uniaxial stress  $\sim 0.5 \text{ GPa}$  and it has been attributed to neutral B [3].

In 6H-SiC, B replaces a Si atom and its ionization energies in the three non-equivalent sites measured by admittance spectroscopy are 0.27, 0.31, and 0.38 eV [56]. In undoped and boron-doped p-type 6H-SiC samples, a photoionization spectrum with a temperature-dependent threshold between  $\sim 0.5$  and 0.7 eV, and a maximum at 1.75 eV has been reported [83]. The difference between the threshold energy and the electrically-measured ionization energy of B (0.3–0.4 eV) is attributed to lattice relaxation. This photoionization spectrum is correlated with the observation near LHeT of three narrow absorption lines at 2.824, 2.863, and 2.890 eV tentatively attributed to excitons bound to neutral B at the three possible sites in 6H-SiC.

## 7.3 Groups-II and -I Acceptors in Group-IV Crystals

Substitutional group-II elements in silicon and germanium are double acceptors with two charge states  $A^0$  and  $A^-$ . In germanium, at a difference with silicon, Mg is a double substitutional acceptor. The group-IB atoms Cu and Au can locate substitutionally in germanium,<sup>5</sup> where they have been identified as triple acceptors [189]. There exist many studies on group-II acceptors in germanium, aimed in the 1960s toward the fabrication of extrinsic photodetectors and photodetector arrays. Groups II and I acceptors can be partially or totally passivated by hydrogen. Under partial passivation, they retain an acceptor behaviour and spectra of these hydrogenated centres are observed and are also discussed here. The energy levels of the  $A^0$  and  $A^-$  charge states of the group-II double acceptors in germanium have been calculated in the

<sup>5</sup> Cu can also locate in an interstitial site, but its solubility on that site is lower than on the substitutional site (Andreev et al. [5]).

EM approximation where the neutral state is described by a mean-field single-particle model [58]. We first consider germanium because it has been the most studied crystal matrix for group-I and group-II acceptors.

### 7.3.1 Germanium

#### 7.3.1.1 The $A^0$ Charge State

Absorption measurements of  $Zn^0$  and  $Cu^0$  were reported in 1960 by Fisher and Fan [60] and results on Cu by Greenaway [65]. This was followed by results on  $Hg^0$  [35, 133], on  $Zn^0$ ,  $Hg^0$ , and  $Cu^0$  [119] and on  $Cd^0$  [120]. Absorption results on  $Be^0$  and  $Mg^0$  were presented in 1983 by Cross et al., but electrical evidence of the p-type behaviour of Mg in germanium had already been given in 1979 by Bannaya et al. [16] and by Ho [78]. In germanium,  $Be^0$  is the shallowest group-II acceptor with  $E_i \sim 25$  meV, followed by  $Zn^0$ ,  $Mg^0$ ,  $Cd^0$ , and  $Hg^0$  (33, 36, 55, and 92 meV, respectively). When observed at low resolution (typically  $1\text{ cm}^{-1}$  or 0.12 meV), the neutral group-II acceptor spectra at LHeT are very similar to those of the group-III acceptors in germanium [119, 120].

The spectroscopic studies on  $Hg^0$  at LHeT soon produced evidence of a ground state splitting by 0.65 meV [36], and this splitting was explained by an electrostatic interaction between two  $j = 3/2$  holes, leading to states with  $J = 0$  and  $J = 2$  by  $j$ - $j$  coupling, to comply with Pauli's principle. This resulted in a  $\Gamma_1$  ( $J = 0$ ) and  $\Gamma_3 + \Gamma_5$  ( $J = 2$ ) levels, with the  $J = 2$  level assumed to be the deepest in energy with respect to the  $VB$ , in accordance with first Hund's rule [36]. There was initially no suggestion of a ground-state splitting of the  $Zn^0$  spectrum [121], but experiments performed between 12 and 30 K revealed a broad low-energy component  $D^*$ , attributed to a transition from a thermalized state to the excited state of line  $D$  [174]. From these results, a ground state splitting of 2.4 meV was deduced for  $Zn^0$ , and it is comparable to the one (1.75 meV) reported by Thewalt et al. [173] for  $Mg^0$ .

For three holes, the case for  $Cu^0$ , it can be shown that the ground-state symmetry is  $\Gamma_8$ , as for the single acceptors so that no splitting of this state is expected in the absence of a perturbation [149].

The low-resolution positions of the lines of the neutral group-II acceptors and of  $Cu^0$  in germanium are given in Table 7.15. In the group-III acceptor spectra in germanium, whose labelling is used for the group-II and Cu neutral spectra, the  $A_4$  and  $A_3$  lines on the one side, and the  $A_2$  and  $A_1$  lines on the other side, are separated by  $\sim 0.1$  meV. These pairs cannot be resolved in the group-II and the Cu neutral spectra, and because  $A_3$  is about three times more intense than  $A_4$  (see Fig. 7.11), the  $(A_4, A_3) - B$  spacing in the group-II and Cu neutral spectra is close to the  $A_3 - B$  spacing of Table 7.10. Similarly, the  $(A_2, A_1) - B$  spacing is close to the  $A_1 - B$  spacing of this table. This is also the case for the  $(I_7, I_6, I_5) - B$  spacing, close to the  $I_6 - B$  spacing of Table 7.10. For these reasons, in the literature, the  $(A_4, A_3)$ ,  $(A_2, A_1)$ , and  $(I_7, I_6, I_5)$  lines of the group-II and Cu neutral spectra in germanium are usually labelled as  $A_4$ ,  $A_3$ , and  $A_2$ , or  $A''$ ,  $A'$ , and  $A$ , respectively.



**Table 7.15.** Low-resolution positions (meV) of lines of the neutral groupII acceptors and of  $\text{Cu}^0$  in germanium near 7 K. When given, the positions of the thermalized lines are the upper ones. The optical ionization energy reported for  $\text{Au}^0$  is 0.21 eV [89]

| Line                                                                      | $\text{Be}^{0a}$   | $\text{Mg}^{0a}$ | $\text{Zn}^{0b}$    | $\text{Cd}^{0b}$ | $\text{Hg}^{0b}$ | $\text{Cu}^{0c}$ |
|---------------------------------------------------------------------------|--------------------|------------------|---------------------|------------------|------------------|------------------|
|                                                                           |                    |                  |                     |                  | 86.41            |                  |
| <i>G</i>                                                                  | 19.9 <sup>b</sup>  | 31.21            | 28.27               | 50.40            | 87.07            | 38.67            |
|                                                                           |                    | $\sim 31.4^*$    | $\sim 27.9^\dagger$ |                  | 88.12            |                  |
| <i>D</i>                                                                  | 21.92 <sup>b</sup> | 32.95            | 30.10               | 52.08            | 88.77            | 40.37            |
| <i>C</i>                                                                  | 22.70 <sup>b</sup> | 33.71            | 30.86               | 52.83            | 89.51            | 41.12            |
| <i>B</i>                                                                  | 23.35 <sup>b</sup> | 34.34            | 31.48               | 53.41            | 90.17            | 41.76            |
|                                                                           | 23.66              |                  |                     |                  |                  |                  |
| ( <i>A</i> <sub>4</sub> , <i>A</i> <sub>3</sub> )                         | 23.76              | 34.68            | 31.84               |                  | 90.52            | 42.07            |
|                                                                           | 23.86              |                  |                     |                  |                  |                  |
| ( <i>A</i> <sub>2</sub> , <i>A</i> <sub>1</sub> )                         | 23.96              | 34.88            | 32.01               |                  | 90.70            | 42.27            |
|                                                                           | 24.16              |                  |                     |                  |                  |                  |
| ( <i>I</i> <sub>7</sub> , <i>I</i> <sub>6</sub> , <i>I</i> <sub>5</sub> ) | 24.26              | 35.14            | 32.23               |                  |                  |                  |
| $E_{\text{io}}^\ddagger$                                                  | 24.84              | 35.78            | 32.92               | 54.85            | 91.61            | 43.20            |

<sup>a</sup> [44], <sup>b</sup> [120], <sup>c</sup> [149], \*  $D^*$  line, estimated from [173], <sup>‡</sup> See text,

<sup>†</sup>  $D^*$  line, estimated from [174]

For  $\text{Hg}^0$ , only the thermalized transitions corresponding to lines *D* and *G* can be observed because of interferences of the thermalized components with other lines. The energy of the  $4\Gamma_8^-$  state (1.44 meV) calculated by [58], corresponding to the final state of line *B* is used to obtain the  $E_{\text{io}}$  values of Table 7.15. At 15 K, where the  $D^*$  lines are observed, the positions of the *D* lines are  $\sim 0.2$  meV larger than the ones at 7 K.

The spectroscopic results of the group-II acceptors other than  $\text{Hg}^0$  are difficult to interpret because at high resolution the lines generally show more than two components. For  $\text{Be}^0$ , a first explanation is a second ground-state splitting between the  $\Gamma_3$  and  $\Gamma_5$  states, illustrated in Fig. 7.14 showing the multiplet structure of some  $\text{Be}^0$  lines at LHeT.

The ground-state splittings deduced from Fig. 7.14 imply an inverted ordering of the ground-state levels, where  $\Gamma_1$  is the deepest state. From the splittings of line *A*, the separation between the  $\Gamma_3$  and  $\Gamma_5$   $\text{Be}^0$  levels is 0.055 meV and they are 0.15 meV above the  $\Gamma_1$  level [172]. However, the ground-state splittings alone cannot explain the six components observed for *D* ( $\text{Be}^0$ ) and a small splitting of the excited states is also assumed.<sup>6</sup>

<sup>6</sup> It has also been proposed that the multiplet structure of the  $\text{Be}^0$  lines in germanium was due to a distortion of the  $\text{Be}^0$  atom from the  $T_d$  site, with a lowering of its symmetry [121].

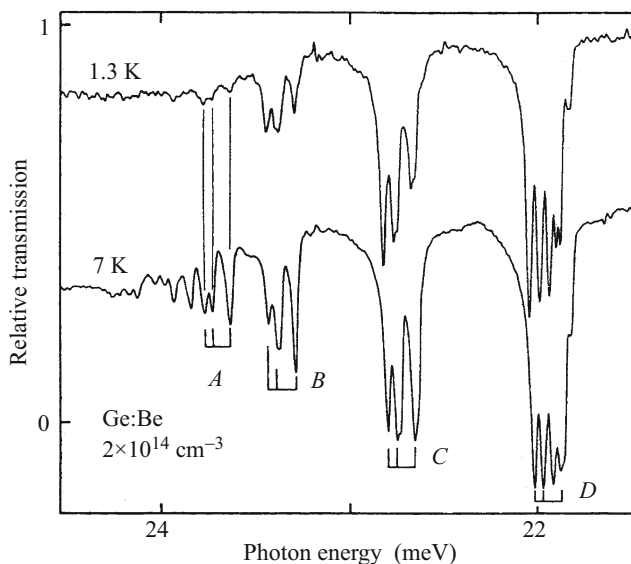


**Fig. 7.14.** Absorption between  $\sim 175.3$  and  $195.6 \text{ cm}^{-1}$  of  $\text{Be}^0$  in germanium at 1.3 and 7 K. The unapodized resolution is  $0.1 \text{ cm}^{-1}$ . The three-component brackets at the bottom of the A to D transitions indicate how the threefold ground state splitting is replicated in all four absorption lines. Reproduced from [172]. Copyright 1987, with permission from Elsevier

The actual situation for  $\text{Zn}^0$  could be still more complicated as high-resolution measurements at 2 K have shown that  $G(\text{Zn}^0)$  is a doublet with a  $0.24 \text{ cm}^{-1}$  ( $30 \mu\text{eV}$ ) separation, and that between 2 and 7 K, the lines D, C, and B of the  $\text{Zn}^0$  spectrum display a shift indicating a small ground state splitting [182].

In germanium, grown in a hydrogen atmosphere and doped with Be and Zn, the spectra of acceptor complexes  $(\text{Be}, \text{H})$  and  $(\text{Zn}, \text{H})$  with ionization energies of 11.29 and 12.53 meV have been observed [113]. They result from the partial passivation of Be and Zn by hydrogen, but no IS has been detected for  $^2\text{H}$ . The ground state of  $(\text{Be}, \text{H})$  is split into two components separated by 0.5 meV, giving two distinct spectra and if no splitting has been observed for  $(\text{Zn}, \text{H})$ , it is none the less expected. Uniaxial stress measurements have shown that these centres have a static trigonal ( $C_{3v}$ ) symmetry [88].

The diffusion of copper in high-purity germanium, grown under a hydrogen atmosphere, results in several hydrogenated acceptor complexes with ionization energies depending on the hydrogen isotope [87]. The results obtained from germanium crystals grown in a  $^1\text{H}_2 + ^2\text{H}_2$  atmosphere are explained by the interaction of two hydrogen nuclei and a hole with the triple-acceptor Cu, and this has been further confirmed by plasma treatments in  $^1\text{H}_2 - ^3\text{H}_2$  mixtures. The ionization energies of these complexes are between 16.8 and 18.2 meV and they show a small positive IS with increasing masses.

These ionization energies are significantly smaller than those of the neutral Cu acceptor (43.2 meV) and this seems to be a general trend of the hydrogenated acceptor (and donor) complexes with respect to the isolated neutral centre. These complexes are tentatively explained by a model in which the hydrogen atoms rotate or tunnel around the Cu atom, with an interaction between this nuclear motion and the acceptor's electronic states. Uniaxial stress measurements show that some of the complexes with two  $^1\text{H}$  atoms have a  $T_d$  symmetry, with a complicated ground state splitting, but that when  $^1\text{H}$  is replaced by a heavier isotope, the resulting complexes have a lower symmetry, with only a single ground-state component [87].

In a germanium sample from an As-doped crystal pulled *in vacuo* and contaminated with Cu, the PTIS spectrum of a CuX centre has been reported by Sirmain et al. [156]. Its first ionization energy is 10.05 meV and the thermalized energy is 9.15 meV. Piezospectroscopic measurements indicate a  $C_{3v}$  symmetry and the dissociation conditions of this complex have led to the tentative attribution of CuX to a  $(\text{Cu}_s, \text{As})$  acceptor complex, which should normally behave as a double acceptor.

### 7.3.1.2 The $A^-$ Charge State

The discrete  $\text{Be}^-$  spectrum is observed in the 44–53 meV region ( $\sim 350\text{--}430\text{ cm}^{-1}$ ) and the  $\text{Zn}^-$  spectrum in the 66–85 meV region ( $\sim 530\text{--}690\text{ cm}^{-1}$ ) and they are superimposed on the two-phonon spectrum of germanium. The  $\text{Zn}^-$  spectrum displayed in Fig. 7.15 includes a part of the photoionization region, which shows Fano resonances involving the optical zone-centre phonon of germanium.

Good-quality spectra of  $\text{Zn}^-$  in germanium have been reported by Piao et al. [138]. The line positions of  $\text{Be}^-$  are given in Table 7.16 and compared with the calculations of Fiorentini and Baldereschi [58].

In a recent investigation [139], the profile of line  $C$  ( $\text{Zn}^-$ ) has been analyzed and fitted with four components  $C^{(1)}$ ,  $C^{(2)}$ ,  $C^{(3)}$ , and  $C^{(4)}$  at 78.107, 78.327, 78.57, and 78.85 meV, respectively. In the light of the piezospectroscopic results obtained in this study, the features  $C^{(1)}$  and  $C^{(2)}$  identified initially as having  $3\Gamma_8^-$  and  $1\Gamma_7^-$  final states (Table 7.16) were re-attributed to  $3\Gamma_8^+$  and  $1\Gamma_7^- + 3\Gamma_8^-$ , respectively. Values of  $E_{\text{io}}(\text{Be}^-)$  and  $E_{\text{io}}(\text{Zn}^-)$ , obtained by adding to the position of line  $B$  the calculated value of the  $4\Gamma_8^-$  state, are 58.14 and 86.66 meV, respectively. These values are comparable to the ones (58.02 and 86.54 meV) obtained by merely adding four times the calculated energy of the single-acceptor  $2\Gamma_8^-$  state to the positions of lines  $D$  ( $\text{Be}^-$ ) and  $D$  ( $\text{Zn}^-$ ). A value of 64 meV has been reported for the thermal ionization energy of  $\text{Be}^-$  by Tyapkina et al. [178], and the reason for the relatively large difference with the optical value is not clear.

Sb-doped germanium samples diffused with copper show absorption thresholds at 0.32 eV in the near IR which can be associated with the onset of the

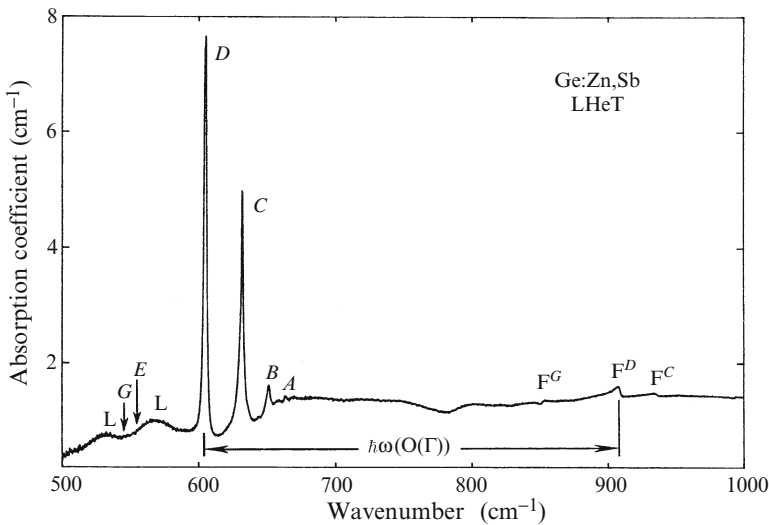


**Fig. 7.15.** Absorption of  $\text{Zn}^-$  in germanium between  $\sim 62$  and  $124$  meV. The features denoted  $F^G$ ,  $F^D$ , and  $F^C$  are Fano resonances associated with the zone-centre  $O(\Gamma)$  phonon of germanium and the corresponding lines. The features denoted by  $L$  are two-phonon lattice absorption bands of germanium. Reproduced from [138]. Copyright 1990, with permission from Elsevier

**Table 7.16.** Measured positions (meV) of the  $\text{Be}^-$  [44] and  $\text{Zn}^-$  lines in germanium at LHeT. Attributions and energy calculations of the final state (third row) from Fiorentini and Baldereschi [58] and private communication quoted by Piao et al. [138]. Some of the values for  $\text{Zn}^-$  have been truncated to keep two significant digits. A  $\text{Zn}^-$  line ( $I_7$ ) with final state  $9\Gamma_8^-$  is observed at  $83.36$  meV [138, 139]

|                  | $G$           | $E$           | $D$           | $C$                            | $a$           | $B$           | $A_4$         | $A_3$         | $A_2$         | $A_1$         |
|------------------|---------------|---------------|---------------|--------------------------------|---------------|---------------|---------------|---------------|---------------|---------------|
|                  | $1\Gamma_8^-$ | $2\Gamma_8^+$ | $2\Gamma_8^-$ | $3\Gamma_8^-$<br>$1\Gamma_7^-$ | $1\Gamma_7^+$ | $4\Gamma_8^-$ | $5\Gamma_8^-$ | $6\Gamma_8^-$ | $3\Gamma_7^-$ | $7\Gamma_8^-$ |
| $\text{Be}^-$    |               |               | 46.50         | 49.78                          |               | 52.18         |               | 53.7          |               |               |
| $\text{Zn}^-$    | 67.80         | 69.06         | 75.02         | 78.12<br>78.33                 | 79.83         | 80.79         | 81.79         | 82.27         | 82.80         | 83.08         |
| $E_{\text{cal}}$ | 18.77         | 17.78         | 11.64         | 8.59<br>8.55                   | 6.98          | 5.92          | 4.91          | 4.46          | 4.08          | 3.66          |

continuum absorption of the  $\text{Cu}^-$  charge state [65], in agreement with the electrical results of [189] and the DLTS results of [155] for the  $\text{Cu}^-/\text{Cu}^{2-}$  level. The onset near  $0.5$  eV observed at  $20$  K by Greenaway [62] should correspond to the  $\text{Cu}^{2-}/\text{Cu}^{3-}$  DLTS level at  $E_c - 0.259$  eV [40].

For shallow multiple acceptors associated with the  $\Gamma_8^+VB$ , the fourfold degeneracy allows one to accommodate a maximum of four holes. Photoconductivity measurements in the very-far IR at LHeT and down to  $1.2$  K have indeed shown that group-II neutral acceptors and  $\text{Cu}^0$  could bind an extra

hole to give the equivalent of  $(1s)^3$  and  $(1s)^4$  configurations [67,68]. The binding energy of this extra hole goes from 5.1 meV for  $\text{Be}^+$  down to 2.0 meV for  $\text{Cu}^+$ . A uniaxial stress can partially lift this degeneracy and these  $A^+$  states are no longer stable and dissociate.

### 7.3.2 Silicon

In this section are presented results on Au, a group-IB element, and on the group-II acceptors. The results on Pt and Mn, two transitions metals whose spectrum bears resemblance with that of Au, are also presented.

The behaviour of group-II FAs in silicon is interesting. Mg behaves as an interstitial double donor and Zn as a substitutional double acceptor. Be shows an acceptor behaviour, but it has been stated that only  $\sim 10\%$  of the Be concentration in silicon is electrically active (quoted by Crouch et al. [45]). Discrete acceptor spectra have been reported at LHeT in Be- and Zn-doped silicon and they include many complexes. In the case of Be, EM acceptor-like spectra associated with four different centres have been reported [45,99]. They are sometimes denoted in the literature Be-I, Be-II, Be-III, and Be-IV, with ionization energies of 192, 146, 200, and 93 meV, respectively. Spectra due to  $(\text{Be}, \text{Li}_i)$  pairs have also been reported [45,137]. Only the first low-energy lines of these spectra are observed, but the line spacings are comparable to those observed for the group-III  $p_{3/2}$  spectra. Some of the  $p_{1/2}$  spectra associated with these centres have also been observed [99,137].

Piezospectroscopic measurements show that the Be-I centre has tetrahedral symmetry which could be attributed to  $\text{Be}^0$  [77]. This attribution was expected from the observation of a red-shifted replica of the 1.7 K spectrum when the temperature is raised to 8 K, attributed to a splitting of the ground state expected for a double acceptor, discussed above in the case of germanium. The replica is split by  $-4 \text{ cm}^{-1}$  ( $-0.5 \text{ meV}$ ) and is observed for all the lines of the  $\text{Be}^0$  spectrum. The direct transition between the  $\Gamma_1$  and  $\Gamma_5$  sublevels of the  $\text{Be}^0$  ground state has also been directly observed at  $4 \text{ cm}^{-1}$  ( $0.5 \text{ meV}$ ) in the very far IR at 1.2 K [137]. A weak temperature-independent component of the  $\text{Be}^0$  spectrum shifted by  $+0.53 \text{ meV}$  has been reported by [77] and attributed to a splitting of the final state. Fano resonances associated with lines of  $\text{Be}^0$  have been reported between 1925 and  $2030 \text{ cm}^{-1}$  ( $\sim 238$  and  $252 \text{ meV}$ ) by Kleverman and Grimmeiss [99].

The  $p_{3/2}$  spectrum of Be-II shows no evidence of a split ground state and it has been suggested that this centre could be a pair of  $nn$  substitutional Be atoms ( $\text{Be}_2$ ), whose trigonal symmetry has been confirmed by the piezospectroscopic measurements of [77]. It may be seen [45] as a divacancy  $V_2$  into which two Be atoms are placed: the two valence electrons of each Be atom satisfies four of the six dangling bonds of  $V_2$  and the two remaining bonds are completed by two electrons of the  $VB$ , leaving two holes. Within this scheme, the  $\text{Be}_2$  pair should then be a double acceptor. An unusual feature is the observation of a much weaker replica of the main spectrum, blue-shifted by

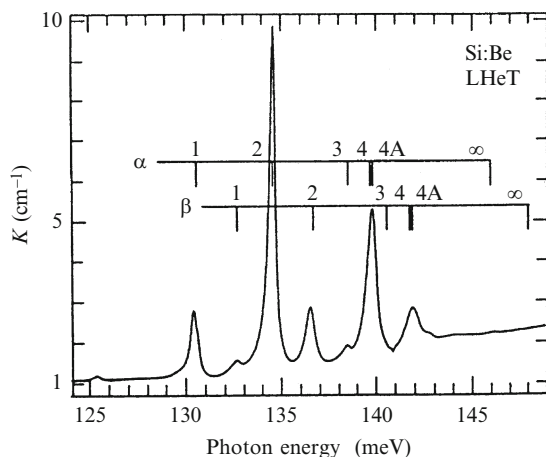


**Fig. 7.16.** Absorption between 1000 and  $1200\text{ cm}^{-1}$  of EM acceptor spectra of the Be-II centre ( $\text{Be}_2^0$ ) in silicon. The main spectrum is denoted  $\alpha$  and the weaker one  $\beta$ . The infinity symbol gives the ionization limit. Numbering 1 of Table 7.1 is used. The lines 4–4A–4B are not resolved in these spectra. The weak feature at  $125.4\text{ meV}$  is not related to  $\text{Be}_2^0$  [77]. Reproduced with permission from Trans Tech Publications

$2\text{ meV}$ , whose relative intensity with respect to the main spectrum is temperature independent. A short discussion of this doublet in relation with a uniform splitting of the excited states is given by Heyman et al. [77]. These two sets of lines of Be-II are displayed in Fig. 7.16.

The Be-IV centre is the (Be, H) complex, as H can be introduced inadvertently. H has been intentionally introduced in Be-doped silicon for an investigation on proton tunnelling and to compare the results with those obtained with (Be,  $^2\text{H}$ ) and (Be, Li) by Muro and Sievers [122]. This study shows *inter alia* that there exists for the (Be, H) complex a splitting of the ground state into five components giving temperature-dependent  $p_{3/2}$  acceptor spectra in the  $620\text{--}750\text{ cm}^{-1}$  ( $77\text{--}93\text{ meV}$ ) region. It also shows that the positive IS when  $^1\text{H}$  is replaced by  $^2\text{H}$  is rather large ( $7.8\text{ cm}^{-1}$  or  $0.97\text{ meV}$ ), compared to those observed for H-related donors. This large difference can be explained by considering the tunnelling of  $^1\text{H}$  and  $^2\text{H}$  into symmetry-equivalent positions around the Be atom, which is related to the tunnel splitting energy.

The temperature and stress dependences of the  $p_{1/2}$  spectra of the (Be,  $^1\text{H}$ ), (Be,  $^2\text{H}$ ), and (Be, Li) complexes have also been investigated [137]. They confirm that the (Be,  $^1\text{H}$ ) and (Be,  $^2\text{H}$ ) complexes undergo either tunnelling or hindered rotor motion.

We have presented here results on the acceptor properties of  $\text{Be}_s$ . Beryllium is also known to produce in silicon substitutional-interstitial pairs which are electrically inactive. These pairs can trap an exciton and the absorption of these excitons will be discussed in due time.

Absorption measurements as a function of temperature show that the  $\text{Zn}^0$  ground state in silicon is split (as for  $\text{Be}^0$  in germanium) into a triplet with

states at 1.9 and 2.8 meV above the fundamental state while the excited states are split twofold [51]. A value of the  $\text{Zn}^0$  ground-state splitting is derived from phonon spectroscopy results showing a peak at 1.92 meV, corresponding presumably to the first excited state of  $\text{Zn}^0$  [160].

An overview of the acceptor spectrum of the (Zn, H) complex has been given by Merk et al. [115], but the positions of the most intense lines of the (Zn, H) spectrum and the hydrogen IS were provided by Suezawa and Mori [165]. Moreover, in this study, a comparison is made between samples doped with  $^{64}\text{Zn}$  and  $^{68}\text{Zn}$  and the result showed for line 2 of the (Zn, H) complex a negative IS of  $\sim 1 \text{ cm}^{-1}$  (0.13 meV) when  $^{64}\text{Zn}$  is replaced by  $^{68}\text{Zn}$ . The hydrogen positive IS when  $^1\text{H}$  is replaced by  $^2\text{H}$  is  $12.1 \text{ cm}^{-1}$  (or 1.5 meV) and it is still larger than the one for Be. This is an indication that in silicon, the same kind of tunnelling of the H atom as the one in the (Be, H) complex also occurs for (Zn, H). As for (Be, H), a splitting of the (Zn, H) acceptor ground state can be inferred from the broadening or asymmetry of the (Zn, H) lines.

The lines of the spectra observed for the neutral group-II acceptors and some of their complexes in silicon are given in Table 7.17. When the ground state is split, only the spectrum from the deepest level is considered. Good spectra of the (Be, H), (Be, D), and (Be, Li) pairs are shown in the paper by Peale et al. [137], but very few line positions are given.

The  $2p'$  transition of the  $p_{1/2}$  spectrum of  $\text{Be}^0$  has been observed and its position deduced from a figure of [77] is  $\sim 1847 \text{ cm}^{-1}$  (229 meV). Similarly, from Fig. 7.8 of [137],  $2p'$  (Be, Li) is found to peak at  $\sim 1158 \text{ cm}^{-1}$  (143.6 meV) at 1.7 K, but at 30 K, a component red-shifted by  $11.1 \text{ cm}^{-1}$  (1.38 meV) reveals the splitting of the ground state of the (Be, Li) pair.

There seems to be no absorption study of Cd in silicon. Two Cd acceptor levels have been detected in DLTS investigations of silicon implanted with radioactive  $^{111}\text{In}$  transmuting into  $^{111}\text{Cd}$  [107]. However, the case of Cd in silicon seems to be more complex than the other group-II elements as a donor state seemingly associated with substitutional Cd has been identified by ESR under TEC at LHeT [128].

There is no report of the absorption spectrum of  $\text{Be}^-$  in silicon, and even though values  $\sim 0.4 \text{ eV}$  have been reported for its ionization energy, there is

**Table 7.17.** Positions (meV) of  $p_{3/2}$  lines of the  $\text{Be}^0$  and  $\text{Zn}^0$  double acceptors and of some of their complexes in silicon at LHeT. The line label is that of [45]

| Line            | (Be, H) <sup>a</sup> | $\text{Be}_2^{\text{ob}}$ | $\text{Be}^{\text{oc}}$ | Be-III <sup>d</sup> | (Be, Li) <sup>b</sup> | $\text{Zn}^{\text{oe}}$ | (Zn, H) <sup>f</sup> | $\text{Zn}(\text{X}_2)^{\text{e}}$ |
|-----------------|----------------------|---------------------------|-------------------------|---------------------|-----------------------|-------------------------|----------------------|------------------------------------|
| 1               | 77.54                | 130.2                     | 176.4                   | —                   | 91.8                  | 303.90                  | $\sim 260.4^*$       | 322.19                             |
| 2               | 81.30                | 134.4                     | 180.3                   | 188.3               | 95.1                  | 307.79                  | 264.14               | 325.95                             |
| 3               | —                    | 136.4                     | 184.3                   | 192.2               | 99.1                  | 311.68                  |                      |                                    |
| 4–4A            | 86.35                | 139.7                     | 185.6                   | 193.5               | 100.4                 | 312.99                  | 269.05               | 331.48                             |
| (5)             |                      |                           |                         |                     |                       |                         | 269.44               |                                    |
| (7)             |                      | 141.9                     |                         |                     |                       |                         |                      |                                    |
| $E_{\text{io}}$ | 92.6                 | 145.9                     | 191.8                   | 199.8               | 106.6                 | 319.3                   | 275.6                | 337.5                              |

<sup>a</sup> [122], <sup>b</sup> [45], <sup>c</sup> [115], <sup>d</sup> [99], <sup>e</sup> [51], <sup>f</sup> [165], \* Estimated from Fig. 2 of this reference

no absolute report of this energy [2]. The ionization energy of  $\text{Zn}^-$  determined from electron-capture measurements is 664 meV at RT [187], but there again, no absorption spectrum of  $\text{Zn}^-$  has been reported. Electric-dipole spin resonance of  $\text{Zn}^-$  reveals that its spin-orbit acceptor splitting  $\Delta_{\text{so}}^{\text{A}}$  is only 0.31 meV [152].

Gold is a group-IB element and platinum is the nearby TM element with a  $5d^9$  electronic configuration. In silicon, they are rapid diffusers and their electronic properties have been actively investigated as they are used to control the lifetimes of free electrons and holes. In silicon, they locate on a substitutional site, but they can also form complexes with other atoms.

Absorption at LHeT of gold and platinum diffused in silicon near 1100°C has been reported by Armelles et al. [8] and Kleverman et al. [100], and one of the observed spectra attributed to the  $0/-$  acceptor level. This level is located approximately at  $E_{\text{v}} + 0.61 \text{ eV}$  ( $E_{\text{c}} - 0.56 \text{ eV}$ ) for Au and at  $E_{\text{v}} + 0.92 \text{ eV}$  ( $E_{\text{c}} - 0.25 \text{ eV}$ ) for Pt. The observed  $p_{3/2}$  spectra are similar to those of the group-II elements in silicon. When the group-III-acceptor lines are denoted 1, 2, 3, etc., the Au and Pt lines are denoted  $I_1$ ,  $I_2$ ,  $I_3$ , etc. [8]. In Au as well as in Pt, line  $I_1$  shows a small splitting similar to the one observed for Be and Cd, presumably due to a ground state splitting. In the range of the Pt  $p_{3/2}$  spectrum, lines which do not fit the EM scheme are also observed and this extends above the  $p_{3/2}$  ionization limit. Most of these additional lines have been attributed to phonon replicas of the  $p_{3/2}$  lines and for a zero-phonon line  $I_i(0)$ , the one- and two-phonon lines are denoted  $I_i(1)$  and  $I_i(2)$ , respectively [100]. The Au and Pt  $p_{3/2}$  spectra at LHeT are compared in Fig. 7.17.

This figure shows no phonon replicas in the Au spectrum. A  $p_{3/2}$  transmission spectrum of Pt at LHeT showing the  $I_1(0)$  splitting is displayed in Fig. 7.18. The measured FWHM of the components of  $I_1(0)$  is  $\sim 1 \text{ cm}^{-1}$  ( $\sim 124 \mu\text{eV}$ ) and the true width should be somewhat smaller, but excited shallower levels are broader.

The widths of the phonon replicas  $I_1(1)$  and  $I_2(1)$  are only 2–4 times larger than the no-phonon lines, and this implies a relatively small coupling with the electronic transitions, which has been discussed by Kleverman et al. [100] in terms of a pseudolocalized phonon in the vicinity of the acceptor atom. The positions of the no-phonon acceptor lines of Au and Pt and of the phonon replicas of Pt in silicon are given in Table 7.18.

From Table 7.18, the energy of the Pt-associated localized phonon resonant with the acoustic phonon band is found to be 7.12 meV or  $57.4 \text{ cm}^{-1}$ .

At higher energies, structures were observed in the Au and Pt PTI spectra by [100] and the first ones, near  $7790 \text{ cm}^{-1}$  (966 meV) and  $5310 \text{ cm}^{-1}$  (658 meV) in the Pt and Au spectra, respectively, were attributed to a split  $2p'$  line of the  $p_{1/2}$  spectrum, partly due to the absorption-like spectra of phonon resonances when measured by photoconductive methods. Recent piezospectroscopic measurements have led to the re-attribution of these structures to a Fano resonance involving a  $1s_{3/2}(\Gamma_8)$  transition and an O( $\Gamma$ ) phonon of silicon [101]. This  $1s_{3/2}(\Gamma_8)$  transition is assumed to take place between



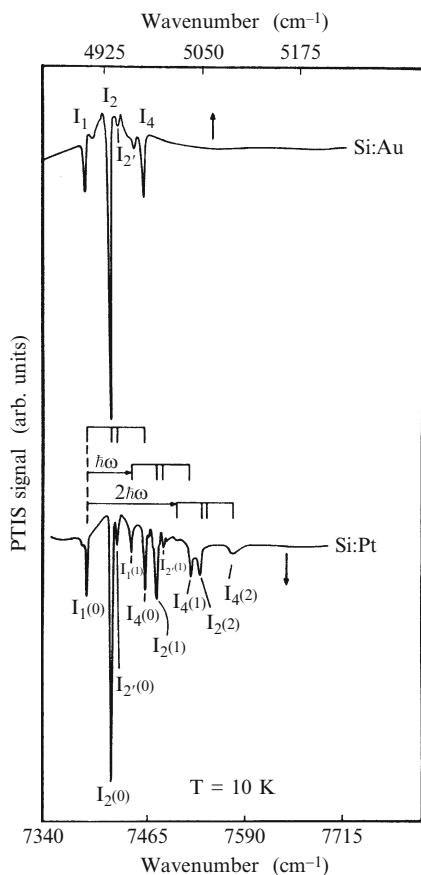


**Fig. 7.17.** Comparison between the Au and Pt  $p_{3/2}$  spectra in silicon obtained from photothermal ionization measurements at LHeT. To facilitate the assignment of the Pt phonon replicas, markers indicating 0, 1, and 2 phonon energies ( $\hbar\omega = 57 \text{ cm}^{-1}$  or 7.1 meV) are included. The Au spectrum extends from about 600 to 650 meV and the Pt one from 910 to 960 meV [100]. Copyright 1988 by the American Physical Society

the deep atomic level and an EM  $1s (\Gamma_8^+)$  state of the kind calculated by Baldereschi and Lipari. This attribution is made from the similarity between the deformation potentials for the  $1s (\Gamma_8^+)$  for boron and those obtained in this study for Au and Pt [101]. From the values of the resonance, the  $1s (\Gamma_8^+)$  transition energy should be  $4796$  and  $7278 \text{ cm}^{-1}$  (594.6 and 902.4 meV) for Au and Pt, respectively, but no lines are observed at these positions. Other Fano resonances involving an O ( $\Gamma$ ) phonon are also observed for both elements at higher energies and the whole structure displayed in Fig. 7.19.

Mn is a TM element with a  $3d^5 4s^2$  configuration close to that of Fe ( $3d^6 4s^2$ ) and this fast diffuser is located on a  $T_d$  interstitial site. At a difference with  $\text{Fe}_i$

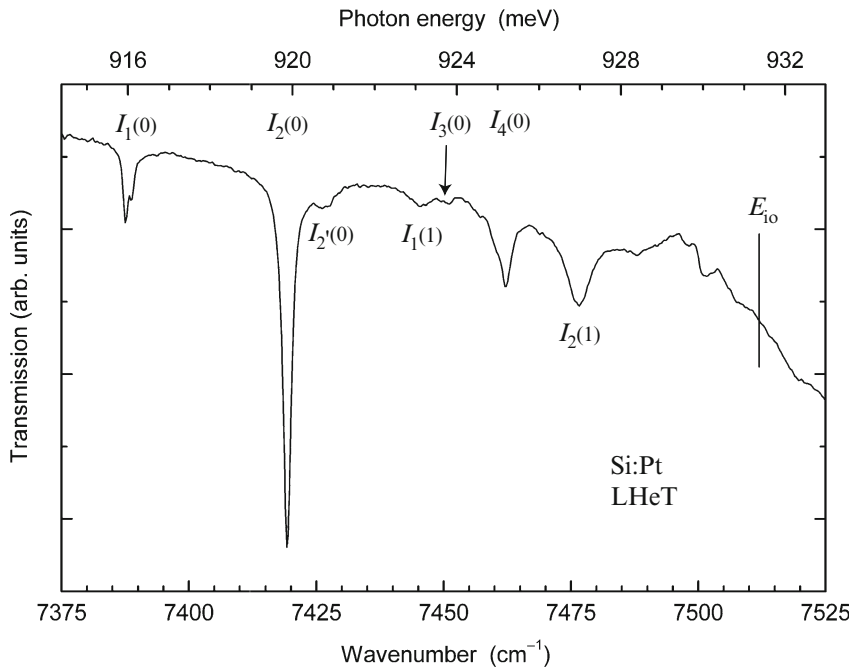


**Fig. 7.18.** Part of the transmission spectrum of  $p_{3/2}$  (Pt) in silicon on an expanded scale at a resolution of  $0.55\text{ cm}^{-1}$  ( $68\text{ }\mu\text{eV}$ ). The features of this spectrum above  $I_{2(1)}$  are not identified. The  $I_{2'}$  label is from [100]. The vertical bar indicates the value of  $E_{\text{io}}$ , obtained by adding 11.5 meV to the position of line  $I_{2(0)}$

**Table 7.18.** Positions (meV ( $\text{cm}^{-1}$  in parentheses)) at LHeT of the no-phonon Au and Pt acceptor lines  $I_1(0)$  in silicon, complemented for Pt by the phonon replicas  $I_1(1)$  and  $I_1(2)$ . The position of  $I_2'(0)$ (Pt) is  $920.74\text{ meV}$  ( $7426.3\text{ cm}^{-1}$ ) [8]

|     | $I_1(0)$  | $I_2(0)$              | $I_3(0)$ | $I_4(0)$              | $E_{\text{io}}$         |
|-----|-----------|-----------------------|----------|-----------------------|-------------------------|
| Au  | 607.36    | 611.27                | 615.27   | 616.45                | 622.8                   |
| 0/– | (4898.7)  | (4930.2)              | (4962.5) | (4972.0)              | $E_c - 0.547\text{ eV}$ |
|     | 607.55    |                       |          | 616.59                |                         |
|     | (4900.2)  |                       |          | (4973.1)              |                         |
| Pt  | 915.935   | 919.86                | 923.81   | 925.1                 | 931.4                   |
| 0/– | (7387.51) | (7419.2)              | (7451.0) | (7461.0)              | $E_c - 0.239\text{ eV}$ |
|     | 916.098   |                       |          | 925.19                |                         |
|     | (7388.75) |                       |          | (7462.2)              |                         |
|     | $I_1(1)$  | $I_2(1)$              | $I_3(1)$ | $I_4(1)$              |                         |
|     | 923.10    | 926.98                |          |                       |                         |
|     | (7445.3)  | (7476.6)              |          |                       |                         |
|     | $I_1(2)$  | $I_2(2)$              | $I_3(2)$ | $I_4(2)$              |                         |
|     |           | 934.18                |          | 939.44                |                         |
|     |           | (7534.7) <sup>a</sup> |          | (7577.1) <sup>a</sup> |                         |

<sup>a</sup> [100]

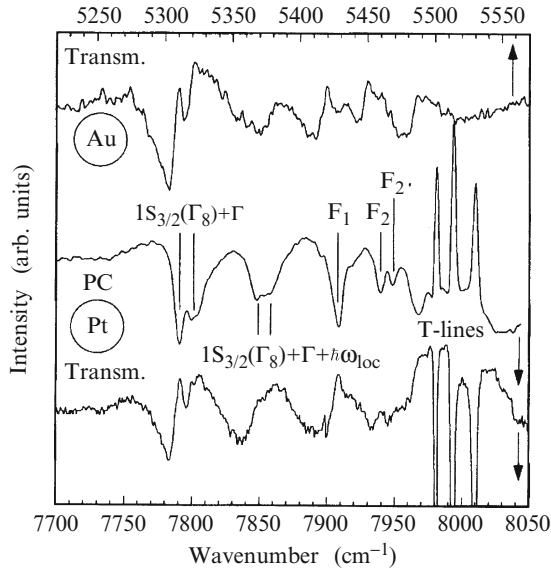


**Fig. 7.19.** Spectra of Au (647.2–690.6 meV) and Pt (954.7–998.1 meV) in silicon at LHeT. Note the difference between the Fano resonance shapes of Pt in the transmission and photoconductive (PC) spectra. The splitting associated with the  $1s_{3/2}(\Gamma_8)$  structure is attributed to the crystal field. The Fano resonances labelled  $F_1$ ,  $F_2$ , and  $F_2'$  include the  $I_{1(0)}$ ,  $I_{2(0)}$ , and  $I_{2'(0)}$  lines of Fig. 7.18. The T-lines are related to a Pt donor centre [101]. Copyright 1997 by the American Physical Society

for which only a donor state is known in silicon, Mn gives a deep acceptor state at  $E_c - 0.13$  eV. Its absorption spectrum at 2 K shows only four well-separated reasonably sharp lines with FWHMs of  $2.5 \text{ cm}^{-1}$  (0.3 meV). When temperature is raised, additional lines with intensities growing with temperature are observed [20].

## 7.4 An Isoelectronic Acceptor: the Be<sub>2</sub> Pair in Silicon

It has been mentioned in Sect. 6.6 that when the electron part of an exciton was bound more strongly to an isoelectronic centre, an isoelectronic acceptor (IA) could form. In Be-doped silicon, two sets of PL lines were reported near 1077 and 1115 meV [75]. The most intense one, consisting of three lines denoted *A*, *B*, and *B'* at 1078.27, 1076.34, and 1075.74 meV, respectively, was attributed from Zeeman measurements to an exciton bound to the isoelectronic (Be<sub>s</sub>, Be<sub>i</sub>) pair with axial symmetry [75, 94], and it was suggested that this centre could be an isoelectronic donor. The PL of lines *A*, *B*, and *B'* of (Be<sub>s</sub>, Be<sub>i</sub>) at 8 K is displayed in Fig. 7.20. The inset in this figure shows how the coupling of the electron ( $j_e = 1/2$ ) with the hole ( $j_h = 3/2$ ) of an exciton bound to an isoelectronic centre with  $T_d$  symmetry gives first a triplet

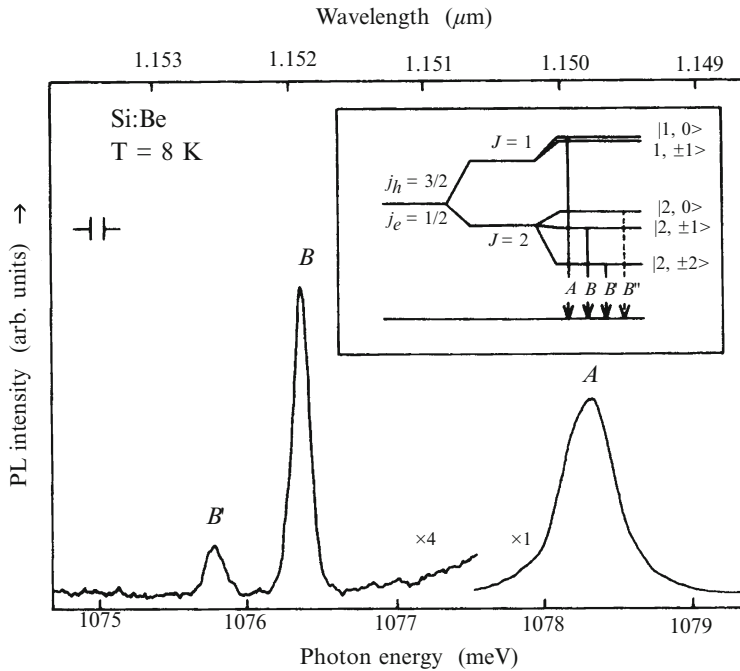


**Fig. 7.20.** Spectrum of the recombination of the exciton bound to the isoelectronic ( $\text{Be}_s$ ,  $\text{Be}_i$ ) centre in silicon showing line  $A$ ,  $B$ , and  $B'$ . The inset shows a schematic energy diagram for the IBE (see text). The additional magnetic-field-induced  $B''$  line is indicated by a broken line (after [94]). Reproduced with permission from the Institute of Physics

( $J = 1$ ) and then a quintuplet ( $J = 2$ ) state, and how the symmetry lowering of the ( $\text{Be}_s$ ,  $\text{Be}_i$ ) pair splits the triplet state into substates with  $M_J = 0$  and  $\pm 1$  denoted  $|1, 0\rangle$  and  $|1, \pm 1\rangle$  and the quintuplet state into substates  $|2, 0\rangle$ ,  $|2, \pm 1\rangle$ , and  $|2, \pm 2\rangle$ . In this inset, it is further shown that  $A$ ,  $B$ , and  $B'$  lines are attributed to the creation or annihilation of an IBE in the  $|1, \pm 1\rangle$  substate for  $A$  line, the  $|2, \pm 1\rangle$  substate for  $B$  line, and the  $|2, \pm 2\rangle$  substate for  $B'$  line. Creation or annihilation from the  $|2, 0\rangle$  substate is forbidden, but is allowed under a magnetic field, giving line  $B''$ .

Line  $A$  was also observed in absorption and PLE measurements near 2 K. In the PLE spectrum of line  $B'$ , other weaker lines were reported at energies between  $\sim 1110$  and  $1114$  meV, and they were attributed first to the transitions toward the excited states of the IBE. Inversely, in the PL measurements at 1.2 K, only line  $B'$  was observed (with a weak contribution of line  $B$ ) while at 15 K, line  $A$  predominated, and at 40 K, two weak PL lines due to recombination from the excited states were also observed [176].

The two weaker lines observed in PL near 1115 meV ( $A_1$  and  $B_1$  at 1117.0 and 1115.21 meV, respectively) were initially attributed to the recombination

of excitons bound to neutral Be-related acceptors. However, the relatively long lifetime measured for line  $B_1$  (2.3 ms) led to ascribe these lines to the recombination of another IBE. A third transition  $B'_1$  with an energy of 1114.53 meV, extrapolated from a fit of the lifetime of  $B_1$  vs. temperature, was also associated with this new IBE. By analogy with the acceptor- $X$  centres in silicon, this IBE was tentatively attributed to a (Be<sub>s</sub>, Be<sub>i</sub>) pair perturbed by a nearby C atom [176].

The “long” lifetime (480  $\mu$ s) measured by [176] for the  $|2, \pm 2\rangle$  excited state of  $B'$  allowed to perform absorption measurements in the far IR similar to those<sup>7</sup> on the S<sub>A</sub> and S<sub>B</sub> IDs. The results of these measurements demonstrated without ambiguity that the (Be<sub>s</sub>, Be<sub>i</sub>) pair was indeed an isoelectronic acceptor [106, 175]. The difference between the far-IR spectra of a Be-doped silicon sample under above-band-gap illumination and under TEC are displayed in Fig. 7.21 at different temperatures and compared with the  $p_{3/2}$

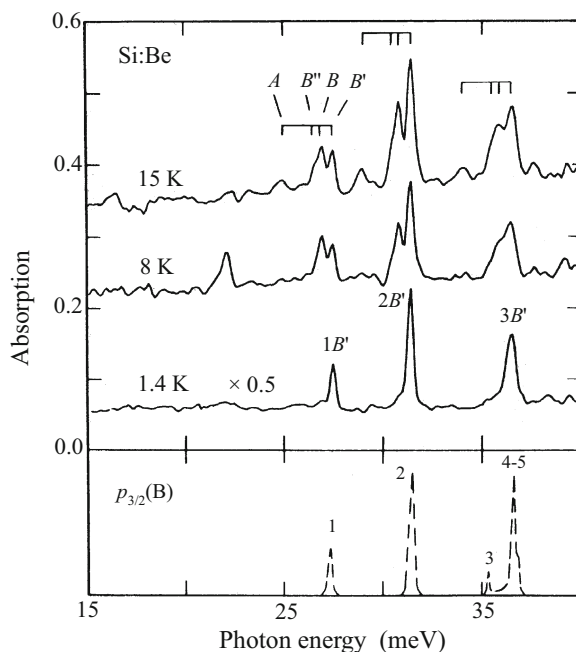


**Fig. 7.21.** Absorption between  $\sim 120$  and  $320 \text{ cm}^{-1}$  of the  $p_{3/2}$  spectrum of the Be<sub>2</sub> pair in Be-doped silicon induced by modulated illumination with 1.92 eV radiation. The ground state of the lines observed at 1.4 K is  $B'$ . Components  $nB$ ,  $nB''$ , and  $nA$  at 15 K arise from thermalization to the  $B$ ,  $B''$ , and  $A$  ground state sublevels of the IBE. The  $p_{3/2}(B)$  dashed spectrum is shifted down by 3.0 meV to position the lines into coincidence (after [106]). Copyright 1984 by the American Physical Society

<sup>7</sup> This far-IR spectrum on the (Be<sub>s</sub>, Be<sub>i</sub>) pair actually provided the first results on the odd-parity states of an IBE shallow-impurity-like centre.

spectrum of boron in silicon. These spectra show the existence of a new acceptor-like spectrum due to illumination.

At the lowest temperature, three acceptor lines denoted  $1B'$ ,  $2B'$ , and  $3B'$  are observed at 27.51, 31.44, and 36.50 meV, respectively, and from comparison with the  $p_{3/2}$  (B) spectrum, their excited states are comparable to the  $1\Gamma_8^-$ ,  $2\Gamma_8^-$ ,  $1\Gamma_6^- + 1\Gamma_7^-$ , respectively, in  $T_d$  symmetry. Their ground state is the IBE  $|2, \pm 2\rangle$  substate, and for higher temperatures, the thermalization of the other sublevels of the IBE ground state gives lines  $nB$ ,  $nB''$ , and  $nA$ , with  $n = 1, 2$ , and 3. In the shallow acceptors numbering 4 of Table 7.2, lines  $1B'$ ,  $2B'$  and  $3B'$  correspond to lines 1, 2, and 4–6 of the  $p_{3/2}$  spectrum of group-III acceptors.

The existence of an IA led to the conclusion that the PL excitation spectrum of line  $B'$  obtained before by Thewalt et al. [176] was indeed a two-hole excitation spectrum of the IA [175]. In this spectrum, line  $A$  is due to the recombination of the IBE from the “excited” ground state  $A$  of the IA, but other lines are due to the IBE recombination leaving the hole bound to the IA in an excited state. The three most intense lines of the two-hole spectrum at 1099.16, 1105.68, and 1111.89 meV correspond to the  $1\Gamma_7^+$ ,  $2\Gamma_8^+$ , and  $3\Gamma_8^+$  even-parity excited states, while two weak lines at 1103.2 and 1107.1 meV, the equivalent of lines 1 and 2 in the far-IR spectrum, correspond to  $1\Gamma_8^-$  and  $2\Gamma_8^-$  odd-parity excited states.

The spacings between the sublevels of the IBE ground state deduced from the splittings of the far-IR lines 1, 2 or 3 at 15 K or from the spacings of the near-IR lines  $A$ ,  $B$ ,  $B'$ , and  $B''$  are similar and they are given in Table 7.19.

It can be assumed that this IA is EM-like, and by adding the calculated EM energy of the  $2\Gamma_8^-$  level (11.5 meV) to the position of line  $2B'$  (line 2 of the  $p_{3/2}$  spectra), an ionization energy  $E_{io}$  of 42.9 meV can be estimated for the ( $\text{Be}_s$ ,  $\text{Be}_i$ ) IA. The energies of the ( $\text{Be}_s$ ,  $\text{Be}_i$ ) IA transitions obtained from the near-IR and far-IR spectra are summarized in Table 7.20 with the corresponding attributions. The above value of  $E_{io}$  can be used to deduce from the experimental values of the IA transitions corresponding values of the energy levels of the excited states, and to compare them with those for the group-III B acceptors. This comparison clearly shows the validity of the IA scheme for the ( $\text{Be}_s$ ,  $\text{Be}_i$ ) IBE.

The binding energy  $E_{IBE}$  for the ( $\text{Be}_s$ ,  $\text{Be}_i$ ) pair is only 95 meV, which is rather small compared to the values of  $E_{IBE}$  for the “C” and “P” O-related

**Table 7.19.** Comparisons of the spacings (meV) of the ground-state sublevels of the ( $\text{Be}_s$ ,  $\text{Be}_i$ ) IBE in silicon obtained by the near-IR and induced far-IR absorption measurements (after [175])

| Sublevels spacing                                  | Near-IR         | Far-IR          |
|----------------------------------------------------|-----------------|-----------------|
| $ 2, \pm 2\rangle -  1, \pm 1\rangle$ ( $B' - A$ ) | $2.53 \pm 0.13$ | $2.50 \pm 0.01$ |
| $ 2, \pm 2\rangle -  2, 0\rangle$ ( $B' - B''$ )   | 0.9             | $0.95 \pm 0.10$ |
| $ 2, \pm 2\rangle -  2, \pm 1\rangle$ ( $B' - B$ ) | $0.60 \pm 0.10$ | $0.62 \pm 0.08$ |

**Table 7.20.** Experimental energies (meV) of the transition to odd-parity and even-parity levels of the  $(Be_s, Be_i)$  IA in silicon measured by the near-IR PL excitation and induced far-IR absorption (after [175]). The last two columns give a comparison of the empirical energies of the excited states of the IA with those of boron. The  $T_d$  symmetry labels are used as an approximation

| Final state                 | Transition energy | Excited state energy ( $Be_s, Be_i$ ) | Excited state energy (boron) |
|-----------------------------|-------------------|---------------------------------------|------------------------------|
| $1\Gamma_7^+$               | 23.42             | 19.5                                  | 22.94                        |
| $1\Gamma_8^-$               | 27.51             | 15.4                                  | 15.26                        |
| $2\Gamma_8^+$               | 29.94             | 13.0                                  | 13.44                        |
| $2\Gamma_8^-$               | 31.44             | [11.5]                                | 11.02                        |
| $3\Gamma_8^+$               | 36.15             | 6.7                                   | 6.38                         |
| $1\Gamma_6^- + 1\Gamma_7^-$ | 36.50             | 6.4                                   | $\sim 5.8$                   |
| $4\Gamma_8^+$               | 38.56             | 4.3                                   | 3.85                         |
| $E_{io}$                    | 42.9              |                                       |                              |

centres or for the (S, Cu) centres. Assuming that the binding energy of the electron part of the exciton to the centre is  $E_{IBE} - E_{io}$ , it is found to be  $\sim 52$  meV, about half the exciton binding energy.

The close similarity between the  $B'$ ,  $B$ ,  $A$  set of lines and the  $B'_1$ ,  $B_1$ ,  $A_1$  set at higher energy had led to assume that the latter one was due to an IBE, possibly due to a  $(Be_s, Be_i)$  pair perturbed by a nearby C atom [176]. A comparison of the PL excitation spectra and the photoinduced far-IR spectra in Be-doped silicon samples with a low and high value of  $[C_s]$  allowed to detect a new IA spectrum with an ionization energy  $\sim 35$  meV in the sample with a high  $[C_s]$  value, in addition to the above-discussed one, and this seems to confirm the above suggestion about the structure of this new IA [105].

Calculations of the atomic structures of the Be-related centres in silicon favour for the  $Be_2$  pair, discussed in this section, a  $(Be_s, Be_i)$  pair along a  $\langle 111 \rangle$  axis [169], and this is confirmed by the experimental results of [76] on a local vibrational mode of the  $Be_2$  pair.

## 7.5 An Acceptor Equivalent of $H^-$ : the $A^+$ Ion

In the weakly compensated n-type semiconductors, a neutral donor can bind an electron at low temperature by thermal ionization of part of the neutral donors and trapping of some of the free electrons by the neutral donors (see Sect. 6.9.1). These  $D^-$  ions have equivalents in p-type semiconductors, and the spectroscopy of the  $A^+$  ions has been investigated for group-III acceptors in silicon and group-II acceptors in germanium. The ionization energies  $E_i$  of positively-charged group-III acceptors in silicon has been measured by acoustic phonon spectroscopy at 1 K by Burger and Lassmann [25], and the values of

$E_i(B^+)$ ,  $E_i(Al^+)$ , and  $E_i(Ga^+)$  are 1.9, 1.7, and 1.6 meV, respectively. These values do not scale with the ionization energies of the neutral acceptors, rather they fit well with the hydrogenic model giving a value of 0.055 for the ratio  $E_i(A^+)/E_i(A^0)$ , where  $E_i(A^0)$  is the EM value of the acceptor ionization energy [63]. Taking  $E_i(A^0) = 31.56$  meV [14] gives  $E_i(A^+) = 1.73$  meV. The value of  $E_i(In^+)$  for the relatively deep In acceptor is 5.8 meV.

In germanium doped with the double acceptor Be, under appropriate filtering allowing RT blackbody illumination, photoconductivity (PC) with a threshold at  $\sim 5$  meV ( $\sim 40$  cm $^{-1}$ ) was observed at temperatures below  $\sim 3$  K. This PC signal, which merged near  $\sim 10$  meV with the PC signal of the shallow acceptors, was attributed to the photoionization of Be $^+$  ions produced by the RT illumination [67]. The hole equivalents of this hypothetical  $(1s)^3$  configuration were also observed in germanium doped with other group-II acceptors and Mn, and the hole equivalent of an hypothetical  $(1s)^4$  configuration was observed in Cu-doped germanium. The trapping of a maximum of four holes by an acceptor is possible because of the fourfold degeneracy of the germanium (and silicon) VB. A uniaxial stress along a [112] axis decouples the VB into two twofold degenerate subbands, and the acceptors coupled to the upper one can accommodate only two holes, precluding the stability of a  $(1s)^3$ -like configuration for a sufficiently high stress. This explains why the low-temperature PC response of Be $^+$  in germanium disappears for values of a [112] stress above 70 MPa [67]. Values of the ionization energies of 4.7, 1.9, 2.9, 12.2, 3.2, and 2.0 meV have been reported for Be $^+$ , Zn $^+$ , Mg $^+$ , Hg $^+$ , Mn $^+$ , and Cu $^+$ , respectively [68, 125, 126]. Variational calculations of these ionization energies using pseudo He or Li atoms have been performed and they provide an upper bound for the ground state energies in each configuration [191].

## 7.6 Acceptors in III-V and II-VI Semiconductors

### 7.6.1 Groups-II and -IV Acceptors in III-V Compounds

In III-V compounds, group-II acceptors are located on the atom-III sublattice and group-IV acceptors on the atom-V sublattice. In GaAs, however, the Si atom can also be found on atom-III sublattice, where it behaves as a donor. Two main types of GaAs LEC crystals can be considered: a) the semi-insulating (SI) crystals, with a Fermi level pinned near  $E_c - 0.8$  eV because of the presence of the As $_{Ga}$  deep donor (EL2), where the residual acceptors are ionized at LHeT under TEC and b) the Ga-rich samples which can be made p-type by doping with shallow acceptors.

For GaAs, spectroscopic data exist for Be $_{Ga}$ , Mg $_{Ga}$ , Zn $_{Ga}$ , Cd $_{Ga}$ , C $_{As}$ , Si $_{As}$ , and Ge $_{As}$  acceptors. The first detailed results on the acceptor spectra in GaAs, including Zeeman measurements, were obtained on epitaxial layers by PTIS [97]. When it was found that the deep donor EL2 in SI GaAs could be converted into an electrically inactive metastable state creating a



non-equilibrium concentration of free holes by illumination with  $\sim 1.1$  eV photons below 120 K, absorption measurements of the residual acceptors in SI samples were also reported [184].

The absorption spectra of EM acceptors in GaAs consist of three to five lines which bear a resemblance with those in germanium, and are noted from the low-energy side *G*, *E*, *D*, *C*, and *B*. The shallow acceptor transitions are observed between 122 and 235  $\text{cm}^{-1}$  (15.1 and 29.1 meV), on the low-energy side of the strong one-phonon absorption of GaAs (269  $\text{cm}^{-1}$  or 33.4 meV at LHeT), in a spectral region where the “static” dielectric constant  $\epsilon_s$  shows a non-negligible increase with energy compared to the true static value due to dispersion, with an effective Rydberg proportional to  $\epsilon_s^{-2}$ . The absorption of  $\text{Be}_{\text{Ga}}$  in GaAs at 1.9 K is shown in Fig. 7.22 and the three lines *G*, *D*, and *C* correspond in order of increasing energies to the  $2P_{3/2}$ ,  $2P_{5/2}$  ( $\Gamma_8$ ), and  $2P_{5/2}$  ( $\Gamma_7$ ) final states of the first column of Table 5.16 for germanium. In SI GaAs, the ionized shallow acceptors are neutralized by converting first the EL2 donor into a metastable state, that does not trap free holes, by illumination at  $1.06 \mu\text{m}$  (1.17 eV) with a  $\text{Nd}^{3+}$  YAG laser. The electronic Raman scattering of

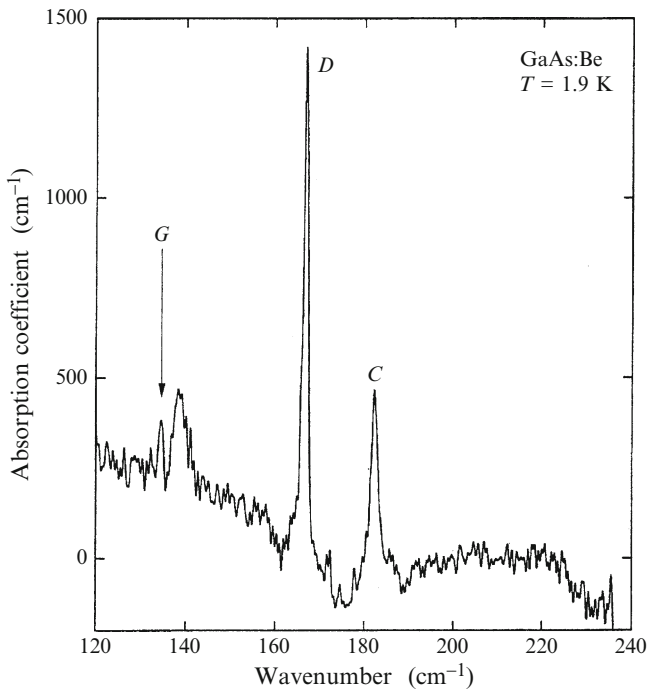


**Fig. 7.22.** Absorption of  $\text{Be}_{\text{Ga}}$  between 14.9 and 29.8 meV in a GaAs sample with  $[\text{Be}] = 2.3 \times 10^{16} \text{ cm}^{-3}$ . The labelling is the same as for the acceptor lines in germanium. The broad feature near  $140 \text{ cm}^{-1}$  is due to the mylar window of the cryostat. The ionization energy of Be corresponds to  $\sim 225 \text{ cm}^{-1}$  or 27.9 meV [109]. Copyright 1996 by the American Physical Society

the C and Zn acceptors associated with illumination at that energy has been reported [183, 186]. The most intense Raman line observed is the  $E$  line, due to a  $1S_{3/2} (\Gamma_8^+) \rightarrow 2S_{3/2} (\Gamma_8^+)$  transition, which is very weak or non-existent in the absorption spectrum.

The measured FWHMs of the acceptor lines are usually broader ( $\sim 1.5 - 2 \text{ cm}^{-1}$  or  $0.19 - 0.25 \text{ meV}$ ) than those observed in silicon and germanium, but a FWHM of  $0.7 \text{ cm}^{-1}$  ( $87 \mu\text{eV}$ ) has been reported by Atzmüller et al. [11] for the  $G$  line of the  $C_{As}$  acceptor.

The positions of the absorption lines of some shallow acceptors in GaAs are given in Table 7.21. The attributions are those of [97]. The  $Ge_{As}$  lines are closer to the one-phonon absorption of GaAs and their positions have been deduced from selective-pair PL measurements [98].

Two lines at  $192.5$  and  $195.3 \text{ cm}^{-1}$  ( $23.87$  and  $24.21 \text{ meV}$ ) have been observed in the  $C_{As}$  spectrum by Kirkman et al. [97] between lines  $B$  and  $A$  of Table 7.21. They have been attributed to the equivalent for GaAs of the  $A_4$  and  $A_3$  lines of Table 7.9 for germanium.

The ionization energies of Be, Mg, Zn, and C are close to the low-energy onset of the one-phonon absorption of GaAs, but those of Si and Ge are within this strong intrinsic absorption and most of the discrete electronic transitions of these latter acceptors are resonant with the one-phonon absorption. Hence, their energies have been deduced from PL measurements near from the GaAs band gap.

**Table 7.21.** Positions ( $\text{meV}$  ( $\text{cm}^{-1}$  in parentheses)) of the shallow acceptor absorption lines observed in GaAs at LHeT

| Line       | Attribution                                 | $Be_{Ga}^a$      | $Mg_{Ga}^b$      | $Zn_{Ga}^c$                   | $C_{As}^b$                    | $Si_{As}^b$      | $Ge_{As}^d$ |
|------------|---------------------------------------------|------------------|------------------|-------------------------------|-------------------------------|------------------|-------------|
| $G$        | $2P_{3/2} (\Gamma_8^-)$<br>or $1\Gamma_8^-$ | 16.66<br>(134.4) | 17.08<br>(137.9) | 19.38 <sup>b</sup><br>(156.3) | 15.19<br>(122.5)              |                  | 26.1        |
| $E$        | $2S_{3/2} (\Gamma_8^+)$<br>or $2\Gamma_8^+$ |                  |                  | 21.6 <sup>e</sup><br>(174)    | 18.41 <sup>c</sup><br>(148.5) |                  | 28.3        |
| $D$        | $2P_{5/2} (\Gamma_8^-)$<br>or $2\Gamma_8^-$ | 20.68<br>(166.8) | 21.06<br>(169.9) | 23.14<br>(186.6)              | 19.36<br>(156.1)              | 27.29<br>(220.1) | 30.1        |
| $C$        | $2P_{5/2} (\Gamma_7^-)$<br>or $1\Gamma_7^-$ | 22.60<br>(182.3) | 23.06<br>(186.0) | 24.92<br>(201.1)              | 21.19 <sup>c</sup><br>(170.9) | 29.15<br>(235.1) | 31.6        |
| $B$        | $3P_{3/2} (\Gamma_8^-)$<br>or $3\Gamma_8^-$ |                  |                  |                               | 22.92<br>(184.9)              |                  |             |
| $A$        | $2P_{1/2} (\Gamma_6^-)$<br>or $1\Gamma_6^-$ |                  |                  | 29.10<br>(234.7)              | 24.87<br>(200.6)              |                  |             |
| $E_{io}$   |                                             | 27.88            | 28.26            | 30.34                         | 26.56                         | 34.49            | 37.3        |
| $1S_{3/2}$ |                                             | 28.0             | 28.4             | 30.7                          | 26.0                          | 34.5             | 40.4        |

The  $Ge_{As}$  transitions are deduced from PL measurements. The attribution of the excited state is indicated.  $E_{io}$  is obtained by adding to the position of line  $D$  the energy of  $7.80 \text{ meV}$  calculated by Fiorentini [57] for the  $2P_{5/2} (\Gamma_8^-)$  state. Below  $E_{io}$ , the last row gives, for comparison, the  $1S_{3/2}$  binding energy derived from different PL measurements. For  $1S_{3/2} (\text{Cd})$ , it is  $34.7 \text{ meV}$  [9]

<sup>a</sup> [109], <sup>b</sup> [97], <sup>c</sup> [11], <sup>d</sup> [98], <sup>e</sup> [186]

Like Si, Sn also displays an amphoteric behaviour in GaAs and the ionization energy of  $\text{Sn}_{\text{As}}$  is rather large (117.1 meV) compared to those of the other group-IV acceptors [150].

Calculated values of the energies of the first EM acceptor states in different semiconductors including GaAs are given in papers by Baldereschi and Lipari [14, 15], where the contribution of the cubic term is taken into account. A value of the EM ground state in GaAs (26.3 meV) is given in [15] and it compares with a value of 32.9 meV obtained by Fiorentini [57]. This value is obtained by considering the dielectric screening and the split-off  $VB$ , with an effective Rydberg of 12.73 meV. This calculation was further refined with site-dependent corrections yielding  $E_{\text{Ga}} = 30.9$  meV and  $E_{\text{As}} = 38.9$  meV, where the index corresponds to the acceptor site. Non-variational calculations of the acceptor energy levels in GaAs have also been performed by Said and Kanehisa [147].

The experimental values of the  $2P_{5/2}(\Gamma_8^-) - 2P_{3/2}(\Gamma_8^-)$  and  $2P_{5/2}(\Gamma_7^-) - 2P_{5/2}(\Gamma_8^-)$  spacings derived from Table 7.21 are compared with the calculated values in Table 7.22.

This table shows that there is a significant dispersion in the experimental spacings, which can be attributed in part to the closeness of the spectra and to the uncertainty in the measurements due to the proximity of the strong one-phonon absorption, and to the dispersion of the dielectric constant in this spectral region, which can also play a role. There is also some dispersion in the calculated values. Semi-empirical ionization energies  $E_{\text{io}}$  of the different acceptors are obtained by adding to the position of line  $D$  of Table 7.21 the value of the  $2P_{5/2}(\Gamma_8^-)$  state (7.20 meV) calculated by Baldereschi and Lipari [14]. It is seen that with the exception of  $\text{Sn}_{\text{Ga}}$ , the ionization energies of the group-II and group-IV acceptors in GaAs are not too far from those calculated with the site-dependent corrections, demonstrating their EM character. At a difference with the group-III acceptors in silicon, the chemical effect implies, however, a small repulsive potential of the atomic core for the hole.

In GaP, selected pair luminescence (SPL), whose principle is explained in Sect. 1.3.3, has been used by Street and Senske [163] to directly measure the transition energies of the  $\text{Mg}_{\text{Ga}}$ ,  $\text{Zn}_{\text{Ga}}$ , and  $\text{C}_{\text{P}}$  acceptors. The advantage of this method is that a value of the ground state energy can also be obtained directly. The absorption by the classical method of a few lines of Be, Mg, Cd, and C acceptors in GaP has also been reported by Kopylov and Pikhtin [103].

**Table 7.22.**  $2P_{5/2}(\Gamma_8^-) - 2P_{3/2}(\Gamma_8^-)$  and  $2P_{5/2}(\Gamma_7^-) - 2P_{5/2}(\Gamma_8^-)$  spacings for different shallow acceptors in GaAs derived from Table 7.15 compared with different calculated spacings

|                                               | $\text{Be}_{\text{Ga}}$ | $\text{Mg}_{\text{Ga}}$ | $\text{Zn}_{\text{Ga}}$ | $\text{C}_{\text{As}}$ | $\text{Si}_{\text{As}}$ | $\text{Ge}_{\text{As}}$ | $\text{EM}^{\text{a}}$ | $\text{EM}^{\text{b}}$ |
|-----------------------------------------------|-------------------------|-------------------------|-------------------------|------------------------|-------------------------|-------------------------|------------------------|------------------------|
| $2P_{5/2}(\Gamma_8^-) - 2P_{3/2}(\Gamma_8^-)$ | 4.02                    | 3.98                    | 3.76                    | 4.17                   |                         | 4.00                    | 4.18                   | 3.7                    |
| $2P_{5/2}(\Gamma_7^-) - 2P_{5/2}(\Gamma_8^-)$ | 1.93                    | 2.00                    | 1.88                    | 1.92                   | 1.86                    | 1.5                     | 1.75                   | 1.9                    |

<sup>a</sup> [14], <sup>b</sup> [147]

**Table 7.23.** Measured energies (meV) of different acceptor transitions from the  $1S_{3/2} (\Gamma_8^-)$  ground state in GaP, where the TO-LO one-phonon region (reststrahlen band) is between 45 and 50 meV

|                               | $2P_{3/2}$        | $2P_{5/2} (\Gamma_8^-)$ | $2P_{5/2} (\Gamma_7^-)$ | $2P_{1/2} (\Gamma_6^-)$ | $1S_{3/2} (\Gamma_8^+)$ | EM <sup>a</sup> |
|-------------------------------|-------------------|-------------------------|-------------------------|-------------------------|-------------------------|-----------------|
| Be <sub>Ga</sub> <sup>a</sup> | 35.8              |                         |                         |                         |                         | 55.3            |
| Mg <sub>Ga</sub> <sup>b</sup> | 39.7              | 43.4                    | 52.3 <sup>a</sup>       |                         | 53.1                    | 60.4            |
| Zn <sub>Ga</sub> <sup>b</sup> | 44.5              | 51.4                    | 53.3                    |                         | 61.0                    |                 |
|                               |                   | 57.1 <sup>a</sup>       | 61.6 <sup>a</sup>       | 64.8 <sup>a</sup>       |                         | 69.7            |
| Cd <sub>Ga</sub> <sup>a</sup> | 82.7              | 89.5                    | 94.1                    | 98.3                    |                         | 102.2           |
| C <sub>P</sub> <sup>b</sup>   | 33.5              | 37.1                    | 39.4                    |                         | 46.9                    |                 |
|                               | 33.7 <sup>a</sup> |                         |                         |                         |                         | 53.2            |

<sup>a</sup> [103], IR absorption, <sup>b</sup> [163], SPL

These results are hampered by the fact that, except for the Cd<sub>Ga</sub> acceptor, the spectra lie in the close vicinity or within the one-phonon absorption region of GaP, and by the high acceptor concentration used, but they are apparently the only absorption results existing for GaP. The positions of different acceptor transitions in GaP are given in Table 7.23.

In this table, the only concordant values between absorption and SPL results are for  $2P_{3/2}$  (C), and a difference of 6–8 meV in the ionization energies is noted. The undifferentiated EM value of the ionization energy for acceptors in GaP, including the cubic contribution, is 49.5 meV in the infinite s-o coupling limit [15]. An electrical measurement of  $E_{\text{ith}}$  (C) in GaP gives  $41 \pm 3$  meV [22].

Absorption lines pertaining to three shallow acceptors have been reported for AlSb [1]. The three lines of the acceptors denoted *A* and *B* are located between 22 and 34 meV on the low-energy side of the one-phonon band (the TO and LO phonon energies are 39.5 and 42.2 meV, respectively) and the two lines of acceptor *C* are located at 91.68 and 94.46 meV. A few other lines have also been observed, but no attribution has been given except for some LO phonon replicas. The spacing between the two highest-energy lines of these three acceptors is the same (2.78 meV), indicating EM excited states. Further piezospectroscopic measurements indicate that these acceptors have  $T_d$  symmetry [1].

The absorption of the *G* and *D* lines of the Zn<sub>In</sub> acceptor in InP have been reported by Causley and Lewis [30], and this appears to be the only known acceptor absorption result for this compound. Their positions are  $241.5 \text{ cm}^{-1}$  (29.94 meV) for the *G* line ( $2P_{3/2} (\Gamma_8^-)$ ) and  $286.0 \text{ cm}^{-1}$  (35.46 meV) for the *D* line ( $2P_{5/2} (\Gamma_8^-)$ ). The scarcity of absorption results is due to the fact that such spectra would be close to the one-phonon absorption of InP (37.7 and 42.8 meV for the TO and LO phonons, respectively). However, shallow acceptor transitions have been identified in InP by selective pair luminescence (SPL) and excitation spectroscopy (Dean et al. [48]). The separation from the  $1S_{3/2}$  ground state of some *S* and *P* acceptor states of Zn<sub>In</sub> and Cd<sub>In</sub> have also been measured by Raman scattering [188].

**Table 7.24.** Positions (meV) of the first energy levels for some acceptors in InP deduced from SPL measurements. The value for  $1S_{3/2} (\Gamma_8^+)$  represents the ionization energy of the acceptor (after [17])

|                  | $1S_{3/2} (\Gamma_8^+)$ | $2P_{3/2} (\Gamma_8^-)$ | $2S_{3/2} (\Gamma_8^+)$ | $2P_{5/2} (\Gamma_8^-)$ | $2P_{5/2} (\Gamma_7^-)$ |
|------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| Mg <sub>In</sub> | 40                      | 15.1                    | 11.5                    | 10                      | 7.8                     |
| Zn <sub>In</sub> | 46.1                    | 15.9                    | 13.8                    | 11.1                    | 8.2                     |
| C <sub>P</sub>   | 41                      | 15.6                    | 12.6                    | 10.4                    | 8.2                     |
| Si <sub>P</sub>  | 37 <sup>a</sup>         |                         | 13.4 <sup>b</sup>       | 11.2 <sup>b</sup>       | 8.3 <sup>b</sup>        |
| EMA              | 39.5                    | 17.7                    | 11.8                    | 10.8                    | 8.3                     |

<sup>a</sup> [141], <sup>b</sup> [86]**Table 7.25.** Positions (meV) of the first lines for some acceptors in InSb at LHeT.  $E_{io}$  is obtained by adding the calculated energy of the  $2P_{5/2} (\Gamma_8^-)$  level to the energy of the  $D$  line

| Line                | $G$                     | $E$                     | $D$                     | $C$                     | $A$                     | $E_{io}$ |
|---------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|----------|
|                     | $2P_{3/2} (\Gamma_8^-)$ | $2S_{3/2} (\Gamma_8^+)$ | $2P_{5/2} (\Gamma_8^-)$ | $2P_{3/2} (\Gamma_7^-)$ | $2P_{1/2} (\Gamma_6^-)$ |          |
| Zn, Cd <sup>a</sup> | 5.7                     | 6.94                    | 7.31                    | 7.93                    | 8.58 <sup>b</sup>       | 9.85     |
| Ge <sup>b</sup>     | 5.9                     | 6.85                    | 7.25                    | 7.80                    | 8.53                    | 9.79     |
| Ag <sup>a</sup>     | 23.5                    | 26.5                    | 27.3                    | 27.9                    |                         | 29.8     |
| EMA                 | 4.24                    | 2.63                    | 2.54                    | 1.91                    | 0.155                   | 8.55     |

<sup>a</sup> [92], <sup>b</sup> [123]

The energy of the first acceptor levels obtained from these measurements are given in Table 7.24.

The ionization energy of Cd in InP is given as 53.6 meV (White et al., unpublished, quoted by Baldereschi and Lipari [13]), but considering an energy of 34.2 meV of the Raman  $2P_{3/2}$  (Cd) line and an average value of the  $2P_{3/2}$  experimental energy levels of Table 7.24,  $E_i$  (Cd) seems to be closer to  $\sim 50$  meV. By adding to the energy of line  $D$  (Zn) measured by absorption [30], the EMA value of the  $2P_{5/2} (\Gamma_8^-)$  level of Table 7.23, one obtains for  $E_i$  (Zn) a value of 46.3 meV close to the value of 46.1 meV from SPL measurements.

In InSb, acceptor absorption spectra have been reported by Kaplan [92] and Murzin et al. [123]. PTIS spectra were also reported by Meisels and Kuchar [114]. The Zn<sub>In</sub> and Cd<sub>In</sub> lines cannot be practically distinguished and Table 7.25 shows that they are very close to those of the Ge<sub>Sb</sub> lines. The last row gives the values of the excited states calculated by Baldereschi and Lipari [14]. An attempt [144], and reference therein) to evaluate the effect of the addition of the inversion asymmetry term (3.27) in the acceptor EM Hamiltonian on the InSb acceptor energy levels shows that this contribution is very small.<sup>8</sup>

<sup>8</sup> In this reference, the value of parameter  $K$  used (corresponding to parameter  $C$  of expression (3.27) expressed in atomic units) is about five times larger than more recent determinations.

### 7.6.2 The $B_{As}$ (78-meV/203-meV) Double Acceptor in GaAs

In GaAs, two unidentified acceptors labelled by their ionization energies as the 68-meV and the 78-meV acceptors, were reported by Elliot et al. [53]. The 78-meV acceptor was identified as the neutral charge state of a double acceptor whose ionization energy rose to 203 meV in the singly-ionized charge state. The absorption spectrum of the 78-meV acceptor is located close to the two-phonon spectrum of GaAs, and three lines of this spectrum at 70.95, 72.94, and 74.5 meV have been observed [53] in undoped p-type GaAs grown from a Ga-rich melt. With the labelling of Table 7.21, they should be ascribed to lines *D*, *C* and *B*, giving  $E_{io} = 78.2$  meV. The 78-meV and the 203-meV spectra have also been observed in B-doped samples cut from SI crystals after initial annealing at 1200°C and different subsequent annealings [166]. A detailed study of the observation of these spectra as a function of additional near-IR illumination and of various isochronal annealings of the sample during the optical measurements was reported in the same reference. The 203-meV spectrum is shown in Fig. 7.23, with three lines at 172.3, 181.0, and 186.3 meV, and a clearly visible elbow at  $\sim 179.6$  meV.

It is tempting to ascribe the 172.3 and 181.0 meV lines of this spectrum, separated by 8.7 meV, to transitions of the  $2P_{5/2}(\Gamma_8^-)$  and  $2P_{5/2}(\Gamma_7^-)$

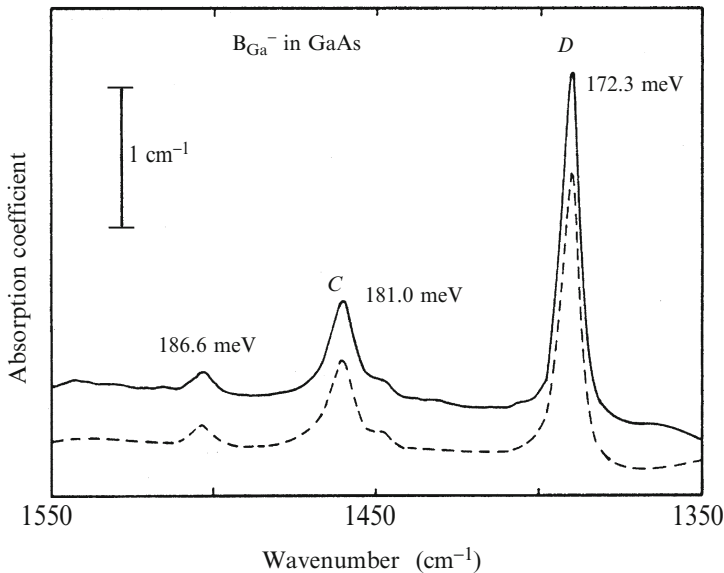


**Fig. 7.23.** Discrete absorption between 192 and 167 meV of the 203-meV- $B_{As}^-$  acceptor spectrum at LHeT in a B-doped GaAs sample annealed at 600°C after an initial annealing at 1200°C. A filter blocking photons with energies above 400 meV has no effect on the absorption coefficient (solid-line spectrum) compared to the dashed-line spectrum obtained without filter (after [166]). Copyright 1994, American Institute of Physics

final states (lines  $D$  and  $C$ ) as their spacing is close to four times the  $2P_{5/2}(\Gamma_7^-) - 2P_{5/2}(\Gamma_8^-)$  spacing of Table 7.22, in qualitative agreement with what is expected for a singly-ionized acceptor spectrum. This double acceptor has been tentatively ascribed to the Ga antisite ( $\text{Ga}_{\text{As}}$ ), but a correlation between PL and DLTS measurements in B-containing GaAs samples and the local vibrational modes due to  $\text{B}_{\text{As}}$  have convincingly proved that the 78-meV and 203-meV levels corresponded to the two charge states of  $\text{B}_{\text{As}}$  [129]. The 68-meV acceptor has been reported to be a dominant intrinsic acceptor in p-type GaAs and its electronic Raman spectrum reported by Wagner et al. [185] but  $\text{Ga}_{\text{As}}$  would be a potential candidate.

### 7.6.3 TMs Acceptors in III-V Compounds

The incorporation of TMs in III-V and II-VI compounds has aroused interest because some of them have a very high solubility in these compounds and because their magnetic moment can lead, by substitution with cations, to diluted magnetic alloys, known as diluted magnetic semiconductors (DMS). In a cubic II-VI compound, within the  $sp^3$  tetrahedral bonding scheme, the substitution of a group-II cation with a  $s^2$  external shell by a  $3d$  TM with electronic structure  $[\text{Ar}] 3d^n 4s^2$  ( $n = 1, 2, \dots, 9$ ) does not lead to any change as the  $d$  electrons do not participate in the bonding. In this aspect, the TM can be regarded as some kind of isoelectronic impurity. The situation in III-V compounds is different because only five  $ns^2np^3$  electrons of the anion are available for tetrahedral bonding, which is then achieved by the adjunction of an electron from the host  $VB$ . This configuration of the TM is often denoted  $\text{TM}^{2+}$  considering only the electrons not involved in the bonding. The presence of a hole results in an acceptor behaviour for these TMs and an EM acceptor spectrum of Mn in GaAs was first observed by Chapman and Hutchinson [34] and other studies followed [110, 168], and references therein). The Lyman EM absorption spectra of Mn in GaAs, GaP, and InP, and of Co and Cu in GaAs have been reported by Tarhan et al. [168]. Figure 7.24 shows the Lyman acceptor spectra at LHeT of Co and Mn in two GaAs samples.

The transition energies for these TMs are given in Table 7.26. For Cu in GaAs, two EM spectra denoted  $\text{Cu}_\text{I}$  and  $\text{Cu}_\text{II}$  are observed, with temperature-independent relative intensities and their possible origin is discussed later. Using the calculated value (5.33 meV) of the acceptor energy level  $2P_{5/2}(\Gamma_7)$  of GaAs [14], one obtains the values of  $E_{\text{io}}$  of Table 7.26. For GaP:Mn and InP:Mn, the values of  $E_{\text{io}}$  are obtained from the corresponding energy level  $2P_{5/2}(\Gamma_8)$  calculated in the same reference.

These TM acceptors display an EM excited level, and for the GaAs host crystal, the line spacings are similar to those measured for shallow acceptors, as can be seen from the comparison between Tables 7.22 and 7.27.

The electronic configurations of Cr and Cu, with only one  $4s$  electron, differ from those of the other  $3d$  TMs (see above). With the same binding process as for Mn and Co, one expects the incorporation of two  $VB$  electrons to complete

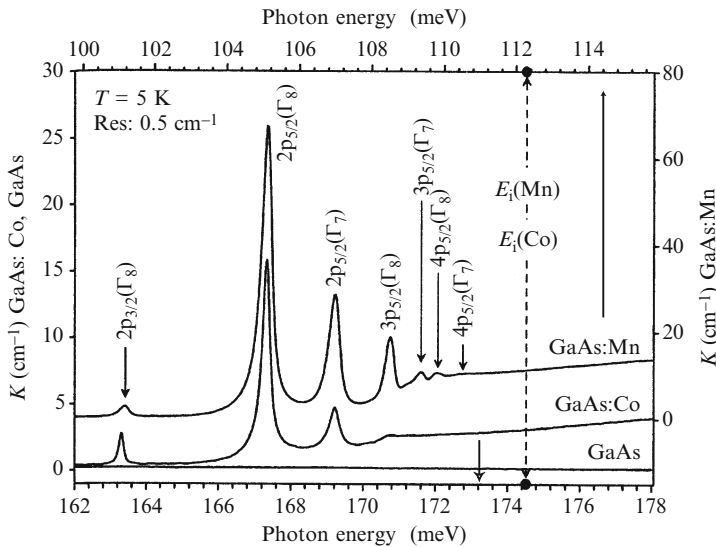


**Fig. 7.24.** Comparison of the acceptor spectra of Co and Mn in GaAs at a resolution of  $62\text{ }\mu\text{eV}$  ( $0.5\text{ cm}^{-1}$ ). The absorption of a pure GaAs sample is shown as a reference. The  $2P_{3/2}$  lines of both spectra are brought into coincidence. The relevant energy scales are indicated by vertical arrows (after [168]). Copyright 2003 by the American Physical Society

**Table 7.26.** Observed positions (meV) at LHeT of the acceptor lines of the EM spectra of some TMs in III-V compounds [168]

|                       | $2P_{3/2}$ | $2P_{5/2}$<br>( $\Gamma_8$ ) | $2P_{5/2}$<br>( $\Gamma_7$ ) | $3P_{5/2}$<br>( $\Gamma_8$ ) | $3P_{5/2}$<br>( $\Gamma_7$ ) | $4P_{5/2}$<br>( $\Gamma_8$ ) | $4P_{5/2}$<br>( $\Gamma_7$ ) | $E_{i0}$ |
|-----------------------|------------|------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|----------|
| GaP:Mn                | 368.84     | 374.71                       | 379.52                       |                              |                              |                              |                              | 387.75   |
| InP:Mn                | 204.66     | 210.06                       | 213.12                       |                              |                              |                              |                              | 220.04   |
| GaAs:Mn               | 101.17     | 105.13                       | 106.99                       | 108.52                       | 109.37                       | 109.82                       | 110.55                       | 112.32   |
| GaAs:Co               | 163.32     | 167.33                       | 169.22                       | 110.74                       |                              |                              |                              | 174.55   |
| GaAs:Cu <sub>I</sub>  | 146.50     | 150.51                       | 152.45                       | 154.72                       |                              |                              |                              | 157.78   |
| GaAs:Cu <sub>II</sub> | 147.36     | 151.37                       | 153.28                       |                              |                              |                              |                              | 158.61   |

**Table 7.27.**  $2P_{5/2}(\Gamma_8) - 2P_{3/2}$  and  $2P_{5/2}(\Gamma_7) - 2P_{5/2}(\Gamma_8)$  spacings (meV) derived from Table 7.26. They are noted here  $\delta(2P_{5/2-3/2})$  and  $\delta(2P_{5/2-5/2})$ , respectively

|                        | GaP:Mn | InP:Mn | GaAs:Mn | GaAs:Co | GaAs:Cu <sub>I</sub> | GaAs:Cu <sub>II</sub> |
|------------------------|--------|--------|---------|---------|----------------------|-----------------------|
| $\delta(2P_{5/2-3/2})$ | 5.87   | 5.40   | 3.96    | 4.01    | 4.01                 | 4.01                  |
| $\delta(2P_{5/2-5/2})$ | 4.81   | 3.06   | 1.86    | 1.89    | 1.94                 | 1.91                  |



tetrahedral bonding, yielding He-like acceptors. However, no striking difference is observed in the ionization energies. A difference originates from the observation of two Cu-related spectra, Cu<sub>I</sub> and Cu<sub>II</sub>. As suggested in the paper by Tarhan et al. [168], it is tempting to ascribe Cu<sub>I</sub> to the  $3d^{10} 4s^2 4p$  Cu<sup>2-</sup> He-like configuration, and Cu<sub>II</sub> to a  $3d^9 4s^2 4p$  Cu<sup>-</sup> H-like configuration involving only one  $3d$  and one  $VB$  electron.

#### 7.6.4 Acceptors in II-VI Compounds

The II-VI compounds have a larger ionicity than the III-V compounds, and it was first assumed that most of the residual donors and acceptors were due to the lattice defects like the anion and cation vacancies ( $V_{II}$  and  $V_{VI}$ ) and to group-II and group-VI interstitial atoms, but it was later found that in most cases, group-I and group-V impurities were involved [118]. In some of these compounds, Li occupies a group-II site, where it is an acceptor, but it can also be present in the interstitial form, leading to self-compensation.

A few acceptor absorption spectra have been identified in ZnSe, ZnTe and CdTe, but most of the results have been obtained by PL. Table 7.28 gives the transition energies for Li and Na in cubic ZnSe deduced from PL excitation spectra and from SPL.

There is some uncertainty on the attribution of  $2P_{3/2}$  (Na) as the experimental  $2P_{3/2} - 2P_{5/2}$  ( $\Gamma_8$ ) spacing for Na is 4.4 meV larger than the one for Li and than an EM estimation of this spacing from Baldereschi and Lipari's calculations [14]. The results of PL experiments on the N acceptor in ZnSe have been reported by Dean et al. [50], giving an estimated ionization energy of 110 meV for this acceptor. The results of PL and SPL experiments on MBE ZnO-doped ZnSe have been interpreted as due to an O-related acceptor with an ionization energy of 84 meV ([37], and references therein). Calculations of the electrical activity of O in ZnSe predict an acceptor behaviour for an interstitial O atom strongly bonded to a Zn atom [31].

More absorption data exist for acceptors in ZnTe, together with PL measurements and they are given in Table 7.29.

A significant difference is observed between the  $E_{i0}$ (Au) values measured by PL and absorption measurements. The energies of the  $3P_{3/2}$ ,  $3P_{5/2}$ ( $\Gamma_8$ ),  $3P_{5/2}$ ( $\Gamma_7$ ), and  $2P_{1/2}$  transitions of Ag measured by Stadler et al. [159] are 113.4, 115.1, 116.4, and 117.2 meV, respectively.

**Table 7.28.** Energies (meV) of the Li and Na acceptor transitions in cubic ZnSe near LHeT. The uncertainty is  $\pm 1$  meV ( $\pm 2$  meV for  $2P_{5/2}$  ( $\Gamma_8$ )) [170]. The value measured by absorption by Nakata et al. [127] for  $2P_{3/2}$  (Li) is  $(72.9 \pm 0.1)$  meV

|    | $2P_{3/2}$ | $2S_{3/2}$ | $2P_{5/2}$ ( $\Gamma_8$ ) | $2P_{5/2}$ ( $\Gamma_7$ ) | $3S_{3/2}$ | $2P_{1/2}$ | $4S_{3/2}$ | $E_i$ |
|----|------------|------------|---------------------------|---------------------------|------------|------------|------------|-------|
| Li | 72.9       | 82.6       | 85.8                      | 93.0                      | 97.8       | 100.1      | 102.5      | 114   |
| Na | 83.1 ?     | 97.6       | 100.4                     | 106.8                     | 110.5      | 113.0      | 114.7      | 128   |

**Table 7.29.** Energies (meV) of acceptor transitions in ZnTe near LHeT. The values of  $E_{\text{io}}$  in parentheses in the last row are obtained directly from PL measurements. The other values are obtained by adding 15.8 meV to the energy of the  $2P_{5/2}(\Gamma_8)$  transition. The EM energies of the excited states are given in the last column

|                      | $\text{Li}_{\text{Zn}}^{\text{a}}$ | $\text{P}_{\text{Te}}^{\text{b}}$ | $\text{As}_{\text{Te}}^{\text{a}}$ | $\text{Cu}_{\text{Zn}}^{\text{c}}$ | $\text{Ag}_{\text{Zn}}^{\text{d}}$ | $\text{Au}_{\text{Zn}}$ | $\text{EMT}^{\text{f}}$ |
|----------------------|------------------------------------|-----------------------------------|------------------------------------|------------------------------------|------------------------------------|-------------------------|-------------------------|
| $2P_{3/2}$           | 37.9                               | 39.6                              | 55.0                               | 124.0                              |                                    |                         | 23.5                    |
| $2S_{3/2}$           | 43.4                               | 45.4                              | 58.6                               | 125.6                              | 100.3                              | 244 <sup>c</sup>        | 17.2                    |
| $2P_{5/2}(\Gamma_8)$ | 44.8 <sup>b</sup>                  | 46.5                              | 63.2                               |                                    | 105.9                              | 255.3 <sup>e</sup>      | 15.8                    |
| $2P_{5/2}(\Gamma_7)$ | 47.7                               | 53.0                              | 66.8                               |                                    | 109.8                              | 259.0 <sup>e</sup>      | 12.5                    |
| $3S_{3/2}$           | 52.8                               | 54.1 <sup>c</sup>                 | 69.4                               | 137.5                              | 111.0                              |                         | 8.6                     |
| $E_{\text{io}}$      | 60.6                               | 62.3                              | 79.0                               | 148.0                              | 121.7                              | 271.1                   |                         |
|                      | (60.5) <sup>c</sup>                | (63.5) <sup>c</sup>               | (79.0) <sup>c</sup>                |                                    | (121) <sup>c</sup>                 | (277) <sup>c</sup>      |                         |

<sup>a</sup> [148] Raman scattering, <sup>b</sup> [124], absorption, Raman scattering, <sup>c</sup> [180], PL, <sup>d</sup> [159], absorption, <sup>e</sup> [112], <sup>f</sup> [147]

**Table 7.30.** Energies (meV) of acceptor transitions in CdTe near LHeT. The transitions are labelled by the final state

|                      | $\text{Li}_{\text{Cd}}^{\text{a}}$ | $\text{Na}_{\text{Cd}}^{\text{b}}$ | $\text{Cu}_{\text{Cd}}^{\text{c}}$ | $\text{Ag}_{\text{Cd}}^{\text{d}}$ | $\text{P}_{\text{Te}}^{\text{b}}$ | EM          |
|----------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|-----------------------------------|-------------|
| $2P_{3/2}$           | 34.0                               | 34.9                               |                                    |                                    | 44.9                              | 33.4 (23.7) |
| $2S_{3/2}$           | 42.8 <sup>c</sup>                  | 43.3                               | 124.4 <sup>d</sup>                 | 87.9                               | 51.0                              | 40.2 (16.9) |
| $2P_{5/2}(\Gamma_8)$ | 44.4                               | 45.0                               | 130.94                             | 92.5                               | 53.1                              | 41.7 (15.4) |
| $2P_{5/2}(\Gamma_7)$ | 47.1                               | 47.5                               | 134.60                             | 96.2                               | 56.6                              | 45.4 (11.6) |
| $3S_{3/2}$           | 49.1 <sup>b</sup>                  | 49.8                               | 136.0 <sup>d</sup>                 | 97.9                               | 58.8                              | 48.4 (10.8) |
| $E_{\text{io}}$      | 59.8                               | 60.4                               | 146.3                              | 107.9                              | 68.5                              | 57.0        |

The calculated transition energies of the last column are the difference between the ground and excited states energies (in parentheses) calculated by [61]. The acceptor ionization energies are obtained by adding 15.4 meV to the energy of the  $2P_{5/2}(\Gamma_8)$  transition

<sup>a</sup> [61], absorption, <sup>b</sup> [118], PL, <sup>c</sup> [159], absorption, <sup>d</sup> [117], absorption and PL

The spectroscopy of acceptors in CdTe has been actively investigated by absorption and PL [118], and references therein). The energies of some acceptor impurity transitions are given in Table 7.30. EM acceptor energy levels in CdTe have been calculated self consistently with adjustments of the  $VB$  parameters and of the dielectric constant of the host crystal. The EM energy obtained for the ground state is 56.8 [118] and 57.0 meV [61]. The EM transition energies to the corresponding excited states are given in the last row of Table 7.30.

The energies of the  $3P_{3/2}$ ,  $3P_{5/2}(\Gamma_8)$ ,  $3P_{5/2}(\Gamma_7)$ , and  $2P_{1/2}$  transitions of  $\text{Cu}_{\text{Cd}}$  measured by Stadler et al. [159] are 136.38, 138.33, 140.64, and 142.65 meV, respectively. The calculated  $2P_{5/2}(\Gamma_7)$ – $2P_{5/2}(\Gamma_8)$  spacing (3.8 meV) differs notably from the experimental one for Li and Na (2.7 and 2.5 meV, respectively). This was noted by Molva et al. [118] and attributed to a resonant coupling of the Li and Na lines with the  $2\text{LO}(\Gamma)$  overtone of CdTe

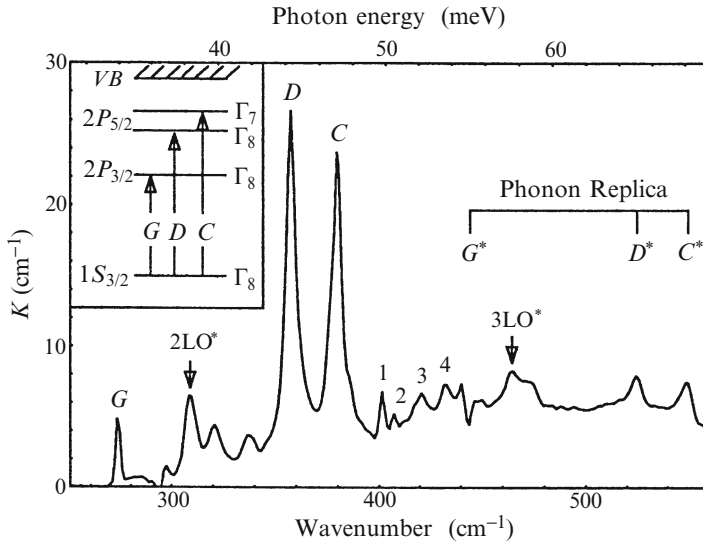


**Fig. 7.25.** Absorption spectrum of Li in CdTe at 1.5 K. The inset shows the attribution of the main electronic lines. The final state of line 1 should be  $3P_{5/2}$  ( $\Gamma_8$ ) and lines 2, 3, and 4 should be attributed to other transitions to  $nP$  states with  $n > 2$ .  $G^*$ ,  $D^*$ , and  $C^*$  are LO ( $\Gamma$ ) phonon replicas of lines  $G$ ,  $D$ , and  $C$ . The lines denoted  $2LO^*$  and  $3LO^*$  are attributed to local phonon modes coupled with the Li acceptors (after [61]). Reproduced with permission from the Institute of Physics

at 42.4 meV. This point is also discussed by Friedrich et al. [61]. The complexity of the Li acceptor spectrum in CdTe can be appreciated in Fig. 7.25.

In II-VI compounds, the cation vacancy  $V_M^{2-}$  is a deep double acceptor and in CdTe, the most recent estimations give  $E_v + 0.76$  eV for  $V_{Cd}^{2-}/V_{Cd}^-$  [29]. It combines with the  $Cl_{Te}$  donor to give a relatively shallow acceptor complex which has been identified by the conjunction of PL and ODMR measurements as a centre with trigonal symmetry and  $E_i \sim 120$  meV [79].

## References

1. B.T. Ahlborn, A.K. Ramdas, Phys. Rev. **187**, 932 (1969)
2. C.A.J. Ammerlaan, in *Properties of Crystalline Silicon, EMIS Datareviews Series No 20*, ed. by R. Hull (INSPEC Publication, London, 1999), pp. 669–675
3. C.A.J. Ammerlaan, R. van Kemp, J. Phys. C **18**, 2623 (1985)
4. E. Anastassakis, Phys. Rev. **186**, 760 (1969)
5. B.A. Andreev, G.G. Devyatikh, V.A. Gavva, D.M. Gordeev, A.V. Gusev, G.A. Maksimov, V.G. Pimenov, V.B. Shmagin, D.A. Timonon, Semicond. Sci. Tech. **9**, 1050 (1994)

6. B.A. Andreev, E.B. Kozlov, T.M. Lifshits, in: *Defects in Semiconductors 18*, ed. by M. Suezawa, H. Katayama-Yoshida (Trans Tech, Switzerland, 1995), Mater. Sci. Forum **196**, 121
7. B.A. Andreev, T.M. Lifshits, High-Purity Subst. (Russian journal) **5**, 7 (1990)
8. G. Armelles, J. Barrau, M. Brousseau, B. Pajot, C. Naud, Solid State Commun. **56**, 303 (1985)
9. D.J. Ashen, P.J. Dean, D.T.J. Hurle, J.B. Mullin, A.M. White, P.D. Greene, J. Phys. Chem. Solids **36**, 1041 (1975)
10. D.E. Aspnes, A.A. Studna, Solid State Commun. **11**, 1375 (1972)
11. R. Atzmüller, M. Dahl, J. Kraus, G. Schaack, J. Schubert, J. Phys. C **3**, 6775 (1991)
12. R.J. Baker, P. Fisher, R.E.M. Vickers, E.E. Haller, W.L. Hansen, in *Proceedings of 7th International Conference on Shallow-Level Centers Semiconductor* Amsterdam 17–19 July 1996), ed. by CAJ, Ammerlaan, B. Pajot (World Scientific, Singapore, 1997) pp. 357
13. A. Baldereschi, N. Lipari, Phys. Rev. B **8**, 2697 (1973)
14. A. Baldereschi, N. Lipari, Phys. Rev. B **9**, 1525 (1974)
15. A. Baldereschi, N. Lipari, J. Lumin. **12/13**, 489 (1976)
16. V.F. Bannaya, G.I. Voronkova, E.S. Milenin, E.A. Petrova, P.V. Sidorenko, Sov. Phys. Semicond. **12**, 754 (1979)
17. D. Barthruff, H. Haspeklo, J. Lumin. **24/25**, 181 (1981)
18. I.L. Beinikhes, Sh. M. Kogan, M. Novak, A.F. Polupanov, in *Shallow Impurities in Semiconductors IV*, ed. by G. Davies (Trans Tech, Switzerland, 1991); Mater. Sci. Forum **65**, 259–264
19. C. Benoit à la Guillaume, J. Cernogora, J. Phys. Chem. Solids **24**, 383 (1963)
20. T. Bever, P. Emanuelsson, M. Kleverman, H.G. Grimmeiss, Appl. Phys. Lett. **55**, 2541 (1989)
21. N. Binggeli, A. Baldereschi, (1989), unpublished results quoted by Lewis et al. (1994)
22. D.P. Bortfeld, B.J. Curtis, H. Meier, J. Appl. Phys. **43**, 1293 (1972)
23. J. Broeckx, Y. Kamiura, P. Clauws, J. Vennik, Solid State Commun. **43**, 499 (1981)
24. R. Buczko, F. Bassani, Phys. Rev. B **45**, 5838 (1992)
25. W. Burger, K. Lassmann, Phys. Rev. B **33**, 5868 (1986)
26. E. Burstein, E.E. Bell, J.W. Davisson, M. Lax, J. Phys. Chem. **57**, 849 (1953)
27. E. Burstein, G. Picus, B. Henvi, R. Wallis, J. Phys. Chem. Solids **1**, 65 (1956)
28. M. Cardona, Solid State Commun. **121**, 7 (2002)
29. A. Castaldini, A. Cavallini, B. Fraboni, P. Fernandez, J. Piqueras, J. Appl. Phys. **83**, 2121 (1988)
30. R.L. Causley, R.A. Lewis, Physica B **302–303**, 327 (2001)
31. D.J. Chadi, J. Cryst. Growth **138**, 295 (1994)
32. H.R. Chandrasekhar, A.K. Ramdas, S. Rodriguez, Phys. Rev. B **14**, 2417 (1976)
33. H.R. Chandrasekhar, A.K. Ramdas, Phys. Rev. B **33**, 1067 (1986)
34. R.A. Chapman, W.G. Hutchinson, Phys. Rev. Lett. **18**, 443 (1967)
35. R.A. Chapman, W.G. Hutchinson, Solid State Commun. **3**, 293 (1965)
36. R.A. Chapman, W.G. Hutchinson, T.L. Estle, Phys. Rev. Lett. **17**, 132 (1966)
37. J. Chen, V. Zhang, B.J. Skromme, K. Akimoto, S.J. Pachuta, J. Appl. Phys. **78**, 5109 (1995)

38. R.M. Chrenko, Phys. Rev. B **7**, 4560 (1973)
39. P. Clauws, J. Broeckx, E. Rotsaert, J. Vennik, Phys. Rev. B **38**, 12377 (1988)
40. P. Clauws, G. Huylebroeck, E. Simoen, P. Vermaercke, F. De Smet, J. Vennik, Semicond. Sci. Tech. **4**, 910 (1989)
41. K. Colbow, Can. J. Phys. **41**, 1801 (1963)
42. A.T. Collins, E.C. Lightowers, Phys. Rev. **171**, 843 (1968)
43. A.T. Collins, A.W.S. Williams, J. Phys. C **4**, 1789 (1971)
44. J.W. Cross, L.T. Ho, A.K. Ramdas, R. Sauer, E.E. Haller, Phys. Rev. B **28**, 6953 (1983)
45. R.K. Crouch, J.B. Robertson, T.E. Gilmer, Jr, Phys. Rev. B **5**, 3111 (1972)
46. L.S. Darken, J. Appl. Phys. **53**, 3754 (1982)
47. G. Davies, R. Stedman, J. Phys. C **20**, 2119 (1987)
48. P.J. Dean, D.J. Robbins, S.G. Bishop, J. Phys. C **12**, 5567 (1979)
49. P.J. Dean, E.C. Lightowers, D.R. Wight, Phys. Rev. **140**, A352 (1965)
50. P.J. Dean, W. Stutius, G.F. Neumark, G.F. Fitzpatrick, R.N. Bhargava, Phys. Rev. B **27**, 2419 (1983)
51. A. Dörnen, R. Kienle, K. Thonke, P. Stolz, G. Pensl, D. Grünebaum, N.A. Stolwijk, Phys. Rev. B **40**, 12005 (1989)
52. A.H. Edwards, W.B. Fowler, Phys. Rev. B **16**, 3613 (1977)
53. K.R. Elliot, D.E. Holmes, R.T. Chen, C.G. Kirkpatrick, Appl. Phys. Lett. **40**, 898 (1982)
54. W. Engeler, H. Levinstein, C. Stannard Jr, J. Phys. Chem. Solids. **22**, 249 (1961)
55. F. Evangelisti, A. Frova, M. Zanini, E.O. Kane, Solid State Commun. **11**, 611 (1972)
56. A.O. Evwaraye, S.R. Smith, W.C. Mitchel, H. Hobgood M.c.D., Appl. Phys. Lett. **71**, 1186 (1997)
57. V. Fiorentini, Phys. Rev. B **51**, 10161 (1995)
58. V. Fiorentini, A. Baldereschi, Solid State Commun. **69**, 953 (1989)
59. D.W. Fischer, J.J. Rome, Phys. Rev. B **27**, 4826 (1983)
60. P. Fisher, H.Y. Fan, Phys. Rev. Lett. **5**, 195 (1960)
61. T. Friedrich, J. Kraus, M. Meininger, G. Schaack, W.O.G. Schmitt, J. Phys.: Cond. Matter. **6**, 4307 (1994)
62. K. Geim, G. Pensl, M. Schulz, Appl. Phys. A **27**, 71 (1982)
63. E.M. Gershenzon, A.P. Mel'nikov, R.I. Rabinovich, N.A. Serebryakova, Sov. Phys. Usp. **23**, 684 (1980)
64. E. Gheeraert, A. Deneuille, J. Mambou, Diam. Relat. Mater. **7**, 1509 (1998)
65. D.L. Greenaway, Proc. Phys. Soc. **76**, 900 (1960)
66. E.E. Haller, W.L. Hansen, F.S. Goulding, Adv. Phys. **30**, 93 (1981)
67. E.E. Haller, R.E. McMurray, L.M. Falicov, N.M. Haegel, W.L. Hansen, Phys. Rev. Lett. **51**, 1089 (1983)
68. E.E. Haller, R.E. McMurray, N.M. Haegel, L.M. Falicov, in *Proceeding 17th ICPS, San Francisco 1984*, ed by J.D. Chadi, W.A. Harrison (Springer, New York, 1985), pp. 679–682
69. T. Hattori, E. Fujii, T. Kurata, Y. Sakaji, A. Mitsuishi, Y. Kamiura, Jpn. J. Appl. Phys. **24**, 682 (1985)
70. T. Hattori, T. Kurata, E. Fujii, A. Mitsuishi, Y. Kamiura, Jpn. J. Appl. Phys. **24**, 689 (1985)
71. T. Hattori, T. Tanaka, A. Mitsuishi, Y. Kamiura, Jpn. J. Appl. Phys. **25**, 358 (1986)

72. T. Hattori, T. Tanaka, A. Mitsuishi, Y. Kamiura, Jpn. J. Appl. Phys. **25**, 1879 (1986)
73. T. Hattori, K. Yamano, A. Mitsuishi, Y. Kamiura, Jpn. J. Appl. Phys. **27**, 776 (1988)
74. T. Hattori, T. Takada, K. Kagawa, A. Mitsuishi, Y. Kamiura, Phys. Stat. Sol. B **120**, K63 (1990)
75. M.O. Henry, E.C. Lightowers, N. Killoran, D.J. Dunstan, B.C. Cavenett, J. Phys. C **14**, L255 (1981)
76. M.O. Henry, K.G. McGuigan, M.C. do Carmo, M.H. Nazare, E.C. Lightowers, J. Phys. Condens. Matter. **2**, 9697 (1990)
77. J.N. Heyman, A. Gieseckus, E.E. Haller, in *Defects in Semiconductors 16*, ed. by G.G. DeLeo, M. Stavola (Trans Tech, Switzerland, 1992); Mater. Sci. Forum **83**, 257
78. L.T. Ho, Appl. Phys. Lett. **35**, 409 (1979)
79. D.M. Hofmann, P. Omling, H.G. Grimmeiss, B.K. Meyer, K.W. Benz, D. Sinerius, Phys. Rev. B **45**, 6247 (1992)
80. C.M. Huggins, P. Cannon, Nature **194**, 829 (1962)
81. K.M. Itoh, J. Muto, W. Walukiewicz, J.W. Beeman, E.E. Haller, H. Kim, A.J. Mayur, M.D. Sciacca, A.K. Ramdas, R. Buczko, J.W. Farmer, V.I. Ozogin, Phys. Rev. B **53**, 7797 (1996)
82. C. Jagannath, Z.W. Grabowski, A.K. Ramdas, Phys. Rev. B **23**, 2082 (1981)
83. J.R. Jenny, M. Skowronski, W.C. Mitchel, H.M. Hobgood, R.C. Glass, G. Augustine, R.H. Hopkins, J. Appl. Phys. **79**, 2326 (1996)
84. R.L. Jones, P. Fisher, J. Phys. Chem. Solids **26**, 1125 (1965)
85. C.E. Jones, D. Schafer, W. Scott, R.J. Hager, J. Appl. Phys. **52**, 5148 (1981)
86. O. Ka, A. Yamada, H. Yoshinaga, Y. Makita, J. Appl. Phys. **78**, 5171 (1995)
87. J.M. Kahn, L.M. Falicov, E.E. Haller, Phys. Rev. Lett. **57**, 2077 (1986)
88. J.M. Kahn, R.E. McMurray, E.E. Haller, L.M. Falicov, Phys. Rev. B **36**, 8001 (1987)
89. W. Kaiser, H.Y. Fan, Phys. Rev. **93**, 977 (1954)
90. Y. Kamiura, J. Broeckx, P. Clauws, J. Vennik, Solid State Commun. **38**, 883 (1981)
91. Y. Kamiura, F. Hashimoto, T. Takada, Y. Sakaji, T. Hattori, in *Proceedings of 11th International Conference Defects and Radiation Effects in Semiconductor, Inst. Phys. Conf Ser. No 59*, ed. by R.R. Hasiguti, 1981, pp. 187–192
92. R. Kaplan, Solid State Commun. **12**, 191 (1973)
93. D. Karaickaj, M.L.W. Thewalt, T. Ruf, M. Cardona, M. Konuma, Phys. Rev. Lett. **89**, 016401/1–4 (2002)
94. N. Killoran, D.J. Dunstan, M.O. Henry, E.C. Lightowers, B.C. Cavenett, J. Phys. C **15**, 6067 (1982)
95. H. Kim, S. Rodriguez, M. Grimsditch, T.R. Anthony, A.K. Ramdas, Physica B **273–274**, 624 (1999)
96. H. Kim, R. Vogelgesang, A.K. Ramdas, S. Rodriguez, M. Grimsditch, T.R. Anthony, Phys. Rev. B **57**, 15315 (1998)
97. R.F. Kirkman, R.A. Stradling, P.J. Lin-Chung, J. Phys. C **11**, 419 (1978)
98. D. Kisker, D.W. Tews, W. Rehm, J. Appl. Phys. **54**, 1332 (1983)
99. M. Kleverman, H.G. Grimmeiss, Semicond. Sci. Tech. **1**, 45 (1986)
100. M. Kleverman, J. Olajos, H.G. Grimmeiss, Phys. Rev. B **37**, 2613 (1988)
101. M. Kleverman, J. Olajos, P. Tidlund, Phys. Rev. B **56**, 1376 (1997)

102. B.O. Kolbesen, Appl. Phys. Lett. **27**, 353 (1975)
103. A.A. Kopylov, A.N. Pikhtin, Solid State Commun. **26**, 735 (1978)
104. Yu. A. Kurskii, Phys. Rev. B **48**, 5148 (1993)
105. D. Labrie, I.J. Booth, S.P. Watkins, M.L.W. Thewalt, Solid State Commun. **63**, 115 (1987)
106. D. Labrie, T. Timusk, M.L.W. Thewalt, Phys. Rev. Lett. **52**, 81 (1984)
107. M. Lang, G. Pensl, M. Gebhard, N. Achttziger, M. Uhrmacher, Appl. Phys. A **53**, 95 (1991)
108. R.A. Lewis, P. Fisher, N.A. McLean, Aust. J. Phys. **47**, 329 (1994)
109. R.A. Lewis, T.S. Cheng, M. Henini, J.M. Chamberlain, Phys. Rev. B **53**, 12 829 (1996)
110. M. Linnarsson, E. Janzén, B. Monemar, M. Kleverman, A. Thilderkvist, Phys. Rev. B **55**, 6938 (1997)
111. N.O. Lipari, M.L.W. Thewalt, W. Andreoni, A. Baldereschi, J. Phys. Soc. Jpn. **49** (Suppl A) 165 (1980)
112. N. Magnea, J.L. Pautrat, K. Saminadayar, B. Pajot, P. Martin, A. Bontemps, Rev. Phys. Appl. **15**, 701 (1980)
113. R.E. McMurray Jr, N.M. Haegel, J.M. Kahn, E.E. Haller, Solid State Commun. **61**, 27 (1987)
114. R. Meisels, F. Kuchar, Phys. Stat. Sol. B **116**, 557 (1985)
115. E. Merk, J. Heyman, E.E. Haller, Mater. Res. Soc. Symp. Proc. **163**, 21 (1990)
116. R.A. Messenger, J.S. Blakemore, Phys. Rev. B **4**, 1873 (1971)
117. E. Molva, J.P. Chamonal, G. Milchberg, K. Saminadayar, B. Pajot, G. Neu, Solid State Commun. **44**, 351 (1982)
118. E. Molva, J.L. Pautrat, K. Saminadayar, G. Milchberg, N. Magnea, Phys. Rev. B **30**, 3344 (1984)
119. W.J. Moore, Solid State Commun. **3**, 385 (1965)
120. W.J. Moore, J. Phys. Chem. Solids **32**, 93 (1971)
121. W.J. Moore, Phys. Rev. B **29**, 7062 (1984)
122. K. Muro, A.J. Sievers, Phys. Rev. Lett. **57**, 897 (1986)
123. V.N. Murzin, A.I. Demeshina, L.M. Umarov, Sov. Phys. Semicond. **6**, 419 (1972)
124. S. Nakashima, T. Hattori, P.E. Simmonds, E. Amzallag, Phys. Rev. B **19**, 3045 (1979)
125. H. Nakata, E. Otsuka, J. Phys. Soc. Jpn. **55**, 391 (1986)
126. H. Nakata, E. Otsuka, E.E. Haller, Jpn. J Appl. Phys. **25**, L57 (1986)
127. H. Nakata, K. Yamada, T. Ohyama, Appl. Phys. Lett. **74**, 3480 (1999)
128. A. Näser, W. Gehlhoff, H. Overhof, R.A. Yankov, Phys. Stat. Sol. B **210**, 753 (1998)
129. R.C. Newman, B.R. Davidson, R. Addinall, R. Murray, J.W. Emmert, J. Wagner, W. Götz, G. Roos, G. Pensl, in *Defects in Semiconductors 17*, ed. by H. Heinrich, W. Jantsch (Trans Tech, Switzerland, 1994); Mater. Sci. Forum **143–147**, 229
130. T. Nishino, M. Takeda, Y. Hamakawa, Solid State Commun. **14**, 627 (1974)
131. A. Onton, PhD thesis, Purdue University, 1967, p. 38
132. B. Pajot, I.L. Beinikhes, Sh. M. Kogan, M.G. Novak, A.F. Polupanov, C. Song, Semicond. Sci. Tech. **7**, 1162 (1992)
133. B. Pajot, Y. Darvriot, Phys. Lett. **21**, 512 (1966)
134. B. Pajot, D. Débarre, D. Roche, J. Appl. Phys. **52**, 5774 (1981)

135. B. Pajot, A. Tardella, in *Neutron transmutation doping of semiconductor materials*, ed by R.D. Larrabee, (Plenum, 1984), pp. 261
136. G.J. Parker, S.D. Brotherton, I. Gale, A. Gill, J. Appl. Phys. **54**, 3926 (1983)
137. R.E. Peale, K. Muro, A.J. Sievers, Phys. Rev. B **41**, 5881 (1990)
138. G. Piao, R.A. Lewis, P. Fisher, Solid State Commun. **75**, 835 (1990)
139. G. Piao, P. Fisher, R.A. Lewis, Phys. Rev. B **61**, 7466 (2000)
140. C. Piccirillo, G. Davies, A. Mainwood, C.M. Pechina, Diam. Relat. Mater. **11**, 338 (2002)
141. G.S. Pomrenke, J. Cryst. Growth **64**, 158 (1983)
142. M. Porrini, M.G. Pretto, R. Scala, A.V. Batunina, H.C. Alt, R. Wolf, Appl. Phys. A **81**, 1187 (2005)
143. A.K. Ramdas, S. Rodriguez, Rep. Progr. Phys. **44**, 1297 (1981)
144. F. Raymond, Solid State Commun. **18**, 171 (1976)
145. J.J. Rome, W.C. Mitchel, G.J. Brown, D.W. Fischer, M.C. Ohmer, T.L. Peterson, Appl. Phys. Lett. **41**, 254 (1982)
146. E. Rotsaert, P. Clauws, J. Vennik, L. van Goethem, Physica **146B**, 75 (1987)
147. M. Said, M.A. Kanehisa, Phys. Stat. Sol. B **157**, 311 (1990)
148. M. Said, M.A. Kanehisa, M. Jouanne, M. Balkanski, J. Phys C **20**, 2917 (1987)
149. E.H. Salib, P. Fisher, P.E. Simmonds, Phys. Rev. B **32**, 2424 (1985)
150. W. Schairer, E. Grobe, Solid State Commun. **8**, 2014 (1970)
151. W. Schelter, W. Hell, R. Helbig, M. Schulz, J. Phys. C **15**, 5839 (1982)
152. H. Schroth, K. Lassmann, S. Voss, H. Bracht, Phys. Rev. Lett. **85**, 417 (2000)
153. W. Scott, J.L. Schmit, Appl. Phys. Lett. **33**, 294 (1978)
154. J. Serrano, A. Wyszomolek, T. Ruf, M. Cardona, Physica B **273–274**, 640 (1999)
155. E. Simoen, P. Clauws, M. Lamon, J. Vennik, Semicond. Sci. Tech. **1**, 53 (1986)
156. G. Sirmain, O.D. Dubon, W.L. Hansen, C.S. Olsen, E.E. Haller, J. Appl. Phys. **79**, 209 (1996)
157. H.P. Soepangkat, P. Fisher, Phys. Rev. B **8**, 870 (1973)
158. B.L. Sopori, Appl. Phys. Lett. **47**, 39 (1985)
159. W. Stadler, D.M. Hofmann, H.C. Alt, T. Muschik, B.K. Meyer, E. Weigel, G. Müller-Vogt, M. Salk, E. Rupp, K.W. Benz, Phys. Rev. B **51**, 10 619 (1995)
160. J. Staiger, P. Gross, K. Lassmann, H. Bracht, N.A. Stolwijk, in *Defects in Semiconductors 17*, ed. by H. Heinrich, W. Jantsch (Trans Tech, Switzerland, 1994); Mater. Sci. Forum **143**
161. M. Steger, A. Yang, D. Karaiskaj, M.L.W. Thewalt, E.E. Haller, I.I.I.J.W. Ager, M. Cardona, H. Riemann, N.V. Abrosimov, A.V. Gusev, A.D. Bulanov, A.K. Kaliteevskii, O.N. Godisov, P. Becker, H.J. Pohl, Phys. Rev. B **79**, 205210 (2009)
162. A. Strachan, in *Properties of Crystalline Silicon, EMIS Datareviews Series No 20*, ed. by R. Hull (INSPEC Publication, London, 1999), p. 457
163. R.A. Street, W. Senske, Phys. Rev. Lett. **37**, 1292 (1976)
164. M. Suezawa, A. Kasuya, K. Sumino, Y. Nishina, J. Phys. Soc. Jpn. **57**, 4021 (1988)
165. M. Suezawa, R. Mori, Phys Stat Sol B **210**, 507 (1998)
166. M. Suezawa, K. Sumino, J. Appl. Phys. **76**, 932 (1994)
167. A. Tardella, B. Pajot, J. Physique **43**, 1789 (1982)
168. E. Tarhan, I. Miotkowski, S. Rodriguez, A.K. Ramdas, Phys. Rev. B **67**, 195202/1–9 (2003)
169. E. Tarnow, S.B. Zhang, K.J. Chang, D.J. Chadi, Phys. Rev. B **42**, 11252 (1990)



170. H. Tews, H. Venghaus, P.J. Dean, *Phys. Rev. B* **19**, 5178 (1979)
171. M.L.W. Thewalt, *Solid State Commun.* **23**, 733 (1977)
172. M.L.W. Thewalt, D. Labrie, I.J. Booth, B.P. Clayman, E.C. Lightowers, E.E. Haller, *Physica* **146B**, 47 (1987)
173. M.L.W. Thewalt, D. Labrie, B.P. Clayman, *Solid State Commun.* **56**, 751 (1985)
174. M.L.W. Thewalt, B.P. Clayman, D. Labrie, *Phys. Rev. B* **32**, 2663 (1985)
175. M.L.W. Thewalt, D. Labrie, T. Timusk, *Solid State Commun.* **53**, 1049 (1985)
176. M.L.W. Thewalt, S.P. Watkins, U.O. Ziemelis, E.C. Lightowers, M.O. Henry, *Solid State Commun.* **44**, 573 (1982)
177. K. Thonke, *Semicond. Sci. Tech.* **18**, S20 (2003)
178. N.D. Tyapkina, M.M. Krivopolenova, V.S. Vavilov, *Sov. Phys. Sol. State* **6**, 1732 (1965)
179. M.K. Udo, C.R. LaBrec, A.K. Ramdas, *Phys. Rev. B* **44**, 1565 (1991)
180. H. Venghaus, P.J. Dean, *Phys. Rev. B* **21**, 1596 (1980)
181. R.E.M. Vickers, P. Fisher, C.A. Freeth, *Solid State Commun.* **65**, 271 (1988)
182. R.E.M. Vickers, P. Fisher, C.A. Freeth, *Phys. Stat. Sol. B* **210**, 839 (1998)
183. J. Wagner, H. Seelewind, *J. Appl. Phys.* **64**, 2761 (1988)
184. J. Wagner, H. Seelewind, P. Koidl, *Appl. Phys. Lett.* **49**, 1080 (1986)
185. J. Wagner, K.H. Ko, J. Lagowski, *Phys. Rev. B* **43**, 5163 (1991)
186. K. Wan, R. Bray, *Phys. Rev. B* **32**, 5265 (1985)
187. A.C. Wang, L.S. Lu, C.T. Sah, *Phys. Rev. B* **30**, 5896 (1984)
188. M. Wenzel, G. Irmer, J. Monecke, *Solid State Commun.* **104**, 371 (1997)
189. H.H. Woodbury, W.W. Tyler, *Phys. Rev.* **105**, 84 (1957)
190. G.B. Wright, A. Mooradian, *Phys. Rev. Lett.* **18**, 608 (1967)
191. Y. Wu, L.M. Falicov, *Phys. Rev. B* **29**, 3671 (1984)
192. Z. Yu, Y.X. Huang, S.C. Shen, *Phys. Rev. B* **39**, 6287 (1989)
193. S. Zwerdling, K.J. Button, B. Lax, L.M. Roth, *Phys. Rev. Lett.* **4**, 173 (1960)

---

## Effects of Perturbations

### 8.1 Introduction

The frequencies of the spectral lines in crystals can be shifted by perturbations and when levels are degenerate, splitting can occur. Discrete levels of impurities and defects are characterized by their energies and their widths, which determine the positions and the FWHMs of the transitions. The degeneracy of the levels is a less obvious parameter related to their symmetry or to the symmetry of the centres in the crystal, and its consequences can only be derived from optical measurements under external perturbations. It has been shown in Chap. 5 that the multi-valley degeneracy of the *CB* of indirect-band-gap semiconductors translated into the same degeneracy of the EM donor states and that this degeneracy was partially lifted by valley-orbit coupling. Similarly, due to the structure of the *VB* maximum, the EM acceptor states also present an intrinsic electronic degeneracy. These degeneracies are the same whatever the atomic structure of the centres because they are due to the band structure of the semiconductor. Another form of degeneracy is due to the atomic symmetry of the centres with equivalent orientations in the crystal, and is logically called orientational degeneracy. An example is the  $\langle 111 \rangle$  oriented chalcogen substitutional donor pairs in silicon, with a fourfold orientational degeneracy. In the preceding chapters, examples of the splitting of the spectra of impurities in crystals under different perturbations have been given. A more systematic treatment of these perturbations, which can be mechanical, electrical or magnetic, is considered in this chapter.

In a crystal, perturbations can be classified as internal and external. The internal perturbations are disturbances from an equilibrium condition, taken as an ideal uniform distribution of impurities or defects which do not modify the crystal lattice and the average electronic density. Mechanical perturbations can be microscopic, like those introduced by impurities or defects producing large local volume changes, which reflect on crystal lattice spacings when their concentration is large, or macroscopic due to residual or accidental stresses. Permanent perturbations can also be produced by unrelaxed stresses

originating from lattice misfits in epitaxially-grown sample and it must be noted that in this case, the perturbation can also be biaxial. Electrical perturbations can be produced by fluctuations in the impurity concentration or due to compensation inhomogeneities, responsible for the already-mentioned inhomogeneous Stark effect.

The external perturbations, on the other hand, are uniaxial or hydrostatic stresses, electric fields and magnetic fields. Strong illumination of samples with radiation at or above band-gap energies, intended to modify the carrier concentration, can also be considered as perturbations (not considered in this chapter).

When an external perturbation is applied along a given crystal direction, it generally reduces the overall symmetry of the crystal by adding an anisotropy axis. The change in symmetry at a given atomic site under an external uniaxial perturbation depends not only on the orientation of the perturbation, but also on its nature: uniaxial stress and electric field are polar vectors which change sign under inversion operation, but a magnetic field is an axial vector which does not. As a consequence, the point group symmetries differ: starting for instance from a donor or an acceptor at a site with  $T_d$  symmetry, a magnetic field along a  $[100]$ ,  $[110]$  or  $[111]$  direction reduces the site symmetry to  $S_4$ ,  $C_{1h}$  or  $C_3$ , respectively, but a uniaxial stress along the same direction reduces the site symmetry to  $D_{2d}$ ,  $C_{2v}$  and  $C_{3v}$ , respectively.

In the general case, a transition involving degenerate levels is split into two or more components under an external perturbation. One usually follows the spectral positions of the component as a function of the amplitude of the perturbation, and this result in “fan” charts of the kind shown in Fig. 8.8. In such charts, there are values of the perturbation for which two components from different transitions can, in principle, intersect. As a function of the symmetries of these components with respect to the perturbation, these components can cross without interaction, but there are cases where the two components interact, giving rise to an anti-crossing or avoided crossing configuration which can be properly dealt with by an appropriate perturbation calculation.

## 8.2 Mechanical Stresses

A detailed presentation of the piezospectroscopy of semiconductors can be found in [124]. Uniaxial stress is the most easily-produced perturbation (for experimental details, see Sect. 4.7.1), and the spectroscopy performed under stress is called piezospectroscopy. The relevant piezospectroscopic parameters for an impurity line are the number of components observed, their polarization characteristics and the amplitude of their shifts and splitting as a function of the value of the stress. Piezospectroscopy is useful when studying degenerate electronic transitions of the EM-like centres as it can lift intrinsic degeneracy. It can also lift the orientational degeneracy of electronic (and vibrational)

transitions. Another interest of piezospectroscopy is that, by modifying the spacing between levels, it is possible to study interactions and resonances between levels. It is restricted to monocrystalline samples of a reasonable size and this explains why some materials have not been investigated by this technique. The maximum stress which can be applied to a material depends on its mechanical properties, but these properties improve at lower temperatures, and stresses that would pulverize a sample at RT can safely be applied at LHeT. A moderate hydrostatic stress does not change the overall crystal symmetry, but it can change the energies of the electronic bands of the crystal as different bands can display opposite pressure coefficients to such stresses: a direct-gap semiconductor like GaAs becomes an indirect-gap semiconductor for hydrostatic pressures above  $\sim 4$  GPa [149]. For much larger hydrostatic stresses, the crystal structure itself can change (above about 12 GPa, cubic silicon turns into tetragonal  $\beta$ -tin structure, with metallic properties), but this kind of perturbation is not considered in this book.

The stress-induced splitting of the levels with intrinsic degeneracy like the triply degenerate levels of vibrational and electronic transitions of cubic centres has been treated by Kaplyanskii [73], and the doubly degenerate levels of trigonal or tetragonal centres in cubic crystals by Hughes and Runciman [63]. From a mathematical aspect, the treatment of the effects of stress must consider the fact that stress is a tensor, so that some piezospectroscopic quantities also have tensor properties. The general textbook by Bir and Pikus [18] on the stress-induced effects in semiconductors includes piezospectroscopic properties and a detailed presentation of the necessary group theoretical tools.

In this section, we first consider the effect of mechanical stresses on EM electronic transitions and present typical examples. The second part develops the relation between orientational degeneracy and splitting under uniaxial stress or other external perturbations.

### 8.2.1 Effects on Electronic Transitions

A stress applied to a crystal results in a strain. A phenomenological description of the electron energy levels under elastic strain was developed by Bardeen and Shockley [12]. It is referred to as the deformation potential approximation (DPA), in which the one-electron Hamiltonian is developed in a Taylor's series of the strain components  $\epsilon_{\alpha\beta}$ . The perturbation is written in cartesian coordinates, for a linear order in strain, as:

$$V = \sum_{\alpha,\beta} V_{\alpha\beta} \epsilon_{\alpha\beta}, \quad (8.1)$$

where  $V_{\alpha\beta}$  are symmetric with respect to  $\alpha$  and  $\beta$ , and used to obtain energy shifts and splitting of specific energy levels.

We consider first the effect of a uniaxial stress on the EM-like electronic spectra of donors with *CB* degeneracy and then the situation for acceptors.

### 8.2.1.1 EM Donors with CB Degeneracy

#### *Shallow Donors in Multi-Valley Semiconductors*

Under stress, a one-valley EM donor state follows the energy shift of the valley it belongs to. A study of the effect of a uniaxial stress on the donor spectra in a multi-valley semiconductor (silicon) has been undertaken by Tekippe et al. [140]. The treatment given below follows this presentation closely, with minor changes in the notations. Following the deformation potential analysis of [60], the shift in energy  $\Delta E^{(j)}$  of valley  $j$  of the *CB* of silicon or germanium with respect to the zero-stress conditions is:

$$\Delta E^{(j)} = \sum_{\alpha, \beta} \left[ \Xi_d \delta_{\alpha\beta} + \Xi_u k_{\alpha}^{(j)} k_{\beta}^{(j)} \right] \epsilon_{\alpha\beta}, \quad (8.2)$$

where  $\Xi_d$  is the deformation potential (DP) for the dilatation in the two directions perpendicular to the valley axis and  $\Xi_u$  the DP for a stretch along the valley axis and a contraction along the two perpendicular directions (shear DP),  $k_{\alpha}^{(j)}$  and  $k_{\beta}^{(j)}$  are the components of a unit vector pointing from the centre of the BZ towards the position of minimum  $j$  and  $\epsilon_{\alpha\beta}$  are the components of the strain tensor. In other descriptions of the strain effects on the *CB* of semiconductors, different notations for the DPs have been used: The deformation potential term  $\Xi_d + \frac{1}{3}\Xi_u$  associated with the hydrostatic component of the stress is represented as  $E_1 + a_1$  by Laude et al. [92], after [26], while  $\Xi_u$  is identical to  $E_2$  for silicon (*CB* minima along  $\langle 100 \rangle$  direction) and to  $2E_2$  for germanium (*CB* minima along  $\langle 111 \rangle$  direction).

Let us consider the case of silicon. The multi-valley structure of the *CB* minimum of silicon is depicted in Fig. 8.1, with six constant energy surfaces along the  $\langle 100 \rangle$  direction  $\Delta$  of the BZ. A force  $\mathbf{F}$  has also been included in this figure, whose direction is defined by polar angles  $\theta$  and  $\phi$ .

When replacing in expression (8.2), the components  $k_{\alpha}^{(j)}$  and  $k_{\beta}^{(j)}$  by the direction cosines  $l, m$  and  $n$  of the external stress, the shift of valley  $j$  becomes:

$$\begin{aligned} \Delta E^{(j)} = & \Xi_d (\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz}) \\ & + \Xi_u (l^2 \epsilon_{xx} + m^2 \epsilon_{yy} + n^2 \epsilon_{zz} + 2(mn \epsilon_{yz} + nl \epsilon_{xz} + lm \epsilon_{xy})). \end{aligned} \quad (8.3)$$

The shift of the centre of gravity (c.g.) of the six valleys deduced from (8.3) is:

$$\langle \Delta E^{(j)} \rangle = \frac{1}{6} \sum_{j=1}^6 \Delta E^{(j)} = (\Xi_d + \frac{1}{3} \Xi_u) (\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz}) \quad (8.4)$$

and it represents the value of the hydrostatic shift of the *CB* minima of silicon (this also holds true, *mutatis mutandis*, for the four *CB* minima of germanium). The shift of valley  $j$  with respect to the centre of gravity can be expressed as:

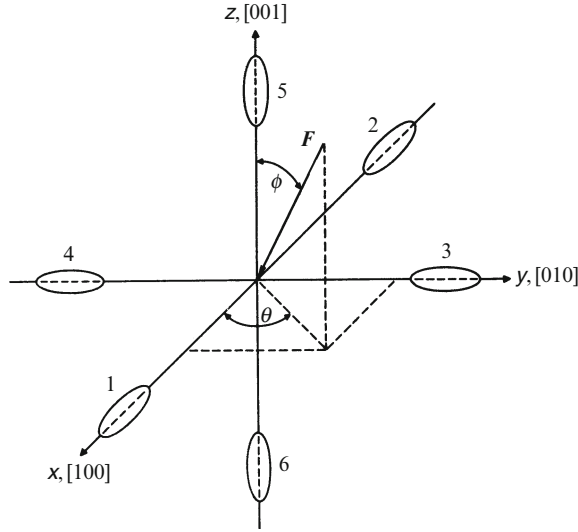


**Fig. 8.1.** Multi-valley structure of the *CB* minimum of silicon showing the constant-energy ellipsoids along  $\langle 100 \rangle$ . For convenience, the direction of an applied compressive force  $\mathbf{F}$  is defined with respect to the orthogonal axes chosen along the  $\langle 100 \rangle$  direction (after [140]). Copyright 1972 by the American Physical Society

$$\delta E^{(j)} = \Xi_u \left[ l^2 \epsilon_{xx} + m^2 \epsilon_{yy} + n^2 \epsilon_{zz} + 2(mn \epsilon_{yz} + nl \epsilon_{zx} + lm \epsilon_{xy}) - \frac{1}{3} (\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz}) \right] \sigma_{xx}. \quad (8.5)$$

The strain tensor is the product of the elastic compliance tensor of the crystal by the stress tensor with components  $\sigma_{\alpha\beta}$ . For cubic crystals, where the non-zero components of the elastic compliance tensor are  $S_{11}$ ,  $S_{12}$  and  $S_{44}$ , it can be expressed<sup>1</sup> as:

$$\begin{bmatrix} \epsilon_{xx} \\ \epsilon_{yy} \\ \epsilon_{zz} \\ \epsilon_{yz} \\ \epsilon_{zx} \\ \epsilon_{xy} \end{bmatrix} = \begin{bmatrix} S_{11} & S_{12} & S_{12} & 0 & 0 & 0 \\ S_{12} & S_{11} & S_{12} & 0 & 0 & 0 \\ S_{12} & S_{12} & S_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{4}S_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{4}S_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{4}S_{44} \end{bmatrix} \begin{bmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \sigma_{zz} \\ \sigma_{yz} \\ \sigma_{zx} \\ \sigma_{xy} \end{bmatrix}. \quad (8.6)$$

<sup>1</sup> In cubic crystals, there are three non-zero compliance components  $S_{11}$ ,  $S_{12}$  and  $S_{44}$  closely related to the second-order elastic moduli  $C_{11}$ ,  $C_{12}$  and  $C_{44}$ :  $S_{11} = (C_{11} + C_{12}) [(C_{11} - C_{12})(C_{11} + 2C_{12})]^{-1}$ ,  $S_{12} = -C_{12} [(C_{11} - C_{12})(C_{11} + 2C_{12})]^{-1}$  and  $S_{44}$  is  $C_{44}^{-1}$ .

Using the expression for the components of the strain tensor derived from (8.6), the shift  $\delta E^{(j)}$  for the silicon *CB* can be rewritten as:

$$\delta E^{(j)} = \Xi_u \left\{ (S_{11} - S_{12}) \left[ l^2 \sigma_{xx} + m^2 \sigma_{yy} + n^2 \sigma_{zz} - \frac{1}{3} (\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) \right] + S_{44} (mn \sigma_{yz} + nl \sigma_{zx} + lm \sigma_{xy}) \right\}. \quad (8.7)$$

The components of the stress tensor in the crystal due to a stress  $\mathbf{T}$  applied along a crystal axis with respect to an orthogonal set of coordinates  $x, y, z$  can be expressed as:

$$\sigma_{\alpha\beta} = \pm \mathbf{n}_\alpha \mathbf{n}_\beta T, \quad (8.8)$$

where  $\mathbf{n}_\alpha$  and  $\mathbf{n}_\beta$  are the direction cosines of the stress in the orthogonal reference frame and  $T$  the magnitude of the stress (the applied force per unit surface). The plus and minus signs are for tension (dilatation) and compression (the usual case), respectively.

When taking  $\mathbf{n}_j$  as a unit vector along the direction from the centre of the BZ to valley  $j$ , expression (8.7) is transformed to give, for a compressive force:

$$\delta E^{(j)} = -\Xi_u T (S_{11} - S_{12}) \left[ (\mathbf{n}_j \cdot \mathbf{n}_F)^2 - 1/3 \right], \quad (8.9)$$

where  $\mathbf{n}_F$  is a unit vector along  $\mathbf{F}$ . For an arbitrary orientation of the compressive force, and following the valley labels of Fig. 8.1, one obtains:

$$\begin{aligned} \delta E^{(1,2)} &= -\Xi_u T (S_{11} - S_{12}) [\cos^2 \theta \sin^2 \phi - 1/3] \\ \delta E^{(3,4)} &= -\Xi_u T (S_{11} - S_{12}) [\sin^2 \theta \sin^2 \phi - 1/3]. \\ \delta E^{(5,6)} &= -\Xi_u T (S_{11} - S_{12}) [\cos^2 \phi - 1/3] \end{aligned} \quad (8.10)$$

For  $\mathbf{F} // [100]$  ( $\theta = 0$  and  $\phi = 90^\circ$ ), valleys 3, 4, 5, and 6 are equivalent and a triply-degenerate  $T_2$  EM level splits into a doublet, as for  $\mathbf{F} // [110]$  ( $\theta = 45^\circ$  and  $\phi = 90^\circ$ ). For  $\mathbf{F} // [111]$ ,  $\theta = 45^\circ$  and  $\phi = 54.736^\circ$  and there is no shift (and no splitting), as can be expected without calculation from symmetry alone and  $\delta E^{(j)}$  is zero for the six valleys.

For germanium, where the *CB* minima are at the *L* point of the surface of the BZ, along a  $\langle 111 \rangle$  direction, the shifts of the four valleys with respect to the shift of the centre of gravity are, for a compressive force, the equivalent of expression (8.9) is [123]:

$$\delta E^{(j)} = -\frac{1}{2} \Xi_u T S_{44} \left[ (\mathbf{n}_j \cdot \mathbf{n}_F)^2 - 1/3 \right]. \quad (8.11)$$

The effect of a force applied along a  $\langle 100 \rangle$  direction is the same for the four valleys, but when applied along  $\langle 110 \rangle$  or  $\langle 111 \rangle$  axes, the shifts are different.

The compliance coefficient  $S_{ij}$  for silicon, germanium, and diamond are given in Table 8.1.

**Table 8.1.** Compliance coefficients ( $\text{GPa}^{-1}$ ) for silicon [55, 112], germanium [28] and diamond [5]

|           | $S_{11}$               | $S_{12}$                | $S_{44}$               |
|-----------|------------------------|-------------------------|------------------------|
| Diamond   | $0.949 \times 10^{-3}$ | $-0.100 \times 10^{-3}$ | $1.734 \times 10^{-3}$ |
| Silicon   | $7.69 \times 10^{-3}$  | $-2.14 \times 10^{-3}$  | $12.58 \times 10^{-3}$ |
| Germanium | $9.67 \times 10^{-3}$  | $-2.42 \times 10^{-3}$  | $14.64 \times 10^{-3}$ |

**Table 8.2.** Shift  $\delta E^{(j)}$  of the  $CB$  minima (valleys) in silicon (units of  $\Xi_u T (S_{11} - S_{12})/3$ ) and germanium (units of  $\Xi_u T S_{44}/6$ ) for a compressive force along the indicated direction. The valley labels for silicon are those of Fig. 8.1; for germanium, valleys 1, 2, 3, and 4 are parallel to the  $[111]$ ,  $[\bar{1}\bar{1}\bar{1}]$ ,  $[\bar{1}\bar{1}1]$ , and  $[\bar{1}1\bar{1}]$  directions, respectively

|                 | Valleys | $F// [100]$      |                    | $F// [110]$      |                    | $F// [111]$      |                    |
|-----------------|---------|------------------|--------------------|------------------|--------------------|------------------|--------------------|
|                 |         | $\delta E^{(j)}$ | Valley point group | $\delta E^{(j)}$ | Valley point group | $\delta E^{(j)}$ | Valley point group |
| Si <sup>a</sup> | 1,2     | -2               | $C_{2v}$           | -1/2             | $C_1$              | 0                | $C_s$              |
|                 | 3,4     | +1               | $C_2$              | -1/2             | $C_1$              |                  |                    |
|                 | 5,6     | +1               | $C_2$              | 1                | $C_{2v}$           |                  |                    |
| Ge <sup>b</sup> | 1       | 0                | $C_s$              | -1               | $C_s$              | -2               | $C_{3v}$           |
|                 | 3       |                  |                    | -1               | $C_s$              | 2/3              | $C_s$              |
|                 | 2,4     |                  |                    | 1                | $C_s$              | 2/3              | $C_s$              |

<sup>a</sup> [140], <sup>b</sup> [125]

For silicon, the value of  $S_{11} - S_{12}$  measured at LHeT is  $9.745 \times 10^{-3} \text{ GPa}^{-1}$ . The effect of a uniaxial stress on the valleys of the  $CB$  translates, in the general case, into a level splitting assumed to be the same for the  $np_0$  and  $np_{\pm 1}$  EM levels and is given in Table 8.2 for particular cases in silicon and germanium. When considering the effect of an external perturbation on a semiconductor with a  $CB$  degeneracy similar to the one in silicon or germanium, another symmetry besides the site symmetry in the real space is the valley symmetry in  $k$ -space, to which is associated the valley point group. This latter group consists of symmetry elements leaving a given valley undisplaced. This is summarized in Table 8.2.

From Table 8.2, the splitting of the  $np$  states in silicon are  $\Xi_u T (S_{11} - S_{12})$  and  $\Xi_u T (S_{11} - S_{12})/2$  for  $\mathbf{F}// [100]$  and  $\mathbf{F}// [110]$ , respectively. For germanium, they are  $\Xi_u T S_{44}/3$  and  $4\Xi_u T S_{44}/9$  for  $\mathbf{F}// [110]$  and  $\mathbf{F}// [111]$ , respectively. The splitting of the  $1s(T_2)$  level in silicon has been calculated by Wilson and Feher [148] for  $\mathbf{F}// [100]$  and it is found to be the same as that of the  $np$  states.

The fundamental group-V donor spectra arise from a  $1s(A_1)$  ground state which is not exactly EM-like because of chemical effects and also because of the  $CB$  degeneracy we are concerned with here. Independent of the chemical



effect, the calculation of the valley-orbit splitting shows that the contribution of all the valleys are the same for the  $1s(A_1)$  state. Therefore, under stress, this state experiences an average shift which is not related to a particular valley, but to the value of the  $1s(A_1) - 1s(E)$  valley-orbit splitting (denoted  $6\Delta_c$ ) in silicon and  $1s(A_1) - 1s(T_2)$  valley-orbit splitting (denoted  $4\Delta_c$ ) in germanium. This shift of the ground state has been calculated explicitly for a compressive force  $\mathbf{F} // [100]$  in silicon [148]. For this configuration, strain induces a mixing of the lowest-energy split components of the  $1s(E)$  state with the  $1s(A_1)$ , giving two states. The dependence with stress of the deepest one is:

$$\delta E_{gs} = \Delta_c \left[ 3 + \frac{1}{2}x - \frac{3}{2} \left( x^2 + \frac{4}{3}x + 4 \right)^{1/2} \right],$$

where  $x = -\Xi_u(S_{11} - S_{12})/3\Delta_c$ . The stress dependence of the other state is also nonlinear with stress, but the highest-energy split component of  $1s(E)$  shows a linear dependence with stress and for  $\mathbf{F} // [100]$ , it is  $\Xi_u T(S_{11} - S_{12})/3$ .

The upper part of Fig. 8.2 shows the experimental splitting of the  $2p_{\pm 1}(P)$  line in silicon at LHeT for increasing stresses along the  $[100]$  direction. The

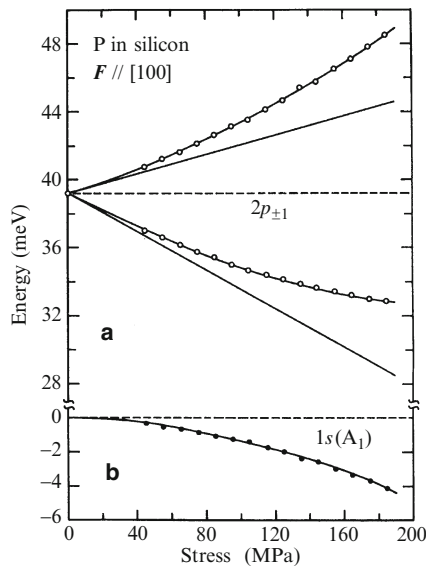


**Fig. 8.2.** (a) Measured stress dependence at LHeT of the two components of the  $2p_{\pm 1}(P)$  line in silicon (*open circles*). The *solid straight lines* are drawn from the energy spacings of the components considering the linear energy spacing with stress of the  $2p_{\pm 1}$  sublevel components divided in the ratio  $+1/-2$  of Table 8.2 with respect to the zero stress position. Above  $\sim 500$  MPa, the energy of the lower component becomes independent of the stress magnitude [38]. (b) stress dependence of the ground state calculated by taking the difference between the positions of the *straight lines* and experimental curves of the *upper part* (after [140]). Copyright 1972 by the American Physical Society

nonlinear shift of the components with stress is due to the shift of the ground state. The experimental stress dependence of the ground state shift is shown in Fig. 8.2 and is obtained by dividing the experimental spacing in a 1/2 ratio with respect to the zero-stress position. At the maximum value of the stress ( $\sim 180$  MPa), the splitting between the two components is  $\sim 16$  meV ( $129 \text{ cm}^{-1}$ ) and its ratio to the valley-orbit splitting of the P donor at zero stress is  $\sim 1.2$ . For stress magnitudes above  $\sim 500$  MPa, the position of the low-energy component becomes stress-insensitive because the negative stress dependences of its initial and final states are the same [38].

Transitions are parity-allowed between the  $1s$  ( $A_1$ ) ground state and the  $np_0$  and  $np_{\pm 1}$  states, but when an anisotropy axis is superimposed, polarization effects of the incident radiation are expected and it becomes necessary to determine the symmetry of the split levels.

Group theory must be used to determine the  $IRs$  of the new site symmetry point groups characterizing the split sublevels; an example of the method followed is given by Ramdas et al. [122]. It starts with the determination of the  $IRs$  for the valley symmetry point group corresponding to the donor wave functions. This can be obtained from the decomposition of the  $IRs$  of the continuous group  $D_{\infty h}$  of the donor Hamiltonian (5.5) for a given valley into the  $IRs$  of the valley symmetry groups. For the donor  $p$ -states which are considered in the following, one must note that the  $IRs$  of  $D_{\infty h}$  are different for the  $m = 0$  and for the  $m = \pm 1$  states. Once obtained, the Frobenius' reciprocity theorem (see for instance [102]) must be used to find the  $IRs$  of the new site symmetry point group which are generated by the  $IRs$  of the valley symmetry groups. Tables 8.3 and 8.4 gives the  $IRs$  of the sublevels of donor states with initial site symmetry  $T_d$  under a uniaxial stress in silicon and germanium. The case when there is no splitting is not considered. As expected, one sees that the stress-split sublevels correspond to specific  $CB$  valleys.

**Table 8.3.**  $IRs$  of the site symmetry point groups of the sublevels of  $np$  donor states in silicon split by a uniaxial stress, deduced from the  $IRs$  of the valley group. The site symmetry group under stress is indicated close to the stress orientation. The magnitudes of the splitting, independent of the value of  $m$ , are given in Table 8.2 (after [2])

| Stress orientation | $m$     | $IRs$ of the valley group                                    | $IRs$ of the $T_d$ site group | $IRs$ of the new site group                  |
|--------------------|---------|--------------------------------------------------------------|-------------------------------|----------------------------------------------|
| [100] $D_{2d}$     | 0       | A of $C_2$ (3, 4, 5, 6)<br>A <sub>1</sub> of $C_{2v}$ (1, 2) | $A_1 + E + T_2$               | $A_1 + B_1 + E$<br>$A_1 + B_2$               |
|                    | $\pm 1$ | 2B of $C_2$ (3, 4, 5, 6)<br>$B_1 + B_2$ of $C_{2v}$ (1, 2)   | $2T_1 + 2T_2$                 | $2A_2 + 2B_2 + 2E$<br>$2E$                   |
| [110] $C_{2v}$     | 0       | A <sub>1</sub> of $C_{2v}$ (5, 6)<br>A of $C_1$ (1, 2, 3, 4) | $A_1 + E + T_2$               | $2A_1$<br>$A_1 + A_2 + B_1 + B_2$            |
|                    | $\pm 1$ | $B_1 + B_2$ of $C_{2v}$ (5, 6)<br>$2A$ of $C_1$ (1, 2, 3, 4) | $2T_1 + 2T_2$                 | $2B_1 + 2B_2$<br>$2A_1 + 2A_2 + 2B_1 + 2B_2$ |

**Table 8.4.** Same as Table 8.3 for germanium (after [125])

| Stress orientation | m       | IRs of the valley group                                  | IRs of the $T_d$ site group | IRs of the new site group                          |
|--------------------|---------|----------------------------------------------------------|-----------------------------|----------------------------------------------------|
| [111] $C_{3v}$     | 0       | $A'$ of $C_s$ (2, 3, 4)<br>$A_1$ of $C_{3v}$ (1)         | $A_1 + T_2$                 | $A_1 + E$<br>$A_1$                                 |
|                    | $\pm 1$ | $A' + A''$ of $C_s$ (2, 3, 4)<br>$E$ of $C_{3v}$ (1)     | $E + T_1 + T_2$             | $A_1 + A_2 + 2E$<br>$E$                            |
| [110] $C_{2v}$     | 0       | $A'$ of $C_s$ (2, 4)<br>$A'$ of $C_s$ (1, 3)             | $A_1 + T_2$                 | $A_1 + B_2$<br>$A_1 + B_1$                         |
|                    | $\pm 1$ | $A' + A''$ of $C_s$ (2, 4)<br>$A' + A''$ of $C_s$ (1, 3) | $E + T_1 + T_2$             | $A_1 + A_2 + B_1 + B_2$<br>$A_1 + A_2 + B_1 + B_2$ |

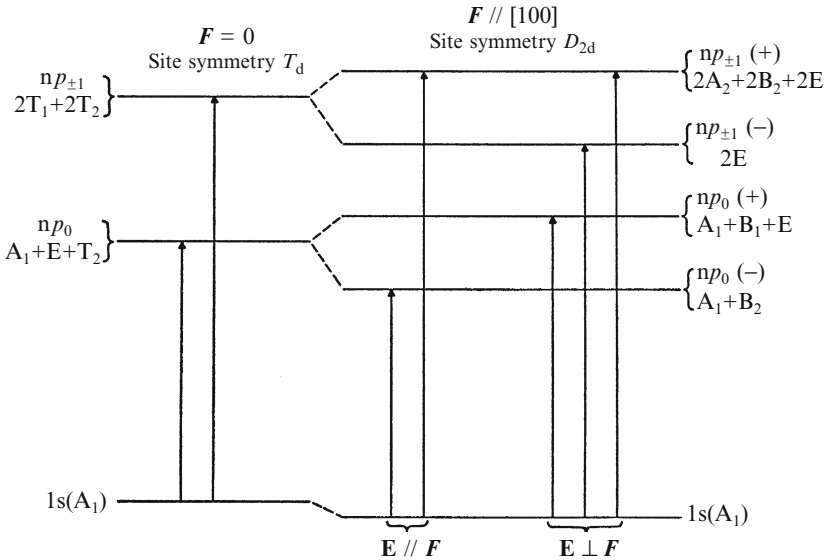


**Fig. 8.3.** Energy levels of shallow donors in silicon (not to scale) showing the allowed transitions between the  $1s(A_1)$  state and the stress-split sublevels of  $np_0$  and  $np_{\pm 1}$  for  $F // [100]$ . In the high-stress limit, the stress dependence of the  $1s(A_1)$ ,  $np_0(A_1 + B_2)$  and  $np_{\pm 1}(2E)$  are the same so that the transitions between these states are stress-independent (after [123]). Reproduced with permission from the Institute of Physics

The selection rules for transitions between the  $1s(A_1)$  state and the stress-split sublevels can be deduced from group theory when one knows the IRs under which the components of the dipole moment (actually,  $x$ ,  $y$ , and  $z$ ) transform. As an example, Fig. 8.3 shows the polarization features of the allowed transitions from the  $1s(A_1)$  state for  $F // [100]$  in silicon. The splitting under stress of the  $1s(T_2)$  donor level in silicon is the same as those of the  $np_0$  and  $np_{\pm 1}$  levels shown in this figure. For  $F // [100]$ , the highest- and lowest-energy

components of  $1s(T_2)$  have symmetries  $B_2$  and  $E$ , respectively, and when the  $1s(B_2)$  level is thermally populated, the energies of the  $1s(B_2) \rightarrow np_{\pm 1}(-)$  transitions are stress-independent.

The polarization rules are deduced from the fact that the dipole moments for  $np_0$  transitions associated with a given valley orientation are along the valley principal axis while for  $np_{\pm 1}$  transitions, they are in a plane perpendicular to this axis. The two components of the  $np_{\pm 1}$  lines are observed for  $\mathbf{E} \perp \mathbf{F}$  while only the transition to the h-e component of the  $np_0$  lines is observed for the same polarization. These symmetry-deduced polarization rules are confirmed by experiment as seen from Fig. 8.4.

The ground state level of the  $\text{Li}_i$  donor in silicon is  $1s(T_2)$ , instead of  $1s(A_1)$  for the shallow substitutional donors (see Table 6.5). Under stress, the  $1s(T_2)$  level splits like the  $np_0$  and  $np_{\pm}$  levels, and the transitions involving this level are not shifted by stress. Shifted transitions are, however, observed in the  $\text{Li}_i$  spectrum, and they are due to one of the components of the stress-split  $1s(E)$  level at LHeT [68]. Piezospectroscopic results have been obtained for the  $(\text{Li},\text{O})$  complexes A and D, and they indicate that these centres have symmetry axes along  $[100]$ ,  $[010]$ , and  $[001]$  directions [68].

It has been pointed out in Sect. 6.2.1 that the near resonance with lattice phonons of the  $2p_0$  line of Bi in silicon produced an anomalous broadening of that line, shown in Fig. 6.3. The strength of this interaction can be changed by a uniaxial stress which tunes the separation between the phonon frequency and

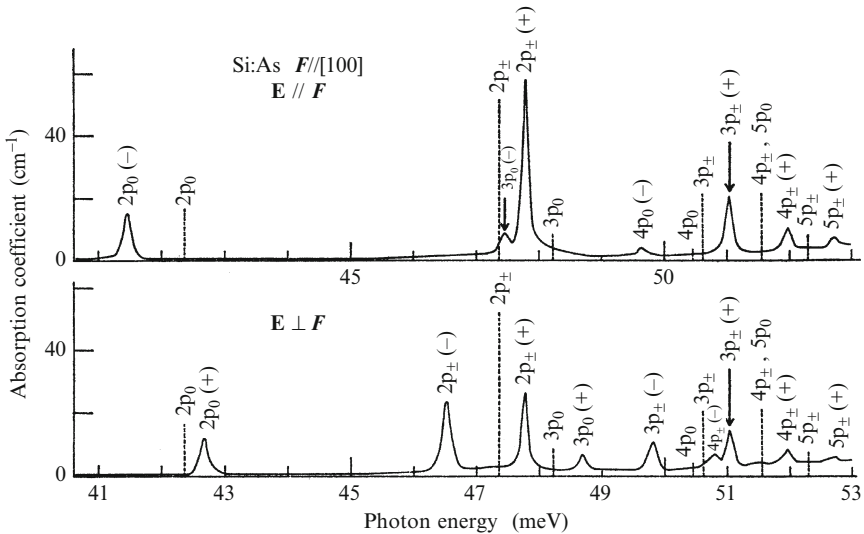


**Fig. 8.4.** Effect of a uniaxial stress along the  $[100]$  axis of a Si:As sample with  $n \sim 3 \times 10^{15} \text{ cm}^{-3}$  on its LHeT absorption spectrum. The propagation vector  $\mathbf{k}$  of the radiation is parallel to  $[011]$ . The dotted lines are the zero-stress positions (after [123]). The estimated stress magnitude is 15 MPa. Reproduced with permission from the Institute of Physics

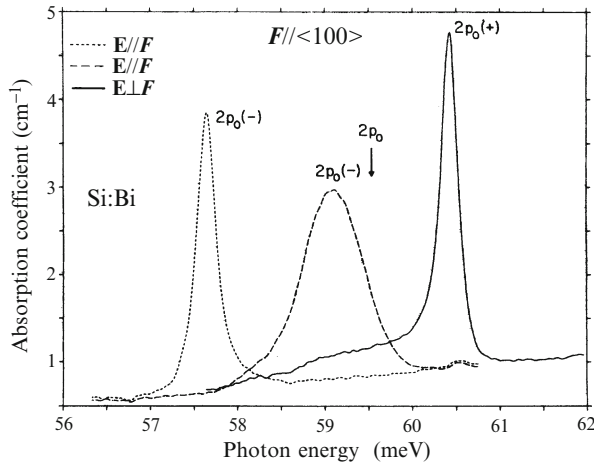


**Fig. 8.5.** Change with stress of the LHeT absorption profile of the  $2p_0$  line of Bi in silicon for  $\mathbf{F} // <100>$ . The *solid* and *dotted* lines are for a stress of 29.6 MPa and the *dashed* line for a stress of 4.7 MPa. For each polarization, only one component is observed (Table 8.4). The zero stress position is indicated by an *arrow* (after [29])

the  $2p_0$  components. The experimental results of [29] show that for sufficiently high stresses, the FWHMs of the  $2p_0(+)$  and  $2p_0(-)$  components are reduced as illustrated in Fig. 8.5. The profile of the low-stress component of Fig. 8.5 (dashed line) is rather symmetric and broad, with a FWHM of 0.85 meV. This is assumed to occur from near coincidence (at 59.1 meV) between the electronic transitions and the  $f\text{TO}(S_1)$  phonon mode. Modelling of this kind of interaction has been investigated by Harris and Prohofsky [56], and by Rodriguez and Schultz [127], and a reasonable fit of the spectroscopic results for the  $2p_0$  line can be obtained. From a simple physical point of view, the broadening of the electronic line can be explained by a drastic reduction of the lifetime of its excited state through an efficient decay via the inter-valley phonon. It is interesting to note that it is also possible to use stress to bring together the  $3p_0(-)$  or  $2p_{\pm 1}(-)$  components of the Bi spectrum and the phonon mode, but then no conspicuous broadening is observed [29].

The selection and polarization rules for the  $np$  donor transitions from the  $1s(A_1)$  state in germanium for a stress along  $<111>$  are given in Fig. 8.6. Here, due the different valley group symmetry and stress orientation, the selection rules differ from those in silicon and one more component is observed for  $\mathbf{E} // \mathbf{F}$ .

The stress splitting of the Sb donor lines in germanium has also been studied in the high-stress limit (HSL) by Baker and Fisher [8]. In this limit, due to thermalization and changes in the relative intensities, the transitions from  $1s(A_1)$  to  $np_0(-)$  (and  $nf_0(-)$ ) of Fig. 8.6 are predominant. They are denoted  $np_0^{(1)}(-)(\infty)$  in this reference and a high-resolution spectrum of Ge:Sb taken

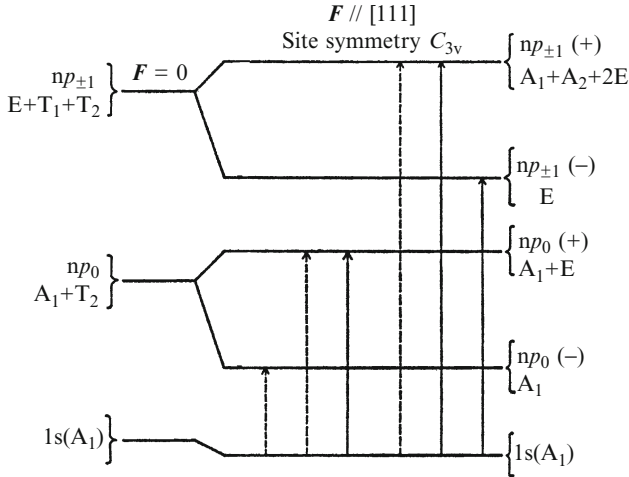


**Fig. 8.6.** Energy levels of donors in germanium (not to scale) showing the allowed transitions between the  $1s(A_1)$  state and the stress-split sublevels of  $np_0$  and  $np_{\pm 1}$  for  $F // [111]$ . The *dashed* and *full* arrows are for  $\mathbf{E}$  parallel and perpendicular to  $\mathbf{F}$ , respectively (after [125]). Copyright 1965 by the American Physical Society

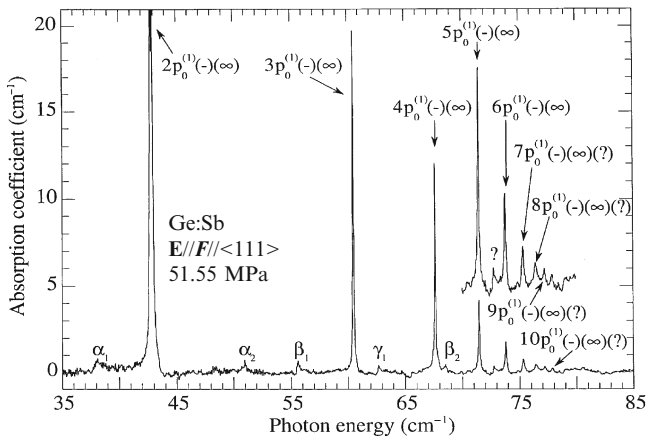


**Fig. 8.7.** Effect of a uniaxial stress of 50.88 MPa parallel to the  $[111]$  axis on the LHeT absorption spectrum between 4.3 and 10.5 meV of a Ge:Sb sample (spectral resolution:  $0.072 \text{ cm}^{-1}$  or  $9 \mu\text{eV}$ ). The *small lines* denoted by *greek letters*, while very probably linked to Sb, have not been further investigated. Reproduced from [8]. Copyright 1996, with permission from Elsevier

in the HSL is shown in Fig. 8.7 (it can be compared with that of Fig. 6.9, taken at zero stress). The value of the stress for this spectrum is such that the ratio of the extrapolated  $np$  stress splitting into the valley-orbit splitting of Sb at zero stress is 17.3 and this justifies the HSL condition.

In the stress studies involving the ( $1sA_1$ ),  $1s(T_2)$  doublet in germanium, one considers a centre of gravity located between the singlet and triplet states, separated from  $1s(A_1)$  by  $3\Delta_c$  and from  $1s(T_2)$  by  $\Delta_c$ . In the HSL, the stress shift coefficient of the  $1s(A_1)$  state with respect to the centre of gravity is  $-\Xi_u TS_{44}/3$ . This is precisely the same stress shift coefficient as the one of the  $np(-)$  states with respect to the  $np$  zero-stress positions. Thus, the zero-field positions of the  $np(-)$  lines can be obtained by adding  $3\Delta_c$  to the positions of the  $np(-)(\infty)$  lines. For the  $2p_0$ ,  $3p_0$ , and  $4p_0$  transitions, there is a very good agreement between the values of Table 6.7 measured at zero field and those deduced from the high-stress spectrum (in the paper by Baker and Fisher [8], the lines identified as  $5p_0$ ,  $6p_0$ ,  $7p_0$ ,  $8p_0$  and  $9p_0$  correspond in fact, to  $4f_0$ ,  $5p_0$ ,  $6p_0$ ,  $6f_0$ , and  $6h_0$ , respectively) using the Faulkner's nomenclature of Table 5.5 for the EM levels. This is an impressive result made possible only by piezoabsorption in the HSL as beyond the  $4p_0$  line, the corresponding zero-field transitions are too weak to be observed. Such measurements with other group-V donors with larger valley-orbit splitting require stresses about one order of magnitude larger to reach the HSL and the germanium matrix may become too fragile.

The above-described piezospectroscopic measurements have led to a better understanding of the shallow donors. They have shown that the values of the shear deformation potential  $\Xi_u$  of 8.8 and 16.4 eV for silicon and germanium, respectively, determined spectroscopically at LHeT for electrons bound to shallow donors [123] agree well with the values of 8.6 eV [92] obtained for  $CB$  electrons by wavelength modulation methods under stress, and of 16.4 eV at LNT obtained from the piezoresistance measurements [11]. Recently, the RT measurement of the hydrostatic DP  $\Xi_d$ , which cannot be obtained from the above-described piezospectroscopic measurement, and of  $\Xi_u$ , have been reported in both silicon and germanium [36, 100]. These quantities were determined from the change in the gate tunnelling currents in Si- and Ge-metal oxide semiconductor field effect transistors (MOSFETs) under a uniaxial mechanical stress. For silicon and germanium,  $\Xi_d$  was found to be  $1.0 \pm 0.1$  and  $-4.3 \pm 0.3$  eV, respectively, and  $\Xi_u$  to be  $9.6 \pm 1.0$  and  $16.5 \pm 0.5$  eV, respectively.

Spectroscopic measurements on silicon and germanium samples through optical surfaces, symmetrically abraded with slurries containing  $15\text{ }\mu\text{m}$   $Al_2O_3$  or #400 grit ( $22\text{ }\mu\text{m}$  average) SiC particles, have revealed the existence of a uniaxial compressive stress perpendicular to the abraded optical surfaces [45], and the magnitude of the stress is inversely proportional to the sample thickness. For a 1 mm-thick silicon monocrystalline sample where the  $\langle 100 \rangle$  axis is perpendicular to the optical surface, the uniaxial stress obtained after abrasion with a  $15\text{ }\mu\text{m}$   $Al_2O_3$  slurry is estimated to be 1 MPa from the splitting of the  $2p_{\pm 1}$  (P) line.

The response to stress of the deep chalcogen-related donors in silicon shows some differences due to the large separation of the deepest  $1s$  state from the other EM-like  $1s$  states, and also to the introduction of degeneracy of the chalcogen pairs, discussed in the following section.

*Isolated Chalcogen Donors in Silicon*

The results presented here are adapted from a detailed investigation of the stress splitting of some S- and Se-related donors in silicon [14]. At a difference with the centres considered in the preceding section, the separation between the  $1s$  ground state and the EM-like  $1s$  states of the deep donors precludes a stress-induced interaction between these states. The experimentally-observed shift rate with stress of a transition is the difference between the shift rates of the excited (e) and ground (g) states, defined by the invariant operators  $V_{A_1} = \frac{1}{\sqrt{3}}(V_{xx} + V_{yy} + V_{zz})$  which, for degenerate excited states, affect only their centre of gravity. The transition stress parameter  $A_1$  is defined as:

$$A_1 = \frac{1}{\sqrt{3}} (\langle e | V_{A_1} | e \rangle - \langle g | V_{A_1} | g \rangle).$$

It can be shown that for a non-EM ground state, the shift in energy relative to the centre of gravity of the  $CB$  is proportional to the stress and is given by  $A_1 (S_{11} + 2S_{12})T$  for a compressive stress and this is the situation for the  $1s(A_1)$  state, whatever the orientation.

The  $1s(E)$  and  $1s(T_2)$  states of an isolated neutral Ch atom in silicon split linearly with stress into two components as indicated in Table 8.5.

The stress-dependence of the components of transitions from the ground state to the higher excited states of  $S^0$  is shown in Fig. 8.8. One can note the linear slope with stress, which differs from that of Fig. 8.2a. This is due to the linear shift with stress of the ground state in the  $S^0$  spectrum. The positive shift with stress of the ground state is evidenced by the negative slope of the line positions for  $\mathbf{F} // [111]$ .

Similar results have been obtained for  $Se^0$ . Figure 8.9 shows the stress splitting of the  $1s(T_2)$  line of  $Se^0$  for different stress orientations. This line, accompanied by the weaker spin triplet  $1s(^3T_2)$  line, is shown at LHeT in Fig. 6.15 in an unstressed silicon sample. It is interesting to see from Fig. 8.9

**Table 8.5.** Shift  $\delta E$  with respect to zero-stress positions of the  $1s(T_2)$  and  $1s(E)$  states of deep donors in silicon for compressive stresses along the  $[100]$  and  $[110]$  axes (units of  $\Xi_u T (S_{11} - S_{12})/3$ ). The components are labelled by the  $IRs$  of the appropriate site symmetry group. When crossing, components of the same symmetry may interact. This can occur with the  $1s(A_1)$  components of the  $1s(T_2)$  and  $1s(E)$  for  $\mathbf{F} // [110]$  as the former is deeper than the latter (after [14])

| $T_d$     | $\mathbf{F} // [100] (D_{2d})$ | $\delta E$ | $\mathbf{F} // [110] (C_{2v})$ | $\delta E$ |
|-----------|--------------------------------|------------|--------------------------------|------------|
| $1s(E)$   | $1s(B_1)$                      | +1         | $1s(A_1)$                      | +1/2       |
|           | $1s(A_1)$                      | -1         | $1s(A_2)$                      | -1/2       |
| $1s(T_2)$ | $1s(E)$                        | +1         | $1s(A_1)$                      | +1         |
|           | $1s(B_2)$                      | -2         | $1s(B_1 + B_2)$                | -1/2       |



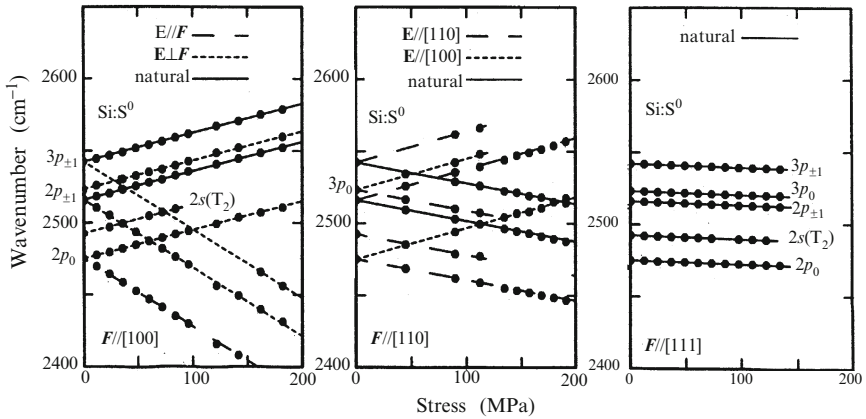


**Fig. 8.8.** Stress dependence of transitions from the ground state to excited states of  $S^0$  in silicon at LHeT. The *lines* are drawn using parameters obtained to fit the  $1s(A_1) \rightarrow 2p_{\pm 1}$  transition. The label “natural” corresponds to the unpolarized radiation. The spectral range is 297.6–328.6 meV (after [14]). Copyright 1989 by the American Physical Society

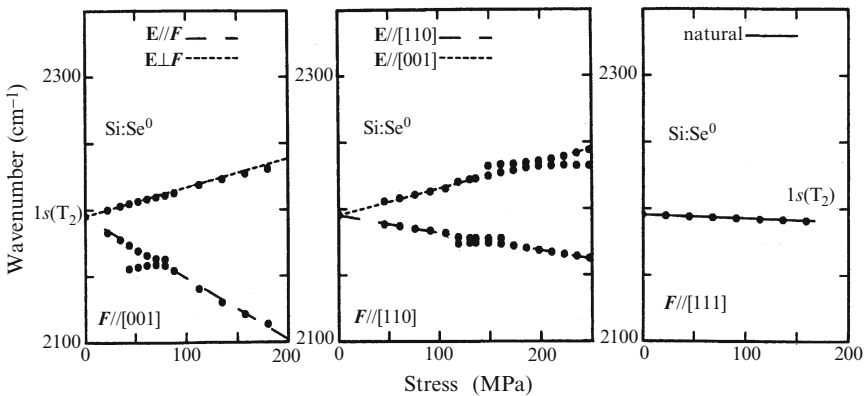


**Fig. 8.9.** Stress dependence of line  $1s(T_2)$  of  $Se^0$  in silicon at LHeT. The *lines* are drawn using parameters obtained to fit the  $1s(A_1) \rightarrow 2p_{\pm 1}$  transition. For  $F//[110]$ , the anti-crossing of the h-e component of  $1s(T_2)$  near 200 MPa is due to its interaction with the h-e component of the  $1s(E)$  level, undetectable at zero stress. The anti-crossing on the low-energy component is due to s-o interaction with the h-e component of the  $1s(^3T_2)$  line located at  $2146.4 \text{ cm}^{-1}$  at zero stress. The spectral range is 260.4–291.4 meV [14]. Copyright 1989 by the American Physical Society

that the low-energy component of  $1s(T_2)$  interacts with the h-e component of the  $1s(^3T_2)$  line and this anti-crossing (or avoided crossing) is attributed to the s-o interaction. This interaction is too small for  $S^0$  and no anti-crossing is observed.

Figure 8.9 shows for  $\mathbf{F} // [110]$ , the anti-crossing of the h-e component of  $1s(T_2)$  ( $\text{Se}^0$ ) with the h-e component of  $1s(E)$  as these components have the same symmetry (see Table 8.5). This interaction allows one to extrapolate the position of the  $1s(E)$  component at zero stress to 2.1 meV ( $\sim 25 \text{ cm}^{-1}$ ) above the  $1s(T_2)$  line and to obtain a value of the position of this symmetry- and parity-forbidden line in good agreement with the one deduced from the Fano resonances [14].

The stress dependences of the transitions from the ground state to the higher excited states of  $\text{S}^+$  and  $\text{Se}^+$  are similar to those shown in Fig. 8.8, and they can be fitted with values of  $\Xi_u$  and  $A_1$  comparable to those obtained for the neutral charge state. The shift under increasing stresses of lines corresponding to the higher excited states of  $\text{Se}^+$  in silicon can be appreciated in the transmission spectra of Fig. 8.10, which are representative of the line splitting of the higher excited states of donors in silicon. In this particular case, it can be seen that the homogeneity of the stress field is good as the widths of the components do not increase substantially with stress.

The  $1s(T_2)$  state of  $\text{S}^+$  and  $\text{Se}^+$  is split by spin-orbit interaction into  $1s\Gamma_7$  and  $1s\Gamma_8$  and the electronic IS of these components has been discussed in Sect. 6.3.1.2. The splitting under stress of this doublet for  $\text{S}^+$  is shown in Fig. 8.11 and it is in contrast with the linear dependences displayed in the preceding figures. Here, the s-o interaction is combined with the stress effects and it cannot be treated in the simple DPA. A discussion of the resultant stress splitting of this doublet is given by Bergman et al. [14].

The net result derived from Fig. 8.11 is the splitting of the  $1s(\Gamma_8)$  level into two components and a reduction of the amplitude of the splitting with respect to the simple DPA, whose expected effects are shown as lighter dashed lines in the figure. A quadratic *ad hoc* term is included in the numerical fit, but it is attributed to a nonlinearity of the interactions rather than to quadratic stress effects.

### *Chalcogen Donor Pairs in Silicon*

Up to now, the centres considered in this chapter were isolated atoms with cubic symmetry, but it has been seen in Chap. 6 that there exists many other donor centres with non-cubic symmetry. These centres, with symmetries lower than cubic, present an orientational degeneracy in addition to the electronic degeneracies related to their atomic structure. The effect of a uniaxial stress on their spectroscopic properties depends also on this additional degeneracy so that it cannot be treated as a whole. The general piezospectroscopic properties of non-cubic centres in cubic crystals have been discussed by Kaplyanskii [73].

Among the chalcogen-related centres in silicon, the chalcogen pairs ( $\text{Ch}_2$ ) are well-characterized by electronic spectroscopy and ESR, and their atomic and electronic structures are well-established. The ESR results have shown that in silicon, they are oriented along a  $\langle 111 \rangle$  crystal axis and their site symmetry is, therefore,  $D_{2d}$  when the two Ch atoms are the same and  $C_{3v}$

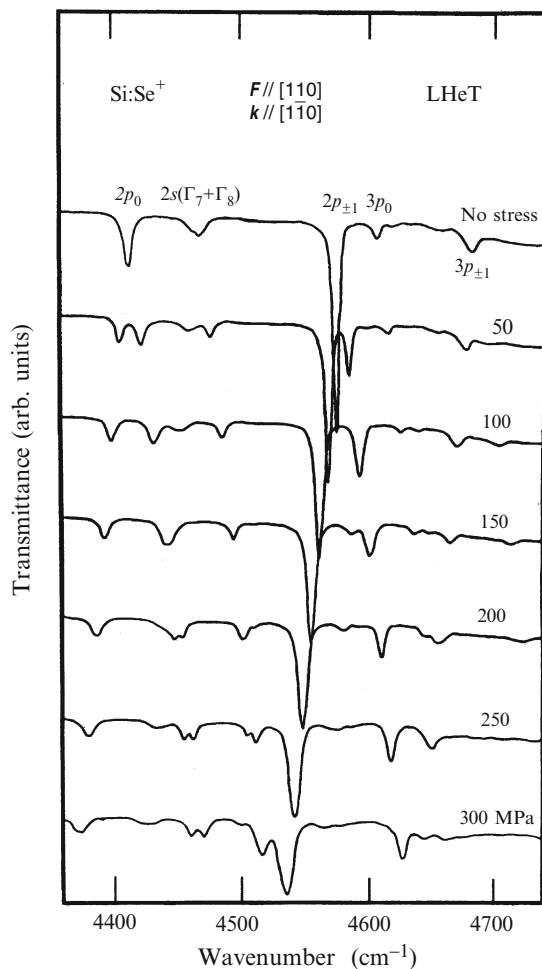


**Fig. 8.10.** Transmission spectra of Se<sup>+</sup> in silicon showing the splitting with increasing stresses of the first  $np$  lines and of the  $2s$  line. The components remain reasonably sharp even for a stress of 300 MPa for which the splitting is of the order of  $100\text{ cm}^{-1}$  or  $12.4\text{ meV}$ . The spectral range is  $541.8\text{--}586.5\text{ meV}$  [14]. Copyright 1989 by the American Physical Society

when different. Piezospectroscopic measurements have been performed on S<sub>2</sub> and Se<sub>2</sub> in the neutral and singly-ionized charge states [14] and the most salient features are presented here.

The effect of stress on the transitions from the deep ground state to EM excited states can be seen as the superposition of a DP contribution similar to the one for the cubic centres and of a ground-state contribution due to orientational degeneracy, characterized by a transition stress parameter  $\mathbf{A}_2$ . The combined shift and splitting of the ground state of a deep donor centre

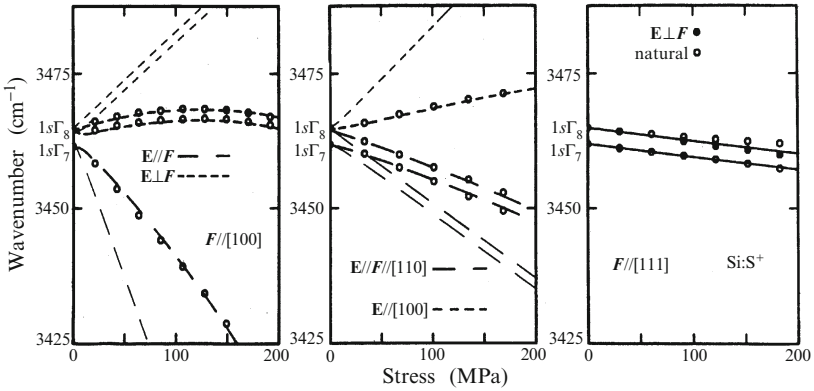


**Fig. 8.11.** Stress splitting of the  $1s\Gamma_7$  and  $1s\Gamma_8$  lines of  $S^+$  in silicon at LHeT. The darker lines are obtained from a numerical fit. The lighter lines correspond to the stress dependence expected from the DPA. The spectral range is 424.6–432.7 meV [14]. Copyright 1989 by the American Physical Society

**Table 8.6.** Effect of a compressive stress on the ground state of deep centres with site symmetries  $C_{3v}$  or  $D_{3d}$ , with an orientational degeneracy of 4 [14]

| Stress direction | Relative intensity | Energy shift                                        |
|------------------|--------------------|-----------------------------------------------------|
| [100]            | 4                  | $A_1 (S_{11} + 2S_{12}) T$                          |
| [110]            | 2                  | $[A_1 (S_{11} + 2S_{12}) + \frac{1}{2}A_2S_{44}] T$ |
|                  | 2                  | $[A_1 (S_{11} + 2S_{12}) - \frac{1}{2}A_2S_{44}] T$ |
| [111]            | 1                  | $[A_1 (S_{11} + 2S_{12}) + A_2S_{44}] T$            |
|                  | 4                  | $[A_1 (S_{11} + 2S_{12}) - \frac{1}{3}A_2S_{44}] T$ |

with orientational degeneracy (we insist on the fact that the effects of these combined contributions are observed only if the ground state of the centre is non-EM like) are given in Table 8.6. For silicon, the value of  $S_{11} + 2S_{12}$  deduced from Table 8.1 is  $3.41 \times 10^{-3} \text{ GPa}^{-1}$ .

It must be borne in mind that the splitting of the ground state given in Table 8.5 is some kind of built-in splitting due to the combination of stress and defect anisotropy such that no thermalization effect is expected for the deep ground states to which this effect applies.

There is practically no difference between the isolated chalcogen-donor and chalcogen-pair spectra for a stress along [100] as the four orientations of the pairs are equivalent with respect to that direction, but the existence of two families of the pairs with different ground-state energies for  $F//$  [110] and  $F//$  [111] produces for the  $np$  lines twice more split components than for the isolated chalcogens with  $T_d$  symmetry, as can be seen in Fig. 8.12 for  $S_2^0$ .

Numerical fits to the  $2p_{\pm 1}$  splitting of the neutral pairs give for  $\Xi_u$  values similar to those for isolated shallow and deep donors and for  $A_1$  and  $A_2$  values

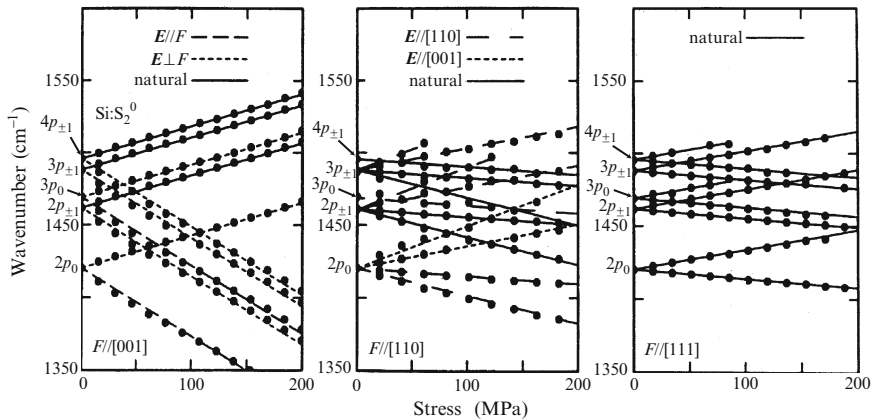


**Fig. 8.12.** Stress dependence of transitions from the ground state to the higher excited states of  $S_2^0$  in silicon at LHeT. Additional splitting with respect to Fig. 8.8 is due to the lifting of orientational degeneracy. The *lines* are drawn using parameters obtained to fit the  $1s(A_1) \rightarrow 2p_{\pm 1}$  transition. The label “natural” corresponds to the unpolarized radiation. The spectral range is 167.4–198.4 meV (after [14]). Copyright 1989 by the American Physical Society

of 0.44 (0.55) and  $-1.5(-1.5)$  eV for  $S_2^0$  ( $Se_2^0$ ), respectively. For  $F// [111]$ , the fit shows that the components with the positive slope are due to the pairs parallel to the stress.

Symmetry-allowed transitions are observed between the  $1s(A_1^+)$  ground state and the  $1s(E^-)$  and  $1s(A_1^-)$  states of the donor pairs (see Fig. 6.14). For  $F// [100]$ , the  $1s(E^-)$  line is expected to split into two components while the  $1s(A_1^-)$  line is merely shifted, and this allowed to establish the ordering of the two levels ([87] and references therein). The results of [14] confirm the point and they show some nonlinear effects due to interactions between sublevels.

The splitting under stress of the first lines of the  $S_2^+$  spectrum is qualitatively similar to that of  $S_2^0$ , but the behaviour of the  $2p_0$  zero-stress doublet confirms that the zero-stress splitting of the  $Ch_2$  pair spectra (see Fig. 6.14 for the one of  $Se_2^0$ ) is due to the non-symmetric central cell potential due to the atomic structure of the pair.

The DLTS measurement of the uniaxial-stress dependence of the electron emission rates of the  $S^0$  and  $S^+$  ground states have allowed determination of the shear DP  $\Xi_u$  associated with these centres, and values in the 10.7–11.6 eV range have been obtained for temperatures between 150 and 220 K [99].

### *Oxygen Thermal Donors in Silicon*

The electronic absorption of the O-related thermal double donors (TDDs) in silicon has been discussed in Sect. 6.4.1.1. The absorption spectra under stress of the first TDD $^0$ s ( $2p_0$  and  $2p_{\pm 1}$  lines) are rather puzzling at first sight [137]. They are characterized by the absence of splitting of the lines for  $F//$

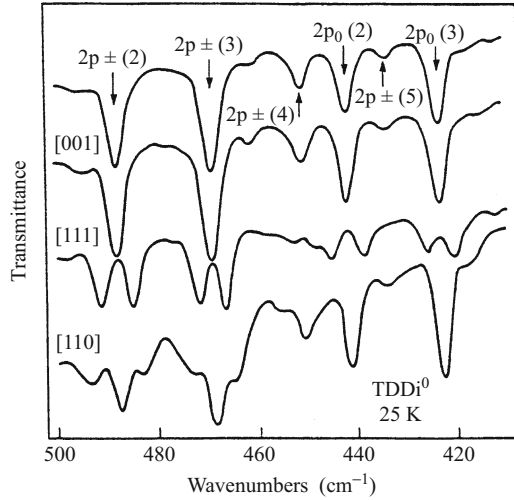


**Fig. 8.13.** Absorption spectrum of the first  $\text{TDDi}^0$  in silicon at 25 K. The upper spectrum is measured at zero stress. For the others, a stress of  $\sim 195$  MPa is applied along the direction indicated. For the [110] stress, the radiation propagates along [001]. The values of  $i$  indicated in parentheses are those of Table 6.23. The spectral range is 62–51 meV (after [137]). Copyright 1985 by the American Physical Society

[100] and by a small splitting for  $\mathbf{F} // [111]$ . For  $\mathbf{F} // [110]$ , the  $2p_0$  lines show no splitting and the  $2p_{\pm 1}$  lines give a triplet. This situation is depicted in Fig. 8.13.

Splitting of the donor lines for  $\mathbf{F} // [111]$  has been associated with orientational degeneracy for the Ch donor pairs and the same origin is assumed for the TDDs. The absence of splitting for  $\mathbf{F} // [100]$  could be understood for a centre with  $T_d$  symmetry with a  $1s(T_2)$  ground state as this state presents the same splitting as the  $np$  states. For donors in silicon, this situation is met for  $\text{Li}_i$ , but a  $1s(E)$  state is close to this ground state so that the observed splitting for  $\text{Li}_i$  results from a combination of transitions from sublevels of these two states [68]. An important point is that equal ground and excited state splitting are preserved for symmetries lower than  $T_d$  for a ground state constructed from wave functions associated with a pair of  $CB$  valleys along the same direction in  $k$ -space [135], and this fundamental assumption is made to explain the piezospectroscopic data on TDDs.

Figure 8.14a shows a level diagram of the allowed transitions from a  $1s(T_2)$  ground state to  $np$  states for  $\mathbf{F} // [100]$ . It shows that for  $\mathbf{E} // \mathbf{F}$ , the only transitions allowed are  $1s(-) \rightarrow 2p_0(-)$  and  $1s(+) \rightarrow 2p_{\pm 1}(+)$ .

The piezospectroscopic measurements of the  $\text{TDD}^0$ s with polarized radiation are particularly instructive. Spectra obtained at 20 and 65 K for  $\mathbf{F} // [100]$  and  $\mathbf{E} // \mathbf{F}$  are compared in Fig. 8.15.

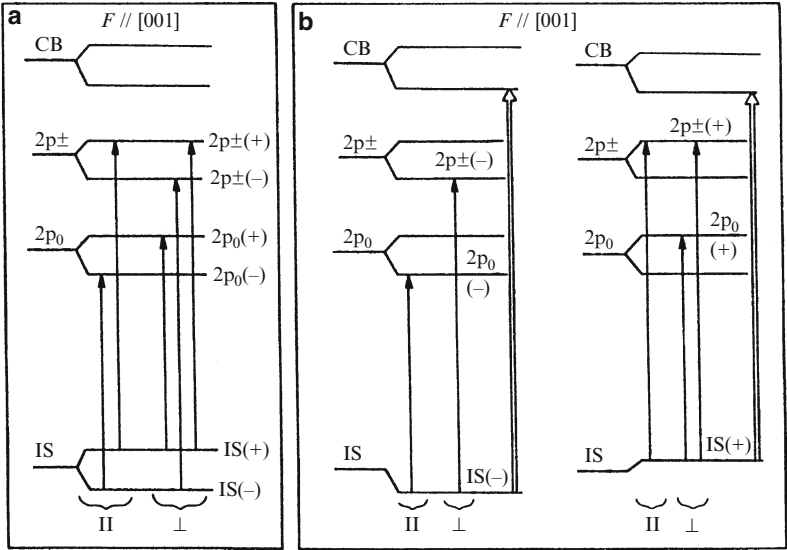


**Fig. 8.14.** (a) Energy level diagram of the transitions from a  $1s$  ( $T_2$ ) donor level of a donor at a  $T_d$  site in silicon for  $F // [100]$ . Allowed transitions for each polarization are indicated. (b) Energy level diagram for the two orientationally degenerate configurations of a donor in silicon with a ground state constructed from a single pair of CB valleys when this degeneracy is lifted for  $\sigma // [100]$ . Double-lined arrows denote thermal ionization transitions (after [137]). Copyright 1985 by the American Physical Society

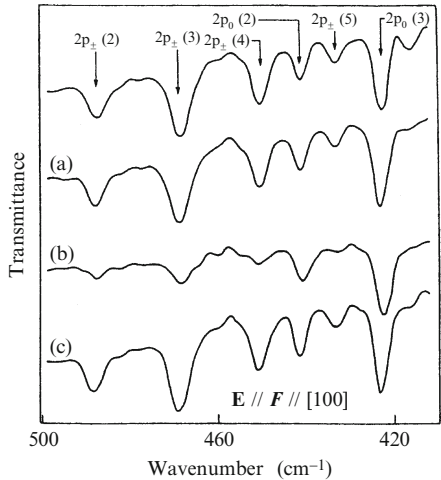


**Fig. 8.15.** Absorption spectrum of the first TDD $^0_i$  in silicon for  $F // [100]$  and  $E // F$ . Upper spectrum measured at 20 K at zero stress. Spectrum (a) measured at 20 K with a stress of 196 MPa, spectrum, (b) at 65 K with stress applied during the temperature raise from 20 K, and spectrum, (c) after cooling-down the sample from 65 to 20 K with the stress maintained. The values of  $i$  indicated in parentheses are those of Table 6.23. The spectral range is 62–51 meV (after [135])

The 65 K spectrum shows no difference with the 20 K spectrum for the  $np_0$  lines, but a decrease in the intensity of the  $np_{\pm 1}$  lines is observed. For a spectrum corresponding to the energy level diagram of Fig. 8.14a, one would expect the inverse because of the thermalization of the population of  $1s(-)$  into  $1s(+)$  (in silicon, the EM  $1s(T_2)$  and  $np$  levels are split by  $\sim 17$  meV ( $\sim 140$  cm $^{-1}$ ) for a stress of 196 MPa parallel to  $[100]$ ). However, for orientationally degenerate donors, there are two families of TDDs with respect to stress: with the conventions of Fig. 8.1 and Table 8.2, the force is oriented along valleys 1 and 2 and the TDDs associated with these valleys<sup>2</sup> correspond to level  $1s(-)$  in Fig. 8.14b while those associated with valleys 3, 4, 5, and 6 correspond to level  $1s(+)$ . Thermalization is thus impossible between  $1s(-)$  and  $1s(+)$ , which correspond to physically distinct centres, and this explains why the  $1s(-)$  level does not depopulate when temperature is raised. Inversely,  $1s(+)$  comes nearer from the  $CB$  and starts depopulating. More insight into the symmetry of the TDDs comes from the existence of a small splitting of the lines for  $\mathbf{F} // [111]$ : this obviously rules out a  $\langle 100 \rangle$  symmetry for the TDDs as in this case no splitting is expected for the stress orientation.

If it is assumed that the TDDs are oriented preferentially along a  $\langle 110 \rangle$  axis, with a  $C_{2v}$  site symmetry, the piezospectroscopic results can be explained satisfactorily on the basis of the stress-induced line shifts and polarizations calculated by Kaplyanskii [73], which are discussed in the next section. This led to propose the  $C_{2v}$  site symmetry for the TDDs in silicon [137]. In expression (8.15), the non-zero components of the piezospectroscopic tensor for  $C_{2v}$  centres, labelled as orthorhombic (or rhombic) I, are  $A_{xx}(A_2)$ ,  $A_{yy}(A_2)$ ,  $A_{zz}(A_1)$  and  $A_{xy} = A_{yx}(A_3)$ . These orthorhombic I centres have a  $C_2$  symmetry axis in the  $\langle 100 \rangle$  direction and the  $1s \rightarrow 2p_0$  transitions have their transition dipole moment oriented along this axis for a  $1s$  state constructed from a pair of valleys along this axis, while the  $1s \rightarrow 2p_{\pm 1}$  transitions have their transition dipole moment oriented in a plane perpendicular to this axis. In a cubic crystal, a  $C_{2v}$  centre has a sixfold orientational degeneracy represented by the six diagonals of a cube (see Fig. 8.16a).

With the notations of this figure, for a stress along  $[110]$ , the shifts  $\Delta_A$ ,  $\Delta_B$ , and  $\Delta_C$  obtained from Table 3 of [73] are  $(A_1 + A_2)/2$ ,  $A_2 - A_3$ , and  $A_2 + A_3$ , respectively. When radiation propagates with  $\mathbf{k} // [001]$ , only subset A contributes to the  $2p_0$  lines while the three subsets contribute to the  $2p_{\pm 1}$  lines. From these results, it can also be inferred that  $A_1$  and  $A_2$  are close to zero. The order of magnitude of  $A_3$  is 3.7 meV GPa $^{-1}$ , the value measured for TDD2<sup>0</sup>.

Uniaxial stress measurements have also been performed on the TDDi<sup>+</sup> and they confirm the conclusions drawn from the results on the TDDi<sup>0</sup> [134]. A detailed presentation of the results on the TDDi<sup>+</sup> is given in this reference. It also provides an interpretation of the observed zero-stress splitting of the  $np_{\pm 1}$

<sup>2</sup> This does not mean that the TDDs are oriented along the  $\langle 100 \rangle$  axes.



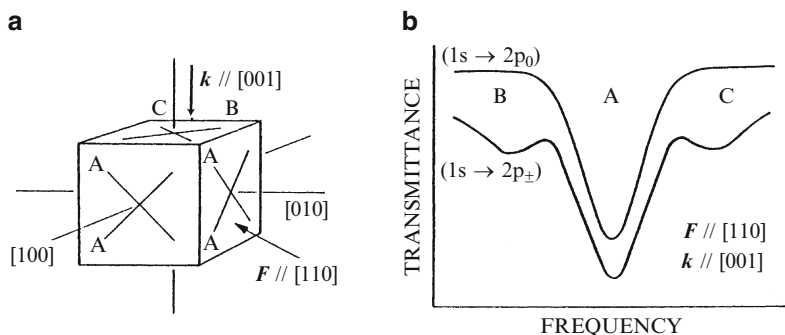


**Fig. 8.16.** (a) The set of  $C_{2v}$  centres in a cubic crystal, represented by the diagonals of a cube with edges along  $\langle 100 \rangle$  direction. For a stress along  $[110]$ , this set divides into three inequivalent subsets A, B, and C. As shown in (b), when radiation propagates with  $\mathbf{k} // [001]$ , there is no contribution of subsets B and C to  $2p_0$  components because  $\mathbf{E}$  is perpendicular to the transition moments, but the three subsets contribute to the  $2p_{\pm 1}$  components (after [135])

lines of the  $TDDi^+$  spectra into two components, relabelled  $np_{\pm 1}^l$  and  $np_{\pm 1}^h$  in Table 6.25, and visible in Figs. 6.24 and 6.25. It is based on the following: to explain the respective splitting of the  $2p_0$  and  $2p_{\pm 1}$  lines in samples stressed along a  $[110]$  direction, it has been stated that the transition dipole moments for the  $np_{\pm 1}$  lines associated with the  $C_{2v}$  donor centres B and C in Fig. 8.16b lie in a (001) plane perpendicular to those for the  $np_0$  lines of these donors, and parallel to the  $[001]$  axis ( $C_2$  axis). Actually, for a given  $C_{2v}$  centre in the (001) plane (consider centre C along  $[110]$ ), the linear combinations of  $np_{\pm 1}$  orbitals rearrange to give  $np_{\pm 1}(\pi p \text{ contributions}^3$  along the main  $[110]$  axis of the centre and  $np_{\pm 1}(\pi')$  contributions along the perpendicular  $[1\bar{1}0]$  axis. For an ideal point-like centre, these two  $np_{\pm 1}$  levels are equivalent, but the directional stresses induced by the anisotropy of the TDDs lift this degeneracy. This effect repeats for the other orientations and the net result is a splitting of the  $np_{\pm 1}$  lines into  $np_{\pm 1}(\pi)$  and  $np_{\pm 1}(\pi')$  components, which is the origin of the effect observed at zero stress. The transition moment of the  $2p_0$  lines along the  $[001]$  axis has no spatial degeneracy and no zero-stress splitting of these lines is, therefore, observed.

The splitting under stress of the  $2p_{\pm 1}^l$  and  $2p_{\pm 1}^h$  components presents an interesting feature when observed for  $\sigma // [111]$  and  $\mathbf{E} // \sigma$ : starting from zero stress, these components are observed to merge with increasing stresses into an apparent single line for some value of the stress, and then to diverge above this value [134, 136]. This can be explained in the following manner: each set of  $np_{\pm 1}(\pi)$  and  $np_{\pm 1}(\pi')$  level is orientationally degenerate and for a stress along  $[111]$ , each level (and therefore each line) splits into a doublet corresponding to the two different TDD subsets. One component of each subset shifts to

<sup>3</sup> The notation  $\pi$  is chosen by analogy with the  $\pi$  orbitals in molecular spectroscopy.

lower energy and the other to higher energy so that two components of the two subsets must invariably cross for some stress value. It turns out that for  $\mathbf{E} // \sigma$ , the selection rules are such that only transitions from the two crossing components are allowed. As a consequence, for that polarization, the  $np_{\pm 1}^l$  and  $np_{\pm 1}^h$  merge with increasing stress into a single line and then diverge for larger stresses. The value of the crossing point depends of the TDD considered as the splitting between  $np_{\pm 1}^l$  and  $np_{\pm 1}^h$  is TDD-dependent (see Table 6.25). For  $\mathbf{E} \perp \sigma$ , the intensities of the crossing components are smaller than those of the outer components of each set. As the low-energy outer component shifts to lower energies and the h-e outer component to higher energies, divergence in energy with stress of the  $2p_{\pm 1}$  doublet is observed at the onset of stress application for that polarization [134].

We have mentioned in Chap. 6 that the  $\text{TDDi}^+$  were paramagnetic. As there are several different TDD species, one would expect ESR spectra related to these different centres, but the Si-NL8 ESR spectrum of the  $\text{TDDi}^+$  displayed in Fig. 8.17(a) shows only two main lines. The observation of only two ESR lines is attributed to the small anisotropy of the  $g$ -factor of these centres with respect to the free electron  $g$ -factor, which reduces the magnetic field expansion of the ESR signal. Figure 8.17b shows the angular dependence of this ESR spectrum for a rotation of the magnetic field in a (110) plane [105]. This angular dependence indicates that the  $\text{TDD}^+$ s must be oriented along  $\langle 110 \rangle$  axes, corresponding to six different directions and that, as a consequence, they must have a  $C_{2v}$  symmetry.

ESR measurements of the Si-NL8 spectrum have been made under uniaxial stress and they show population effects consistent with the orientational

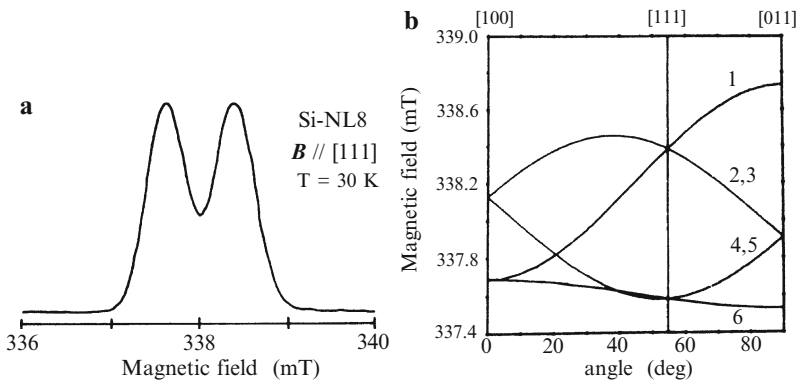


**Fig. 8.17.** (a) ESR absorption of the NL8 spectrum of the  $\text{TDD}^+$ s in silicon at 30 K in a p-type CZ silicon sample with  $[B] > 10^{15} \text{ cm}^{-3}$  annealed for 6 h at  $460^\circ\text{C}$  (ordinates of the ESR signal in arbitrary units). (b) Angular dependence of the  $\text{TDD}^+$ s ESR spectrum for a rotation of the magnetic field in a [110] plane. The integers denote the six  $C_{2v}$ -oriented donors (after [105]). Copyright 1989 by the American Physical Society

degeneracy of a  $C_{2v}$  centre, and they have indeed proved that the centres responsible for the NL8 spectrum were the  $TDD^+$ s [95].

DLTS measurements on Schottky structures containing  $TDD^+$ s show an electron emission peak vs temperature corresponding to an ionization energy of 0.15 eV, this corresponds to the emission from the first  $TDDi^+$  [80], as can be checked from a comparison with Table 6.23. The results of DLTS measurements on the  $TDD^+$ s under stress are consistent with the IR absorption measurement ([79] and references therein). From the DLTS principles, electronic reorientation between different orientations of the centres can occur through the  $CB$ , which is not possible directly in the absorption measurements. This allows determination of the ground state splitting, and a value of the shear DP  $\Xi_u$  of  $\sim 9$  eV is obtained, not far from 8.8 eV derived from the piezospectroscopic measurements [123].

In the above-described experiments, a uniaxial stress was used to change the electronic energy levels, but equipartition of the TDD concentrations among the different configurations was maintained. It is possible to modify this equipartition by maintaining the CZ silicon samples under stress during the TDD formation treatment and cooling it under stress to RT. In this case, one expects the TDDs to grow in configurations, minimizing their formation energies with respect to stress, producing a sample with TDD populations depending on the stress orientation with respect to TDD orientations. This has been performed for stresses applied along the [001] and [110] directions [146]. The result is shown for a stress along [001] in Fig. 8.18.

For an aligning stress along [001] at 460°C, the  $TDDi$  are formed preferentially in the (011) plane. The dipole moment for the  $2p_0$  line of the  $TDDi$

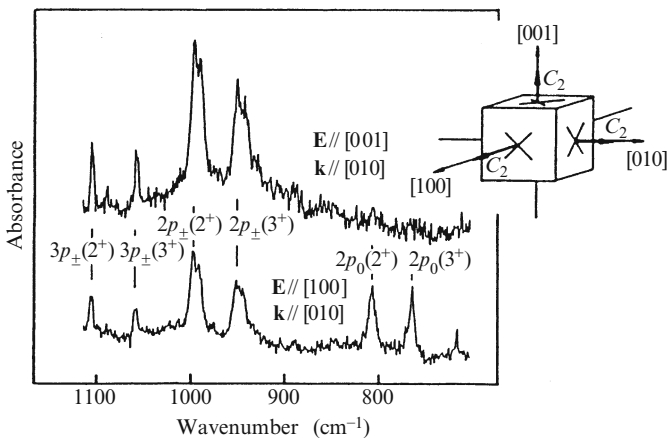


**Fig. 8.18.**  $TDDi^+$  absorption at LHeT in a CZ silicon sample annealed 110 min at 460°C under an aligning stress of 600 MPa along [001]. The  $C_2$  axes of the different orientations are indicated. The spectral range is 136.4–86.8 meV. See text. Reprinted with permission from [146]. (Copyright 1987, American Institute of Physics)

formed in this plane are along the valleys parallel to the  $[100]$  and  $[010]$  axes. Thus, for  $\mathbf{E} // [001]$ , there will be practically no contribution of  $2p_0$  in the spectrum, but the contribution of the  $np_{\pm 1}$  lines will be maximum. The inverse occurs for  $\mathbf{E} // [100]$ , but as the  $np_{\pm 1}$  lines are proportionally more intense than the  $2p_0$  lines, their intensities are reduced, but they remain clearly visible.

### 8.2.1.2 EM Acceptors

The EM acceptor levels are calculated from the  $VB$  parameters and, by analogy with the situation for EM donors, we consider first the splitting of the  $VB$  under a uniaxial stress. A stress along a  $\langle 100 \rangle$  or  $\langle 111 \rangle$  direction reduces the point group symmetry of the diamond structure to  $D_{4h}$  or  $D_{3d}$ , respectively. In the linear regime, the strain-induced part  $H'$  of the  $VB$  Hamiltonian corresponding to (8.1) can be written as [57]:

$$H' = D_d \sum_i \epsilon_{ii} + 2D_u \sum_i \epsilon_{ii} (I_i - 1/3 I^2) + 4D'_u \sum_{i < j} \epsilon_{ij} \{I_i I_j\}, \quad (8.12)$$

where  $I$  and  $I_i$  are the angular momentum matrices,  $D_d$  is the  $VB$  isotropic deformation potential (DP), and  $D_u$  and  $D'_u$  the uniaxial DPs, which are positive quantities defined by Kleiner and Roth [82] considering electrons. Bir et al. [16], and references therein, considering holes in the  $VB$ , have used an isotropic DP  $a$  equal to  $D_d$  and uniaxial DPs  $b$  and  $d$ , equal to  $-\frac{2}{3}D_u$  and  $-\frac{2}{\sqrt{3}}D'_u$ , respectively.<sup>4</sup> The  $a, b$  and  $d$  DPs are the only ones used now.

Under a stress of intensity  $T$ , defined as negative for compression, the  $\Gamma_8^+$  ( $J = 3/2$ )  $VB$  of silicon or germanium, taken as the energy origin, splits into an upper  $VB$  ( $m_J = \pm 1/2$ ) corresponding to the absolute  $VB$  maximum and a lower  $VB$  ( $m_J = \pm 3/2$ ). For a stress along  $[100]$ , the Bloch functions of the upper ( $m_J = \pm 1/2$ ) and lower ( $m_J = \pm 3/2$ )  $VB$ s transform as the  $\Gamma_6^+$  and  $\Gamma_7^+$  IRs of the  $D_{4h}$  group, and the energies  $E(\Gamma_7^+)$  and  $E(\Gamma_6^+)$  in the small stress regime are given by:

$$E_{\pm 1/2}(\Gamma_6^+) = \frac{2}{3}D_u(S_{11} - S_{12})T = -b(S_{11} - S_{12})T = -E_{\pm 3/2}(\Gamma_7^+).$$

Similarly, for a stress along  $[111]$ , the symmetry is reduced to  $D_{3d}$ , and the functions of the upper and lower  $VB$ s transform as the  $\Gamma_4^+$  and  $\Gamma_5^+ + \Gamma_6^+$  IRs of the  $D_{3d}$  group, respectively. The energies  $E(\Gamma_4^+)$  and  $E(\Gamma_5^+ + \Gamma_6^+)$  are then given by:

$$E_{\pm 1/2}(\Gamma_4^+) = \frac{1}{3}D'_u S_{44}T = -\frac{1}{2\sqrt{3}}d = -E_{\pm 3/2}(\Gamma_5^+ + \Gamma_6^+),$$

<sup>4</sup> The  $VB$  deformation potentials  $a, b$ , and  $d$  are defined in p. 311 of the book by Bir and Pikus [17]. The correspondence between the two notations is given in note 35 of [59].

where the  $S_{ij}$  are the components of the elastic compliance tensor. The absolute maximum of the  $VB$  corresponds to  $m = \pm 1/2$  and the values of the splitting  $\delta E_{3/2-1/2}$  between the two states are given by:

$$\delta E_{1/2-3/2}[100] = 2|b|(S_{11} - S_{12})T = \Delta_{100} \quad (8.13)$$

$$\delta E_{1/2-3/2}[111] = \frac{1}{\sqrt{3}}|d|S_{44}T = \Delta_{111}. \quad (8.14)$$

The expression for the splitting  $\Delta_{110}$  for a stress along  $\langle 110 \rangle$  is more complicated (see [58]) and it is not considered here. A relatively simple relation can, however, be derived among  $\Delta_{100}$ ,  $\Delta_{110}$ , and  $\Delta_{111}$ , namely:

$$4(\Delta_{110})^2 = (\Delta_{100})^2 + 3(\Delta_{111})^2$$

and it shows that if any two splitting among  $\Delta_{100}$ ,  $\Delta_{110}$ , and  $\Delta_{111}$  are equal, then, the three are. This situation is referred to as stress isotropy [32]. The hydrostatic DP  $a$  produces a uniform shift of the levels, independent of the stress orientation, equal to  $a(S_{11} + 2S_{12})T$ , denoted  $\Delta_{000}$ .

Under large strains, the two bands associated with the  $m_J = \pm 1/2$  and  $\pm 3/2$  states decouple along the stress direction. Their separation is always given by (8.13) or (8.14) but the constant energy surfaces for the upper  $VB$  ( $m_J = \pm 1/2$ ) become prolate ellipsoids. Quantitatively, for germanium, the  $VB$  splitting  $\Delta_{111}(T)$  is  $3.73 \times 10^{-2}|T|$  (MPa) [59]. The stress-dependent effective masses  $m_{//}$  along the stress direction is smaller than  $m_{\perp}$  perpendicular to the stress direction. For shallow acceptors, this high-stress limit bears resemblance with those for shallow donors, but with a value of the parameter  $\gamma = m_{\perp}/m_{//}$  larger than unity, and this facilitates the calculation of their energy levels as the Hamiltonian is similar to the one given by (5.5) [25].

Broeckx and Vennik [24] have solved variationally for germanium the acceptor Hamiltonian containing the stress interaction term (8.12) for stresses parallel to the  $\langle 100 \rangle$  and  $\langle 111 \rangle$  axes in the 1–1000 MPa range. The results show that throughout the low stress region, up to  $\sim 200$  MPa in germanium, the acceptor ground state splitting is linear, given by (8.13) and (8.14), but the energy levels show an upward quadratic shift. With increasing stress, the energies no longer follow a simple power law with stress, due to interactions with the even-parity excited states. The energy splitting of the first odd-parity states remains linear at very low stress, but quadratic shifts are also present. The intermediate stress region is dominated by interactions between states with the same symmetry, leading to a complicated pattern. In the high-stress region, above 500 MPa, the energy spectrum simplifies again, because of decoupling of the  $VB$  in the stress direction mentioned in the preceding paragraph, and the energies of the levels with respect to the  $VB$  become stress-independent. The situation for a stress parallel to  $\langle 100 \rangle$  is shown in Fig. 8.19. The labellings on the left-hand side correspond to the excited states of lines  $G$ ,  $D$ ,  $C$ ,  $B$ ,  $A_4$ ,  $A_3$ ,  $A_2$ , and  $A_1$  of the group-III acceptors in germanium in the order of decreasing energy.

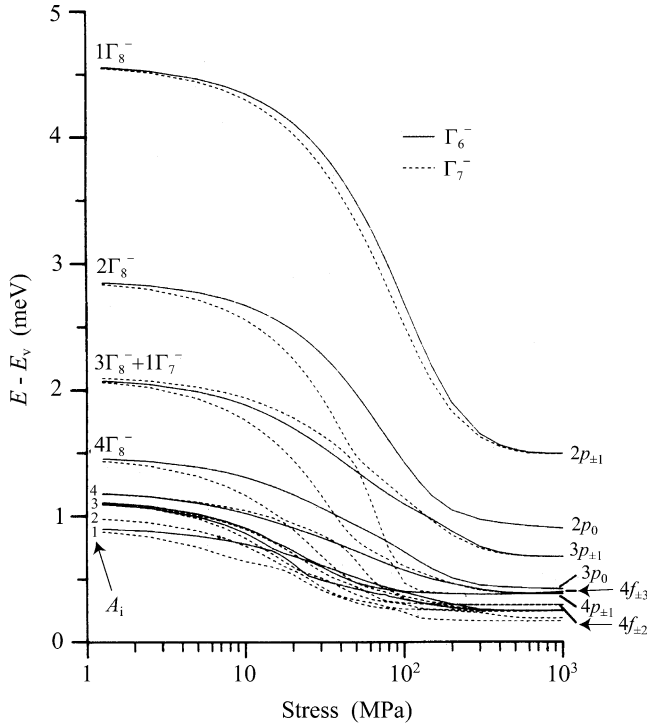


**Fig. 8.19.** Stress dependence of the computed binding energies for the first odd-parity excited acceptor states in germanium for  $F//\langle 100 \rangle$ . The energy origin is the top of the  $\Gamma_6^+$  ( $m_J = \pm 1/2$ ) VB ( $D_{4h}$  symmetry). The labelling on the LHS corresponds to the attributions of zero-stress acceptor lines of germanium given in Table 7.9. The one on the RHS corresponds to the high-stress limit (after [24]). Copyright 1987 by the American Physical Society

Energies and wave functions of shallow acceptor states in silicon and germanium for stresses along the  $\langle 100 \rangle$  and  $\langle 111 \rangle$  axes have also been calculated by Buczko [27] using the full stress-dependent Hamiltonian up to the high-stress limit. The results of these calculations will be discussed in comparison with the experimental results.

The absorption lines of the shallow acceptor spectra in silicon and in germanium have been well-identified (see Tables 7.2 and 7.9) and a qualitative understanding of their splitting under stress can be derived from their symmetry. For uniaxial stresses along  $\langle 100 \rangle$ ,  $\langle 110 \rangle$  and  $\langle 111 \rangle$  axes, the symmetry of an acceptor on a  $T_d$  site is lowered to  $D_{2d}$ ,  $C_{2v}$ , and  $C_{3v}$ , respectively. The zero-stress levels of the acceptors associated with the  $\Gamma_8^+$  VB belong to three IRs of the double group of  $T_d$ , namely  $\Gamma_8$ ,  $\Gamma_7$ , and  $\Gamma_6$ . Under stresses along  $\langle 100 \rangle$ ,  $\langle 110 \rangle$  or  $\langle 111 \rangle$  directions, the  $\Gamma_8$  levels split into a doublet and there is no splitting of the  $\Gamma_7$  and  $\Gamma_6$  levels. This situation, which also prevails

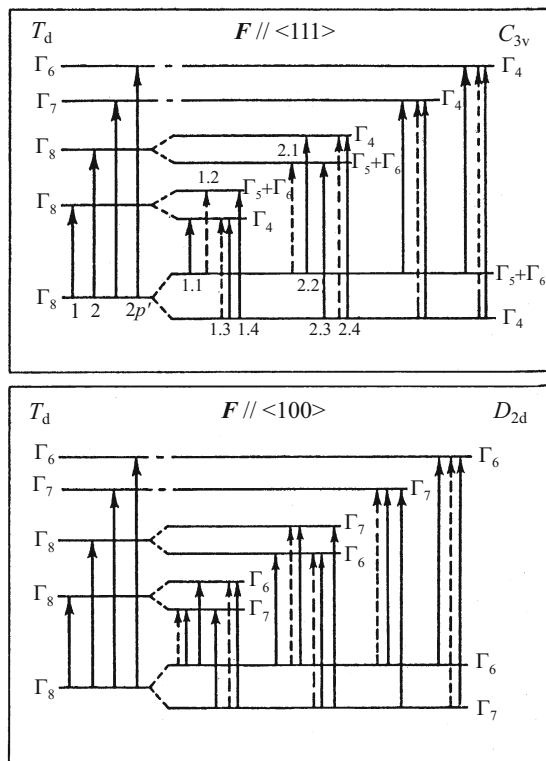


**Fig. 8.20.** Allowed transitions from a  $\Gamma_8$  acceptor ground state to  $\Gamma_8$ ,  $\Gamma_7$ , and  $\Gamma_6$  excited states of the double group  $T_d$  for compressive forces along  $\langle 111 \rangle$ , and  $\langle 100 \rangle$ . The IRs of the double groups are indicated next to the levels. The superscripts for the even- and odd-parity states have been omitted. The dashed and full arrows are for transitions with  $\mathbf{E} // \mathbf{F}$  and  $\mathbf{E} \perp \mathbf{F}$ , respectively [115]. The labels of some of the transitions for  $F // \langle 111 \rangle$  are the same as those of components of the spectrum of boron in silicon in Fig. 8.21. Copyright 1967 by the American Physical Society

for acceptors in diamond, is represented in Fig. 8.20 for  $F // \langle 100 \rangle$  and  $F // \langle 111 \rangle$ . The ordering of the  $\Gamma_8$  ground state sublevels shown in this figure has been deduced from the piezospectroscopic measurements of [115] on different group-III acceptors in silicon. Two orderings are given for sublevels of the  $\Gamma_8$  excited states. These reversed orderings are in agreement with the polarization properties of the split components of lines 1 and 2 for  $F // \langle 111 \rangle$  and the transitions are labelled according to the components of these two lines, shown in Fig. 8.21. A qualitative comparison with the experimental spectrum is no longer valid for  $F // \langle 100 \rangle$  because the excited state of line 1 shows no detectable splitting for the group-III acceptors in silicon for this specific stress orientation [115].

The energies of the sublevels of a  $\Gamma_8$  acceptor level with  $T_d$  symmetry split by stresses along  $\langle 100 \rangle$  and  $\langle 111 \rangle$  are given in Table 8.7.

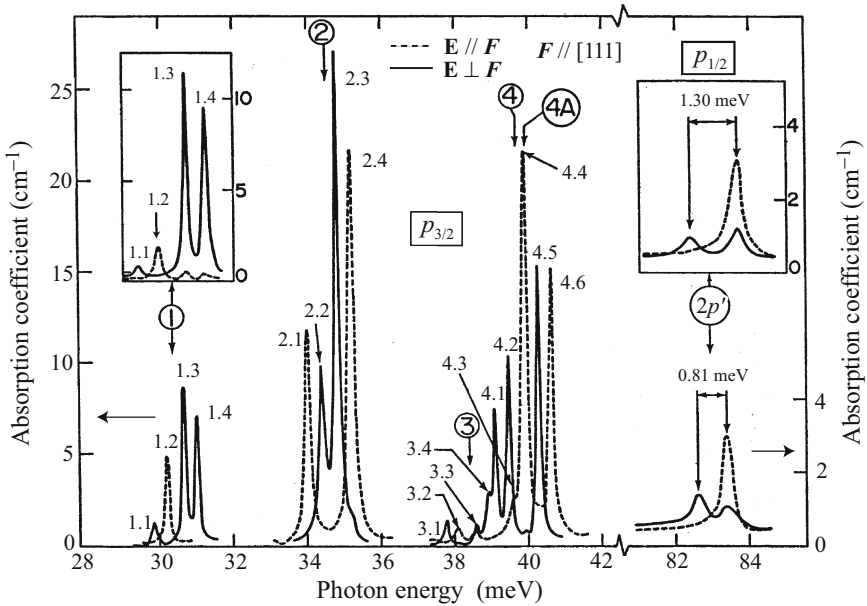


**Fig. 8.21.** Absorption at LHeT of lines 1– 4A and  $2p'$  of B in silicon ( $p$  is  $1.1 \times 10^{15} \text{ cm}^{-3}$  at RT) under a  $\langle 111 \rangle$  uniaxial stress. The *encircled numbers* together with the *vertical arrows* indicate the positions of the lines at zero stress. The *two insets* show the effect of a larger stress [115]. The estimated stress is 27 MPa, and 44 MPa for the insets. Copyright 1967 by the American Physical Society

**Table 8.7.** Energies and symmetries of the stress-split sublevels of a  $\Gamma_8$  level of an acceptor with  $T_d$  symmetry in a group-IV semiconductor (after [32])

| $F$ parallel to       | Sublevels symmetry                 | Energy                                | $J$       |
|-----------------------|------------------------------------|---------------------------------------|-----------|
| $\langle 100 \rangle$ | $\Gamma_6$ ( $D_{2d}$ )            | $\Delta_{000} + b(S_{11} - S_{12})T$  | $\pm 3/2$ |
|                       | $\Gamma_7$ ( $D_{2d}$ )            | $\Delta_{000} - b(S_{11} - S_{12})T$  | $\pm 1/2$ |
| $\langle 111 \rangle$ | $\Gamma_5 + \Gamma_6$ ( $C_{3v}$ ) | $\Delta_{000} + (d/2\sqrt{3})S_{44}T$ | $\pm 3/2$ |
|                       | $\Gamma_4$ ( $C_{3v}$ )            | $\Delta_{000} - (d/2\sqrt{3})S_{44}T$ | $\pm 1/2$ |

There is a distinct set of DPs  $a$ ,  $b$ , and  $d$  for each  $\Gamma_8$  level, and for each  $\Gamma_6$  and  $\Gamma_7$  levels, there is one isotropic DP  $a$ .

Figure 8.21 shows a composite truncated spectrum of boron in a silicon sample in which a stress along  $\langle 111 \rangle$  is produced by differential contraction between the sample and the copper jig. Because of the relatively low resolution used in this study, only lines 4 and 4A/6 were resolved and line 4B/5 was not considered (it was in 1967), but this figure gives none the less a very good global idea of the stress splitting of acceptors at low stress in silicon. A comparison can be made with the zero stress  $p_{3/2}$  spectrum of Fig. 7.1.



The stress-split components are well resolved and this splitting can be interpreted from symmetry considerations considering that the ground state of the  $p_{3/2}$  and  $p_{1/2}$  spectra is a  $\Gamma_8$  state and that the odd-parity excited states have  $\Gamma_8$ ,  $\Gamma_7$ , and  $\Gamma_6$  symmetries. This figure shows that if the amplitudes of the splitting of lines 1 and 2 are comparable, the polarization properties of their components are different, due to a reverse ordering of the split levels. This is due to the fact that the  $1\Gamma_8$  and  $2\Gamma_8$  excited states of the transitions giving lines 1 and 2 correspond to different  $nL_J$  configurations ( $2P_{3/2}$  and  $2P_{5/2}$ ).

The interpretation of the acceptor spectra in silicon under uniaxial stress has considered the splitting of lines 1 and 2 and of the  $2p'$  lines of the B, Al, and In acceptors. It is based on the assumption that the splitting of the  $1\Gamma_8$  acceptor ground state and excited states can be fitted into expressions like (8.13) or (8.14) for the  $\Gamma_8^+ VB$ , but with values of the DPs  $b$  and  $d$  depending on the  $\Gamma_8$  state considered. These DPs are denoted  $(b_0, d_0)$  for the  $1\Gamma_8^+$  ground state and  $(b_1, d_1)$  and  $(b_2, d_2)$  for the  $1\Gamma_8^-$  and  $2\Gamma_8^-$  states, respectively.

The stress dependence of the splitting of the  $\Gamma_8^+$  ground state is conveniently measured from the splitting observed for the  $2p'$  line, attributed to this state. The splitting displayed in Fig. 8.22 for  $2p'(\text{B})$  for three stress orientations show that within experimental error, the ground-state splitting is independent of the stress direction.

A similar stress isotropy of the ground-state splitting is also observed for the other acceptors, but with different values of the ground state DPs  $b_0$  and  $d_0$ .

The DPs  $b_i$  and  $d_i$  for the  $1\Gamma_8^+$  ground state and for the  $1\Gamma_8^-$  and  $2\Gamma_8^-$  excited states pertaining to lines 1 and 2 were determined for the B, Al, and In acceptors in silicon by [32] for stresses up to 140 MPa along  $\langle 100 \rangle$ ,  $\langle 110 \rangle$ , and  $\langle 111 \rangle$ . Such stresses allowed the study of the anti-crossing behaviour of components of different lines with the same symmetry. The results of the detailed piezospectroscopic measurements on B in silicon performed for lower values of the stress (up to 40 MPa) have also been reported by Lewis et al. [97]. They provide values of the DPs  $b_i$  and  $d_i$  for the  $1\Gamma_8^+$  ground state and several excited states. In Table 8.8 are presented experimental values of the uniaxial DPs  $b_i$  and  $d_i$  of the first acceptor levels in silicon, where they are compared with calculated values.

The values of  $b_0$  and  $d_0$  ( $-1.42$  and  $-3.7$  eV, respectively) for B obtained from ESR under a small uniaxial stress [110] are slightly smaller<sup>5</sup> than those in Table 8.8. A determination of the DPs  $b$  and  $d$  of the  $\Gamma_8^+ VB$  of silicon from the spectroscopic values of  $b_0$  and  $d_0$  of  $1\Gamma_8^+(\text{B})$  using correction factors calculated [16, 138] gives  $\sim -2.0$  and  $-4.7$  eV for  $b$  and  $d$ , respectively. There is a good agreement between the values obtained by other methods and by calculation (see Table V of the paper by Chandrasekhar et al. [32]).

---

<sup>5</sup> In this reference, the ground state DPs are denoted  $b'$  and  $d'$ .

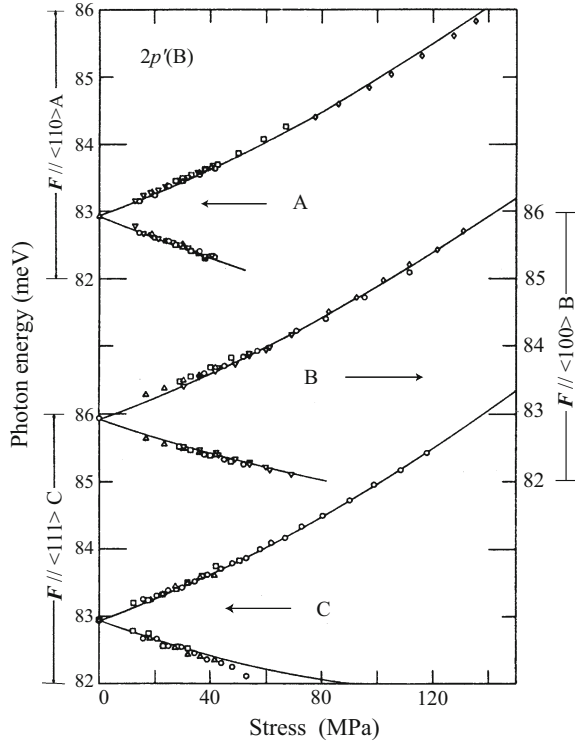


**Fig. 8.22.** Stress dependence of the components of the  $p_{1/2}2p'$  line of B in silicon at LHeT. A:  $F//\langle 110 \rangle$ , B:  $F//\langle 100 \rangle$ , C:  $F//\langle 111 \rangle$ . The different symbols correspond to different spectral runs. The zero stress position of  $2p'$  is 82.90 meV (after [32])

**Table 8.8.** Uniaxial deformation potential constants (eV) of acceptor ground and excited states in silicon deduced from piezospectroscopic measurements compared with the calculated ones. The corresponding lines of the spectrum are indicated in parentheses

|    |   | $1\Gamma_8^+$ (GS) |       | $1\Gamma_8^-(1)$ |       | $2\Gamma_8^-(2)$ |       | $3\Gamma_8^-(3)$ |       | $5\Gamma_8^-(7)$ |       |
|----|---|--------------------|-------|------------------|-------|------------------|-------|------------------|-------|------------------|-------|
|    |   | $b_0$              | $d_0$ | $b_1$            | $d_1$ | $b_2$            | $d_2$ | $b_3$            | $d_3$ | $b_7$            | $d_7$ |
| B  | a | -1.61              | -4.50 | 0.20             | -2.31 | 1.61             | 2.64  |                  |       |                  |       |
|    | b | -1.46              | -3.91 | -0.055           | -1.76 | 1.53             | 1.36  | 0.03             | -2.1  | 0.01             | -2.1  |
| Al | a | -1.43              | -3.84 | 0.10             | -3.11 | 1.43             | 2.56  |                  |       |                  |       |
|    | b | -1.43              | -3.84 | 0.10             | -3.11 | 1.43             | 2.56  |                  |       |                  |       |
| In | a | -0.98              | -2.68 | $\sim 0$         | -3.22 | 1.76             | 2.54  |                  |       |                  |       |
|    | c | -1.39              | -4.17 | -0.025           | -1.84 | 1.09             | 2.04  | 0                | -1.70 | 0                | -1.65 |

<sup>a</sup> [32], <sup>b</sup> [97], <sup>c</sup> [27], calculated

If the isotropic coefficients  $a_i$  cannot be obtained separately from the above-described piezospectroscopic measurements, the differences  $a_i - a_0$  can be. For boron, these differences are  $-0.41$ ,  $0.86$ ,  $-2.17$ , and  $-1.0$  eV for lines 1, 2, 3, and 7, respectively [97].

At a difference with line  $2p'$ , the stress splitting observed for lines 1 and 2 is a combination of the ground and excited state splitting. Anti-crossing behaviour between components of different zero-stress lines can be observed when they have the same symmetry. This is the case for component 1.4 of line 1 and component 2.1 of line 2 of B in silicon (see Fig. 7 of the paper by Chandrasekhar et al. [32]).

In the  $p_{3/2}$  Ga spectrum of Fig. 7.3, an anomalous broadening of line 2(Ga) is observed, together with a rather sharp, but weak X feature near from the energy of the  $O(\Gamma)$  phonon in silicon. This feature is attributed to a splitting of line 2 due to the interaction with the  $O(\Gamma)$  phonon. This resonant interaction has been further studied under uniaxial stress by Chandrasekhar et al. [34]. The X feature is seen to be split by stress and its relative sharpness at zero stress is attributed to its interaction with phonons close to the  $\mathbf{q} = 0 \Gamma$  point while line 2 interacts with a larger phonon distribution.

There are several reports on the piezospectroscopy of group III acceptors and on  $\text{Zn}^-$  in germanium in the low-stress limit, aimed at confirming the symmetry of the excited states and in determining the DPs ([123], and references therein, [143]). We pick here in the study by Vickers et al. an interesting comparison shown in Fig. 8.23 between the splitting of the  $D$  and  $C$  lines of gallium in germanium. The splitting of the  $D$  line in four components is consistent with the  $2\Gamma_8^-$  excited state of this line, which displays under stress an ordering of the sublevels reversed with respect to the one of the  $1\Gamma_8^+$  ground state. These orderings are the same as those shown schematically in Fig. 8.20 for line 2. The splitting of line  $C$  is much more complex, showing ten components which can be attributed to a zero-stress  $3\Gamma_8^- + 3\Gamma_8^+ + 1\Gamma_7^-$  combination of excited states. The deformation potential  $b_0$  of the  $1\Gamma_8^+$  ground state of Ga in germanium derived from this measurement is  $-1.2$  eV and it is significantly smaller than the value of  $b$  ( $-2.2$  eV) measured for the  $\Gamma_8^+ VB$  of germanium by Hensel and Suzuki [59].

The relative intensities of the stress-induced components have been obtained by calculating the matrix elements of the dipole moment operator for the different components of the multiplets. This has been performed for the three categories of zero stress transitions and for the stress-induced components of the  $\Gamma_8 \rightarrow \Gamma_8$  transitions, the intensities depend on parameters defined in terms of ratios of the magnitudes of matrix elements appropriate to the different unperturbed multiplets ([123], and references therein).

The results of PTIS experiments on high-purity p-type silicon under stresses up to 550 MPa have been described by [38]. Lines reported between 258 and  $350 \text{ cm}^{-1}$  (32 and 43.4 meV) for a stress of 550 MPa along the  $\langle 111 \rangle$  axis have been attributed to the different donor-like transitions with an

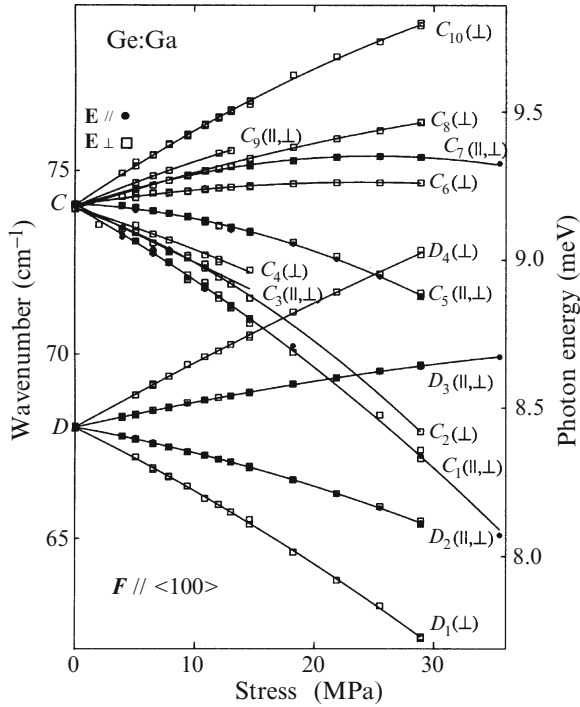


**Fig. 8.23.** Stress dependence measured at LHeT of the components of the  $C$  and  $D$  lines of Ga in germanium for  $F // \langle 100 \rangle$ . The *solid curves* are the results of the second-order regression fit. The indications  $\perp$  and  $//$  correspond to  $E \perp F$  and  $E // F$ , respectively. The ground-state splitting is given directly by the  $D_3 - D_1$  or  $D_4 - D_2$  separation. Reproduced with permission from [143]. Copyright 1988, with permission from Elsevier

effective-mass anisotropy factor  $\gamma$  of 4.9 due to the decoupling of the  $VB$ , and a qualitative agreement with a crude EM calculation is obtained.

Piezospectroscopic results of residual B and Al in germanium for stresses between  $\sim 300$  and  $640$  MPa along the  $\langle 100 \rangle$  and  $\langle 111 \rangle$  axes have been reported by Kazanskii et al. [77] using PTIS. They were able to determine directly the shift with stress  $T$  of the ionization energies  $E_i$  of these acceptors at 2 K (see Fig. 8.24).

This shift represents the separation between the highest energy component of the ground-state doublet and the  $m_J = \pm 1/2$   $VB$ , and it is found to decrease with stress, and is faster for stress along  $\langle 100 \rangle$  than along  $\langle 111 \rangle$ . For large stresses,  $E_i$  can be expanded in inverse power of the stress or strain amplitude [54]. Its value  $E_{i\infty}$  for very large stresses, obtained from a best fit of the experimental data, is  $6.4$  meV for Al compared to the zero-stress value of

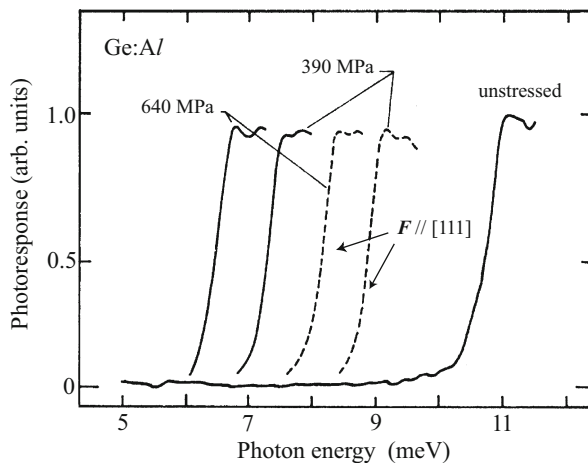


**Fig. 8.24.** Shift with stress of the photoconductivity threshold energy of the Al acceptor in germanium at 2 K. This threshold represents the ionization energy of Al. The *solid lines* are for  $\mathbf{F} // [100]$ . The vertical scale is different for each curve. Reproduced with permission from [77]. Copyright 1977, with permission from Elsevier

11.1 meV, and it is very close to the value measured<sup>6</sup> for  $T = 640$  MPa for  $\mathbf{F} // \langle 100 \rangle$ . For such stresses, the discrete acceptor spectrum simplifies because of the  $VB$  decoupling, and under the experimental conditions, only three lines denoted  $L_1$ ,  $L_2$ , and  $L_3$  in order of decreasing energy are observed for the highest stress (Fig. 8.25).

From a comparison with their calculated values of the acceptor levels in germanium in the high-stress limit, lines  $L_1$ ,  $L_2$ , and  $L_3$  have been attributed to the  $3p_0$ ,  $2p_0$ , and  $2p_{\pm}$  donor-like transition, respectively, by Broeckx and Vennik [24]. The energies at 640 MPa are close to those calculated by these authors and by Buczko [27]. As for  $E_i$ , these transitions have been assumed to follow with stress an inverse power law and their energies become stress-independent at high stress. On the one hand, this is in agreement with the near independence from the stress of the calculated energies of the odd-parity energy levels at high stress, displayed in Fig. 8.19, and on the other hand, with the same independence determined experimentally for the ground state energy and reported above [77].

### 8.2.1.3 Stress-Induced Inhomogeneous Broadening

A distribution of stresses in a crystal sample produces random splitting of the electronic levels and the net result is, to the first order, an inhomogeneous broadening of the electronic lines.

<sup>6</sup> The values of  $E_i$  of Kazanskii et al.'s paper are measured at half height of the photoresponse signal.

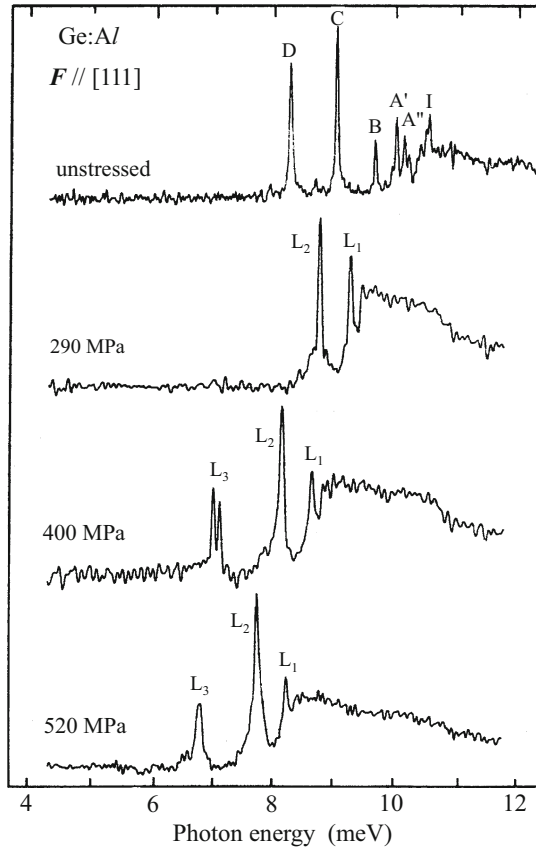


**Fig. 8.25.** Influence of stress along a  $\langle 111 \rangle$  axis on the spectrum of Al in germanium at 7 K. The zero-stress line noted I should correspond to line  $I_6$  of Table 7.9. Reproduced with permission from [77]. Copyright 1977, with permission from Elsevier

Distribution of stresses is found in the immediate vicinity of dislocations in semiconductors and it is the origin of the so-called dislocation broadening. This effect was recognized and discussed in conjunction with the conditions for the observation of ESR spectra in silicon [17, 84]. An example of this effect on an absorption line is shown in Fig. 8.26, displaying the profiles at LHeT of the  $G(\text{Al})$  line in germanium samples cut in two different regions of a Ge:Al ingot.

The profile of the line in the more dislocated sample is observed to be broadened. There are also additional splitting of the line ( $\sim 0.054$  and  $0.093 \text{ cm}^{-1}$ ) ( $\sim 6.7$  and  $12 \mu\text{eV}$ ). This doublet splitting can be due to the effect of inhomogeneous stress induced by dislocations [142].

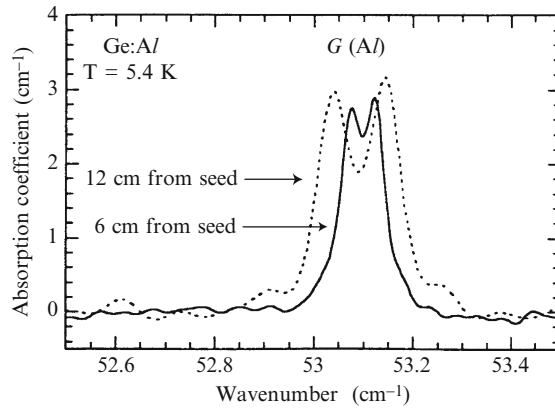


**Fig. 8.26.** Profiles of line  $G(Al)$  in CZ  $^{nat}Ge$  samples cut at 6 cm from the seed end, at a resolution of  $0.037\text{ cm}^{-1}$  (solid curve) and at 12 cm from the seed end and more heavily dislocated than the first, at a resolution of  $0.074\text{ cm}^{-1}$  (dashed curve). The spectral range goes from 6.497 to 6.646 meV. For the doublet splitting, see text (after [9]). Copyright 1997, with permission from World Scientific Publishing Co. Pte. Ltd, Singapore

Another source<sup>7</sup> of random stress in semiconductors is the presence of FAs with atomic radii significantly smaller or larger than the one(s) of the atom(s) of the crystal. When these atoms are electrically inert, an increase of the FWHMs of the lines of shallow donor or acceptor spectra can be attributed to this kind of inhomogeneous stress broadening. This effect has been reported for the spectra of phosphorus in silicon doped with Sn, where an increase of the FWHM of  $2p_{\pm 1}(P)$  from  $\sim 0.3\text{ cm}^{-1}$  in silicon without Sn to  $\sim 2\text{ cm}^{-1}$  in samples with  $[Sn] = 1.7 \times 10^{19}\text{ cm}^{-3}$  was measured [106]. In germanium co-doped with Ba (this element is electrically inert in germanium [51], and its atomic radius is 215 pm compared to 125 pm for Ge), a splitting of  $\sim 0.06\text{ meV}$  ( $0.5\text{ cm}^{-1}$ ) of the  $D(Ga)$ ,  $C(Ga)$ , and  $B(Ga)$  lines was reported and attributed to the effect of Ba doping [6]. Such a splitting is similar to the above-reported one for  $G(Al)$ , while larger, and it has been discussed in terms of inhomogeneous stress effect.

### 8.2.2 Uniaxial Stress and Orientational Degeneracy

The splitting under stress of non-degenerate electronic and vibrational transitions of impurity centres depend almost exclusively on the symmetry of these centres through their orientational degeneracy, already defined as the

<sup>7</sup> It must also be noted that a stress distribution can also be generated at low temperature in crystal samples tightly fixed to a metal sample holder *in vacuo* in order to ensure a good thermal contact.

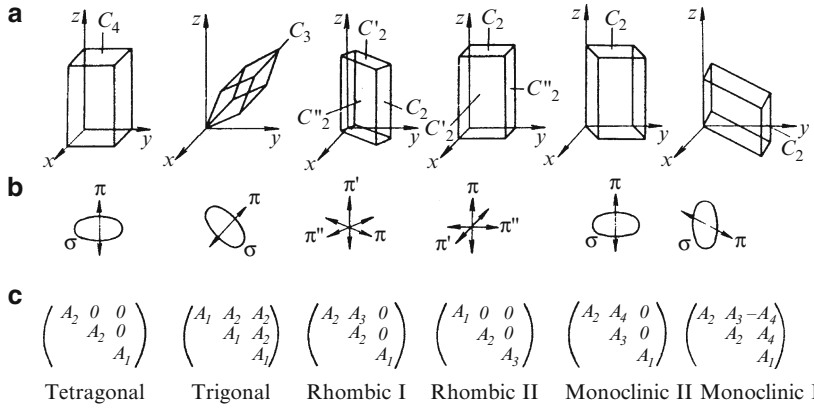


**Fig. 8.27.** (a): Polyhedra having the symmetries of the different non-cubic centres in a cubic crystal. (b): Dipole oscillators of the centres. (c): Corresponding piezospectroscopic tensors.  $C'_2$  and  $C''_2$  also indicate axes perpendicular to the symmetry planes  $\sigma'_v$  and  $\sigma_v$  (after [74]). The type of centres are those of Table 8.9. Reproduced with permission from EDP Sciences

number of distinct equivalent orientations that a centre can take in a crystal. It depends on the symmetries of the centre and of the crystal in which it is embedded. Further, it is necessary to classify the possible symmetries of centres in crystals. This has been done for cubic crystals by Kaplyanskii [73] to study their stress splitting, but it can be extended to other kinds of perturbations [74].

In cubic crystals, one can distinguish six kinds of centres whose symmetries are those of the polyhedra shown in Fig. 8.27. In this figure are also indicated the components  $A_{ij}$  of the piezospectroscopic tensor defined in (8.15).

In Table 8.9, these polyhedra are defined by their edges  $a_1$ ,  $a_2$ , and  $a_3$  (along the  $z$  [001] axis) and the angles  $\alpha$ ,  $\beta$ , and  $\gamma$  between these edges (angle  $\gamma$  taken as the one between  $a_1$  and  $a_2$ ), and the triclinic centres have been added.

More generally, in a diamond-type crystal, the orientational degeneracy  $R$  of a centre whose symmetry corresponds to a subgroup of order  $g$  of the full cubic group  $O_h$  is  $R = G/g$ , where  $G$  is the order (48) of  $O_h$ . This orientational degeneracy is shared by the electronic and vibrational lines associated with the centre, in addition to their possible intrinsic degeneracies. Under non-isotropic perturbations, such as oriented stresses and magnetic or electric fields, orientational degeneracy can be partially or totally lifted by defining sub-families of centres with the same orientational degeneracy  $R_i$  with respect to perturbation and a line splitting is observed. Similar orientational degeneracies also occur in non-cubic crystals. For a few centres with non-cubic symmetries there can exist, however, high-symmetry orientations along which stress has no effect on the initial orientational degeneracy.



**Table 8.9.** Main symmetry characteristics of the non-cubic centres in cubic crystals. The notations of Fig. 8.27 are indicated first for the centre type. Columns 2 and 3 refer to the polyhedra of Fig. 8.27. Possible point-group symmetries for the related centres are given in the last column

| Type of centre | Restrictions on the lengths of the edges and angles                      | Symmetry axes                                                              | Point groups                                    |
|----------------|--------------------------------------------------------------------------|----------------------------------------------------------------------------|-------------------------------------------------|
| Tetragonal     | $a_1 = a_2 \neq a_3$<br>$\alpha = \beta = \gamma = 90^\circ$             | $C_4$ along $[001]$                                                        | $D_{4h}, D_4, C_{4v}, D_{2d}, C_{4h}, C_4, S_4$ |
| Trigonal       | $a_1 = a_2 = a_3$<br>$\alpha = \beta = \gamma \neq 90^\circ < 120^\circ$ | $C_3$ along $[111]$                                                        | $D_{3d}, D_3, C_{3v}, C_{3i}, C_3$              |
| Rhombic I      | $a_1 \neq a_2 \neq a_3$<br>$\alpha = \beta = \gamma = 90^\circ$          | $C_2$ along $[110]$<br>$C'_2$ along $[001]$<br>$C''_2$ along $[1\bar{1}0]$ | $D_{2h}, D_2, C_{2v}$                           |
| Rhombic II     | $a_1 \neq a_2 \neq a_3$<br>$\alpha = \beta = \gamma = 90^\circ$          | $C_2, C'_2, C''_2$ along $\langle 100 \rangle$ directions                  | $D_{2h}, D_2, C_{2v}$                           |
| Monoclinic II  | $a_1 \neq a_2 \neq a_3$<br>$\alpha = \beta = 90^\circ \neq \gamma$       | $C_2$ or a normal to $\sigma_v$ along $[001]$                              | $C_{2h}, C_{1h}, C_s$                           |
| Monoclinic I   | $a_1 \neq a_2 \neq a_3$<br>$\alpha = \beta = 90^\circ \neq \gamma$       | $C_2$ or a normal to $\sigma_v$ along $[110]$                              | $C_{2h}, C_{1h}, C_s$                           |
| Triclinic      | No restriction                                                           |                                                                            | $C_1$                                           |

Centres with different symmetries are characterized by a piezospectroscopic tensor  $\mathbf{A}$  whose components are determined by symmetry considerations [73]. The shifts  $\Delta$  with stress of a transition of a centre referenced in an orthogonal system is:

$$\Delta = A_{xx}\sigma_{xx} + A_{yy}\sigma_{yy} + A_{zz}\sigma_{zz} + 2(A_{xy}\sigma_{xy} + A_{yz}\sigma_{yz} + A_{zx}\sigma_{zx}), \quad (8.15)$$

where  $A_{ij}$  are the components of the piezospectroscopic tensor, which depend on the orientational degeneracy of the centre in the crystal. The components  $\sigma_{ij}$  of the stress tensor are defined by:

$$\sigma_{ij} = \mathbf{n}_i \mathbf{n}_j T, \quad (8.16)$$

where  $\mathbf{n}_i$  and  $\mathbf{n}_j$  are the direction cosines of the stress in the reference frame and  $T$  is the magnitude of the compressional stress. The values of  $\Delta$  for the different orientations of non-cubic centres are given in Table 3 of Kaplyanskii's paper [73]. The shift of the centre of gravity of the split components is independent of the stress direction and is equal to one third of the shift for a hydrostatic stress of the same magnitude. The stress splitting of doubly degenerate states of centres with tetragonal and trigonal symmetry has been treated by Hughes and Runciman [63].

The number of independent components  $A_{ij}$  in expression (8.15) depends on the symmetry of the centre and the values of these components on the interaction of the centre with the crystal.

The centres with trigonal and rhombic I crystallographic symmetries are considered in detail. A trigonal centre has a  $C_3$  symmetry axis along a  $\langle 111 \rangle$  direction and the piezospectroscopic tensor  $\mathbf{A}_{\text{trig}}$  has two independent components  $A_1$  and  $A_2$ . A rhombic I centre has one  $C_2$  axis along a  $\langle 110 \rangle$  direction and the piezospectroscopic tensor  $\mathbf{A}_{\text{rhomb}}$  has three independent components  $A_1$ ,  $A_2$  and  $A_3$ . (see Fig. 8.27).

The reference frames chosen for the definition of the direction cosines  $n_j$  of stress depend on the sub-family of the centres considered. The general piezospectroscopic parameters for the trigonal and orthorhombic I centres are given in Tables 8.10 and 8.11.

The shift of the centre of gravity  $\Delta_{\text{cg}}$  of the split components is independent of the orientation of stress and is given by:

$$\Delta_{\text{cg}} = \frac{1}{R} \sum_{i=1} R_i \Delta_i,$$

where the sum is taken on the sub-families for one of the stress orientations. It can be checked that for the trigonal and orthorhombic I symmetries,  $\Delta_{\text{cg}}$  is  $A_1$  and  $(A_1 + 2A_2)/3$ , respectively [73]. It corresponds to the response of the line to a hydrostatic pressure.

If spectroscopy under uniaxial stress is a method which allows determination of the orientational degeneracy of many centres, this property (and the symmetry of the centres) can also be determined for paramagnetic ones

**Table 8.10.** Piezospectroscopic characteristic of trigonal centres in cubic crystals.  $R_i$  denotes the residual orientational degeneracies under stress. The direction cosines  $n_x$ ,  $n_y$ , and  $n_z$  of the stress in the reference frames associated with each sub-family are those given in [73] and the shift  $\Delta_i$  per unit stress is calculated using expression (8.15)

| Stress direction                                               | $R_i$ | $n_x, n_y, n_z$                       | $\Delta_i$    | Intensities for<br>$\mathbf{E} // \sigma : \mathbf{E} \perp \sigma$ |                  |
|----------------------------------------------------------------|-------|---------------------------------------|---------------|---------------------------------------------------------------------|------------------|
|                                                                |       |                                       |               | $\pi$ dipoles                                                       | $\sigma$ dipoles |
| [100]                                                          | 4     | 1, 0, 0                               | $A_1$         | 1:1                                                                 | 1:1              |
| [111]                                                          | 1     | $1/\sqrt{3}, 1/\sqrt{3}, 1/\sqrt{3}$  | $A_1 + 2A_2$  | 3:0                                                                 | 0:3              |
|                                                                | 3     | $1/\sqrt{3}, -1/\sqrt{3}, 1/\sqrt{3}$ | $A_1 - A_2/3$ | 1:4                                                                 | 8:5              |
| Intensities for<br>$\mathbf{E} // [110] : [001] : [1\bar{1}0]$ |       |                                       |               |                                                                     |                  |
| [110]                                                          | 2     | $1/\sqrt{2}, 1/\sqrt{2}, 0$           | $A_1 + A_2$   | 2:1:0                                                               | 1:2:3            |
|                                                                | 2     | $1/\sqrt{2}, -1/\sqrt{2}, 0$          | $A_1 - A_2$   | 0:1:2                                                               | 3:2:1            |

**Table 8.11.** Same as Table 8.8 for rhombic I centres (from [73])

| Stress direction | $R_i$ | $n_x, n_y, n_z$                       | $\Delta_i$              | Intensities for<br>$\mathbf{E} // \sigma : \mathbf{E} \perp \sigma$ |                  |
|------------------|-------|---------------------------------------|-------------------------|---------------------------------------------------------------------|------------------|
|                  |       |                                       |                         | $\pi$ dipoles                                                       | $\sigma$ dipoles |
| [100]            | 4     | 1, 0, 0                               | $A_2$                   | 2:1                                                                 | 0:1              |
|                  | 2     | 0, 0, 1                               | $A_1$                   | 0:1                                                                 | 1:0              |
| [111]            | 3     | $1/\sqrt{3}, 1/\sqrt{3}, 1/\sqrt{3}$  | $(A_1 + 2A_2 + 2A_3)/3$ | 4:1                                                                 | 1:1              |
|                  | 3     | $1/\sqrt{3}, -1/\sqrt{3}, 1/\sqrt{3}$ | $(A_1 + 2A_2 - 2A_3)/3$ | 0:3                                                                 | 1:1              |
| [110]            |       |                                       |                         | Intensities for<br>$\mathbf{E} // [110] : [001] : [1\bar{1}0]$      |                  |
|                  |       |                                       |                         |                                                                     |                  |
| [110]            | 1     | $1/\sqrt{2}, 1/\sqrt{2}, 0$           | $A_2 + A_3$             | 1:0:0                                                               | 0:1:0            |
|                  | 4     | $1/\sqrt{2}, 0, 1/\sqrt{2}$           | $(A_1 + A_2)/2$         | 1:2:1                                                               | 2:0:2            |
|                  | 1     | $1/\sqrt{2}, -1/\sqrt{2}, 0$          | $A_2 - A_3$             | 0:0:1                                                               | 0:1:0            |

from the number of components of their ESR spectrum for high-symmetry orientations of the magnetic field: for a monoclinic I centre with  $C_{1h}$  symmetry and spin 1/2, in a diamond-type crystal, the maximum number of ESR components for  $\mathbf{B}$  in a  $\{110\}$  plane is 7, but it reduces to 2, 3, and 4 for  $\mathbf{B} // \langle 100 \rangle$ ,  $\langle 111 \rangle$ , and  $\langle 110 \rangle$ , respectively (see also Fig. 8.17).

### 8.3 Effect of Magnetic Fields

The perturbation produced by a magnetic field on the electronic spectra in atomic and solid-state spectroscopies is known as the Zeeman effect [152] and it produces a splitting of the lines. The magnetic field is an axial vector with the symmetry of the DC current loop by which it is produced, and when the direction of current (or time) is reversed, the direction of the magnetic field is also reversed and time-reversal symmetry is broken. This results in the splitting of the degenerate Kramers doublets of the electronic levels. Another consequence is the lowering of the point group symmetry with respect to a uniaxial stress: the point group symmetry for a cubic crystal with  $\mathbf{B} // [001]$ ,  $[111]$  or  $[110]$  directions are  $S_4$ ,  $C_3$ , and  $C_{1h}$  ( $C_s$ ), respectively. A general presentation of the effect of a magnetic field on Bloch electrons is given in the review by Ramdas and Rodriguez [123].

Considering the simple case of an electron bound to a shallow electronic ion in a crystal with static dielectric constant  $\epsilon_s$ , when the magnetic field  $\mathbf{B}$  is oriented along the  $z$  axis, the EM Hamiltonian at a non-degenerate band extremum characterized by an effective mass  $m^*$  is:

$$H_{eB} = \frac{\hbar^2 k^2}{2m^*} + \frac{e\hbar B}{2m^*} L_z + \frac{e^2 B^2}{8m^*} (r^2 - z^2) - \frac{e^2}{4\pi\epsilon_0\epsilon_s r}. \quad (8.17)$$

**Table 8.12.** Values of the critical field  $B_0$  (T) for EM donors and acceptors in some semiconductors. As a magnetic-field dependence of the effective masses is not considered and because of the spread in the published values of the  $VB$  parameter  $\gamma_1$ , these values should be regarded as estimates. For the H atom,  $B_0$  is  $2.35 \times 10^5$  T

|              |           | C <sub>diam</sub> | SiC | Si   | Ge  | GaP | GaAs | InP | InSb | CdTe |
|--------------|-----------|-------------------|-----|------|-----|-----|------|-----|------|------|
| EM donors    | $B_0$ (T) | 695               | 149 | 65.5 | 6.4 | 126 | 6.6  | 10  | 0.14 | 22   |
| EM acceptors | $B_0$ (T) | 555               | 315 | 98.7 | 5.6 | 115 | 34   | 44  | 5.8  | 89   |

In  $H_{eB}$ ,  $L_z$  is a constant of the motion and the eigenvalues can be characterized by the quantum number  $N$  of the Landau levels and by  $m$ , associated with the eigenvalues of  $L_z$ . If the magnetic field is strong enough, the Coulomb term can be taken as a perturbation and the Landau levels must be considered first. The validity of this approximation is characterized by the value of the dimensionless effective magnetic field parameter  $\gamma_B$  equal to  $\hbar\omega_c/2R_\infty^*$  or  $\mu_B B/m^* R_\infty^*$  already introduced for donors in Sect. 5.2.3, but here,  $m^*$  is expressed in units of  $m_e$ . The value  $B_0 = m^* R_\infty^*/\mu_B$  (denoted also  $\beta_0$ ) of the magnetic field for which  $\gamma_B = 1$  must be considered as a boundary above which the low-field limit is no longer applicable.

With  $m^*$  in units of  $m_e$ ,  $\gamma_B = 4.2544 \times 10^{-6} (\epsilon_s/m^*)^2$  B(T). For shallow donors in multi-valley semiconductors,  $m^*$  is the electron transverse effective mass  $m_{nt}$  of Table 3.4 and for QHDs in direct-band-gap semiconductors, it is the effective mass  $m_n$  at the  $\Gamma$  minimum of the  $CB$  of Table 3.6. For the shallow acceptors where the effective Rydberg  $R_{\infty a}^*$  is defined as  $R_\infty/\gamma_1 \epsilon_s^2$ ,  $B_0$  is equal to  $R_{\infty a}^*/\gamma_1 \mu_B$ . Values of  $B_0$  for shallow donors and acceptors in different semiconductors are given in Table 8.12.

In the Zeeman experiments, two effects can be distinguished: the linear one, which produces a splitting of the zero-field lines, and the quadratic Zeeman effect, producing a shift of the Zeeman components.

### 8.3.1 Shallow Donors in Multi-Valley Semiconductors

The symmetry classification of the components of the odd-parity donor states with  $m = 0$  and  $\pm 1$  split by a magnetic field in silicon and germanium has been given by [122].

When neglecting spin, which gives the same splitting for all the levels, the linear Zeeman effect of shallow donors is essentially the splitting by the magnetic field of EM states with  $m \neq 0$ , that is, the  $np_{\pm 1}$  lines in the experimental spectra. Their splitting is:

$$\Delta E_{\pm} = \frac{2\mu_B B}{m_t} \cos \beta, \quad (8.18)$$

**Table 8.13.** Splitting  $\Delta E_{\pm}$  of the Zeeman components of the  $1s(A_1) \rightarrow np_{\pm 1}$  donor transitions in silicon in units of  $2\mu_B B/m_t$  as a function of the orientation of the magnetic field  $\mathbf{B}$  with respect to the valleys (D: doublet, S: singlet). The orientations of the pair of valleys are those of Fig. 8.1. Y (yes) and N (no) correspond to the observation conditions resulting from polarization.  $\mathbf{k}$  is the propagation vector of the radiation. The number of components for each polarization is given in the last line for each orientation of  $\mathbf{B}$

| <b>B</b> parallel to | valley                                        | splitting | $\Delta E_{\pm}$ | <b>k</b> // <b>B</b> | <b>k</b> $\perp$ <b>B</b> |                           |
|----------------------|-----------------------------------------------|-----------|------------------|----------------------|---------------------------|---------------------------|
|                      |                                               |           |                  |                      | <b>E</b> // <b>B</b>      | <b>E</b> $\perp$ <b>B</b> |
| [001]                | 5,6                                           | D         | 1                | Y                    | N                         | Y                         |
|                      | 1,2,3,4                                       | S         | 0                | Y                    | Y                         | Y                         |
|                      | Number of components:                         |           |                  | 3                    | 1                         | 3                         |
| [111]                | 1,2,3,4,5,6                                   | D         | $1/\sqrt{3}$     | Y                    | Y                         |                           |
|                      | Number of components:                         |           |                  | 2                    | 2                         |                           |
|                      | <b>E</b> // [001] <b>E</b> // [1 $\bar{1}$ 0] |           |                  |                      |                           |                           |
| [110]                | 5,6                                           | Ss        | 0                | N                    | Y                         | Y                         |
|                      | 1,2,3,4                                       | D         | $1/\sqrt{2}$     | Y                    | Y                         | Y                         |
|                      | Number of components:                         |           |                  | 2                    | 3                         | 3                         |

where  $\beta$  is the angle between the magnetic field and the principal directions of the valleys of the  $CB$ , and  $m_t$  the transverse effective mass of the donor electron expressed in units of  $m_e$  [53, 93]. In this expression, any magnetic-field dependence of  $m_t$  is neglected. The splitting of a  $np_{\pm 1}$  line in silicon for specific values of angle  $\beta$  is given in Table 8.13, but it is also valid for donors in 3C-SiC and for P in diamond. In this table, the direction of the magnetic field varies from [001] to [110] in a  $(0\bar{1}1)$  plane and the notation for the pairs of valleys is the same as in Fig. 8.1.

In the Voigt configuration ( $\mathbf{k} \perp \mathbf{B}$ ), for  $\mathbf{B} // [001]$ , only one line is observed for  $\mathbf{E} // \mathbf{B}$ , and in the Faraday configuration ( $\mathbf{k} // \mathbf{B}$ ), for  $\mathbf{B} // [110]$ , the number of components depends on the polarization. For a general orientation of  $\mathbf{B}$  in the  $(0\bar{1}1)$  plane, the split structure is a quartet, but for a random orientation of the magnetic field, it becomes a sextet, as shown in Fig. 2a of [116].

The splitting with the magnetic field orientation of a  $np_{\pm 1}$  line in germanium associated with the four ellipsoids oriented along  $\langle 111 \rangle$  directions has been calculated and put in a graphical form by [53]. It is given here in the form of Table 8.14.

For a random orientation of  $\mathbf{B}$ , the split structure of a  $np_{\pm 1}$  donor line in germanium is an octet.

**Table 8.14.** Same as Table 8.13 for the  $1s (A_1) \rightarrow np_{\pm 1}$  donor transitions in germanium. The four valleys of the germanium  $CB$  are denoted 1, 2, 3, and 4 for  $[111]$ ,  $[\bar{1}\bar{1}\bar{1}]$ ,  $[1\bar{1}\bar{1}]$ , and  $[\bar{1}\bar{1}1]$  orientations, respectively

| B parallel to                                                     | valley  | splitting | $\Delta E_{\pm}$ | $\mathbf{k} // \mathbf{B}$ | $\mathbf{k} \perp \mathbf{B}$ |                               |
|-------------------------------------------------------------------|---------|-----------|------------------|----------------------------|-------------------------------|-------------------------------|
|                                                                   |         |           |                  |                            | $\mathbf{E} // \mathbf{B}$    | $\mathbf{E} \perp \mathbf{B}$ |
| [001]                                                             | 1,2,3,4 | D         | $1/\sqrt{3}$     | Y                          | Y                             |                               |
| Number of components:                                             |         |           |                  | 2                          | 2                             |                               |
| $\mathbf{E} // [1\bar{1}1] \quad \mathbf{E} // [0\bar{1}\bar{1}]$ |         |           |                  |                            |                               |                               |
| [211]                                                             | 2       | S         | 0                | N                          | Y                             | Y                             |
| [211]                                                             | 1       | D         | $\sim 0.95$      | Y                          | Y                             |                               |
| [211]                                                             | 3,4     | D         | $\sim 0.47$      | Y                          | Y                             |                               |
| Number of components:                                             |         |           |                  | 4                          | 5                             | 5                             |
| [111]                                                             | 1       | D         | 1                | Y                          | N                             | Y                             |
| [111]                                                             | 2,3,4   | D         | $1/3$            | Y                          | Y                             | Y                             |
| Number of components:                                             |         |           |                  | 4                          | 2                             | 4                             |
| [110]                                                             | 1,2     | D         | $\sqrt{2/3}$     | Y                          | Y                             |                               |
|                                                                   | 3,4     | S         | 0                | Y                          | Y                             |                               |
| Number of components:                                             |         |           |                  | 3                          | 3                             |                               |

The quadratic shift of the Zeeman components has been calculated for silicon and germanium by a perturbation method [117]<sup>8</sup>, [139] and by a full calculation [108]. The physical interpretation of this second-order effect in terms of the ratio  $\gamma$  of the transverse and longitudinal effective masses of the donor electron is far from simple.

### 8.3.1.1 Silicon

The experimental magnetospectroscopy of shallow impurities in silicon has first been investigated in 1959–1960 at the M.I.T. group [93,154] using classical electromagnets. Commercial magneto-optical cryostats using superconducting solenoids became available at the end of the 1960s and results obtained with these systems were published by Pajot et al. [116], and later on by Mu et al. [108] using the PTIS detection and magnetic fields up to 10 T ( $\gamma_B = 0.145$ ).

PTI spectra of P in silicon showing low-field Zeeman splitting in the Faraday configuration are displayed in Fig. 8.28.

The asymmetry of the triplet splitting of  $2p_{\pm 1}$  due to the quadratic effect is clearly visible in Fig. 8.28b. The increase of the intensity of the  $3p_0$  line in (c) compared to (a) is due to its interaction with the  $2p_+$  component. The field dependence of the splitting of the first  $np_{\pm}$  lines of P in silicon up to 10 T

<sup>8</sup> In this reference, the sign between the last two terms of  $H_2$  and in front of the expression for  $H_b$  should be  $-$ , and in the expression for  $H_c$ ,  $B$  should be squared.

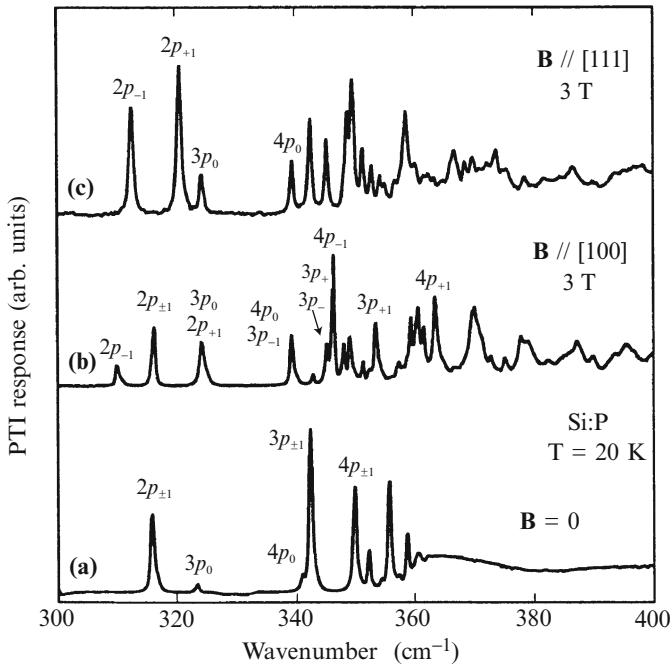


**Fig. 8.28.** PTI spectra of P in silicon between  $\sim 37.2$  and  $49.6$  meV. The components  $3p_-$  and  $3p_+$  in (b) are attributed to the central component  $3p_{\pm 1}$  split by quadratic effects. The spectral resolution is  $0.15 \text{ cm}^{-1}$  ( $\sim 19 \mu\text{eV}$ ).  $[P] = 9.3 \times 10^{12} \text{ cm}^{-3}$  (after [108]). Copyright 1993 by the American Physical Society

is shown in the paper by Shen et al. [129] for  $\mathbf{B} // \langle 100 \rangle$ . The resolution used and the relatively small FWHMs of the components allow to observe a small splitting of the central component of the  $2p_{\pm}$  line attributed<sup>9</sup> to a quadratic effect. The splitting shown for the  $3p_{\pm}$  line is somewhat different from the one measured by classical absorption for the same orientation, and shown in Fig. 4 of [116]. Anti-crossing behaviours have been observed between the  $2p_+$  component and the  $3p_0$  line for  $\mathbf{B} // \langle 111 \rangle$  and calculated between interacting components by Pajot et al. and by Mu et al. Such an effect can be appreciated in Fig. 8.29 with the repulsion between the  $3p_0$  line and the  $2p_+$  component for  $\mathbf{B} // \langle 111 \rangle$ .

This effect, which is accompanied by an increase of the intensity of the  $3p_0$  line, which becomes  $2p_+$ -like, and by a decrease of the intensity of the  $2p_+$  component, which becomes  $3p_0$ -like, has been discussed by Shen [129]. The quadratic contribution to the Zeeman effect of P in silicon has also been measured and compared with the calculations [108, 116, 117].

<sup>9</sup> This splitting could also be produced by a small deviation of the orientation of the sample with respect to  $\mathbf{B}$ , with  $\mathbf{B}$  remaining in a (110) plane.

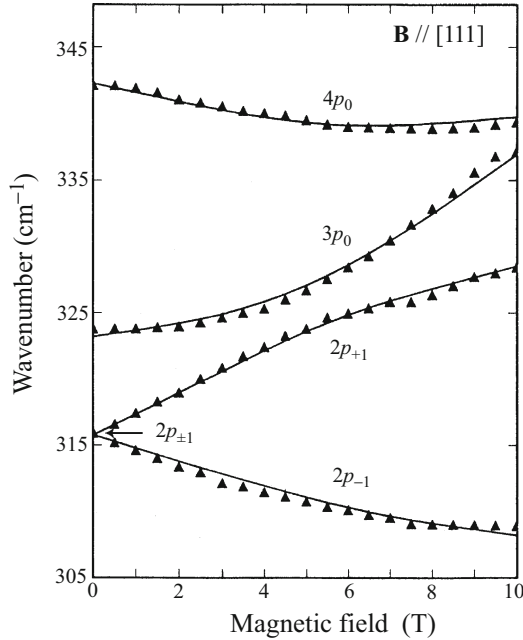


**Fig. 8.29.** Comparison of the observed magnetic field dependence of the interaction between the  $2p_{+1}$  component and the  $3p_0$  transition of P in silicon (*solid triangles*) with the calculated one for  $\mathbf{B} // [111]$  (after [108]). In Fig. 4 of the original publication, the wave number scale is shifted downward by  $\sim 10 \text{ cm}^{-1}$

Expression (8.18) has been used to derive values of the transverse effective mass of donor electrons in silicon from experiments on the P donor for different orientations of the magnetic field [116]. The low-field data give  $m_t = (0.195 \pm 0.002) m_e$ , a value slightly larger than the one derived for the free electrons from the CR experiments (see Table 3.4).

Spectral lines due to the transitions from the  $1s (A_1)$  ground state to the  $1s (T_2)$  and  $1s ({}^3T_2)$  excited states were reported for the  $\text{Se}^0$  and  $\text{Te}^0$  double donors in Chap. 6 (Table 6.12 and Fig. 6.15). The  $1s ({}^3T_2)$  excited state corresponds to a  $1s (A_1) 1s (T_2)$  configuration with parallel spins and the transition from the ground state is only possible if s-o interaction is present. The Zeeman effect of the  $\text{Se}^0$  and  $\text{Te}^0$   $1s ({}^3T_2)$  line was investigated experimentally by Peale and Muro [120], who also provided a modelling of their results on the basis of s-o interaction. It is based on an analogy with the  ${}^3P$  term of a free atom, which allows one to write the s-o interaction as:

$$H_{\text{so}} = \lambda (\mathbf{L} \cdot \mathbf{S}), \quad (8.19)$$

where  $\lambda$  is the s-o coupling parameter for the  ${}^3T_2$  term. In expression (8.19),  $\mathbf{L}$  is an effective angular momentum whose value is 1, always by analogy with



a free atom [1]. An effective total angular momentum,  $\mathbf{J}=\mathbf{L}+\mathbf{S}$ , is introduced corresponding to three s-o split levels with  $J = 0, 1$ , and  $2$ . The *IRs* of  $T_d$  are  $A_2$  ( $J = 0$ ),  $T_2$  ( $J = 1$ ), and  $E + T_1$  ( $J = 2$ ) and transitions from the  $1s$  ( $A_1$ ) state are only possible to the  $T_2$  state with  $J = 1$ .

The magnetic field splits this state into a triplet with  $M_J = +1, 0$ , and  $-1$ , whose energy levels  $E_M$  depend on  $\lambda$  and on the orbital and spin  $g$  factors  $g_L$  and  $g_S$ . The transition to the  $M_J = 0$  state is a so-called  $\pi$  transition with  $\mathbf{E} // \mathbf{B}$  polarization, which can be observed only in the Voigt configuration while those to the  $M_J = \pm 1$  states are  $\sigma$  transitions with  $\mathbf{E} \perp \mathbf{B}$  polarization, which are seen only in the Faraday configuration. The linear Zeeman term of a  $^3T_2$  state with a magnetic field  $\mathbf{B}$  may be written as:

$$H_Z = g_L \mu_B \mathbf{L} \cdot \mathbf{B} + g_S \mu_B \mathbf{S} \cdot \mathbf{B}.$$

With the justified assumption that  $g_L \sim 0$ , the expressions for  $E_{\pm 1}$  and  $E_0$  (see [120] for the derivation) are finally given as:

$$E_{\pm 1} \cong \pm g_S \mu_B B - \left[ \lambda^2 + \frac{1}{4} (g_S \mu_B B)^2 \right]^{1/2} \quad (8.20a)$$

and

$$E_0 \cong -\lambda (1 - 1/2\alpha^2 + 3/8\alpha^4 - 7/16\alpha^6 + \dots), \quad (8.20b)$$

where  $\alpha = g_S \mu_B B / \lambda$ . These expressions predict an isotropic splitting of the  $1s$  ( $^3T_2$ ) components, with a central component showing a nonlinear effect. The validity of this prediction is demonstrated in Fig. 8.30, showing the Zeeman splitting of the  $1s$  ( $^3T_2$ ) line of Fig. 6.15. In the Voigt configuration, both the  $\pi$  central component and the  $\sigma$  doublet are observed, but in the Faraday configuration, only the  $\sigma$  doublet is observed.

These results and those obtained at zero field allow one to determine the experimental values of the s-o interaction parameters, which are, as expected, larger for  $\text{Te}^0$  than for  $\text{Se}^0$  [120]. These measurements have been extended to higher values of the magnetic field and also to the s-o-split  $1\Gamma_7$  and  $1\Gamma_8$  components of the  $^2T_2$  state of  $\text{S}^+$  and  $\text{Se}^+$  [121].

### 8.3.1.2 Germanium

The first Zeeman measurement on donors in germanium for  $\mathbf{B} // \langle 100 \rangle$  for fields up to  $\sim 1.7$  T were reported in 1959 by Fan and Fisher [41], from which they deduced  $m_t = (0.077 \pm 0.005) m_e$ , a value close to the one obtained from CR measurements for free electrons (Table 3.4). Oscillatory magnetoabsorption as a function of the field or of the frequency, explained by the field dependence of the Zeeman components, was reported by Boyle [20]. The experimental results of Boyle and Howard [21] on the splitting of  $2p_{\pm 1}(\text{As})$  for fields up to 3 T were compared with variational calculations and a connection with the high-field limit established. Extensive measurements of the Zeeman

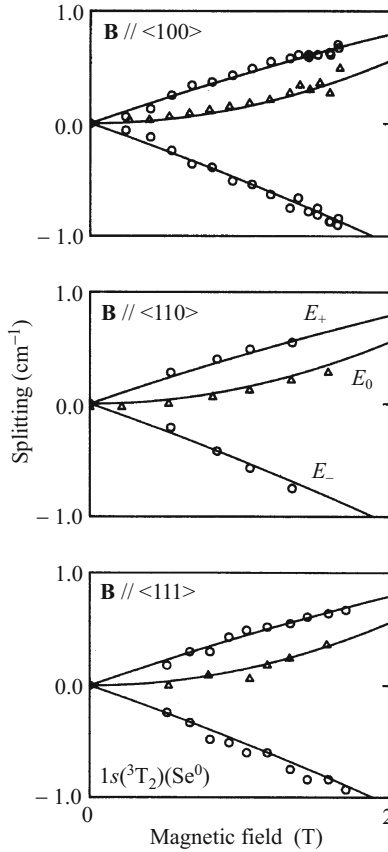


**Fig. 8.30.** Magnetic-field dependence of the Zeeman splitting of the  $1s(^3T_2)$  line of  $\text{Se}^0$  in silicon measured at 1.7 K in the Voigt configuration for three orientations of the sample. The theoretical curves (*solid lines*) are the same for each orientation (after [120]). Copyright 1988 by the American Physical Society

effect of the As and Sb donors in germanium at a temperature of  $\sim 2$  K were reported in several papers by Horii and Nisida ([62], and references therein) for fields up to 4.6 T ( $\gamma_B \sim 0.7$ ) parallel to a  $\langle 111 \rangle$  axis, and the Zeeman splitting was found to be given by expression (8.18). The spectra were characterized by the importance of the quadratic Zeeman effect, and for the Sb donor by the contribution of transitions from the  $1s(T_2)$  components separated from  $1s(A_1)$  by only 0.32 meV. The magnetic field dependence of the positions of the split components of the first lines of the As donor spectrum is shown in Fig. 8.31, where the solid and dashed lines are guides to the eye. In this figure are also shown the magnetic field dependences of components denoted  $a$ ,  $b$ , and  $c$ . Because of its slope,  $a$  is probably due to  $4f_{+B}$ , while  $b$  and  $c$  have been interpreted as donor levels associated with higher-energy Landau levels [62].

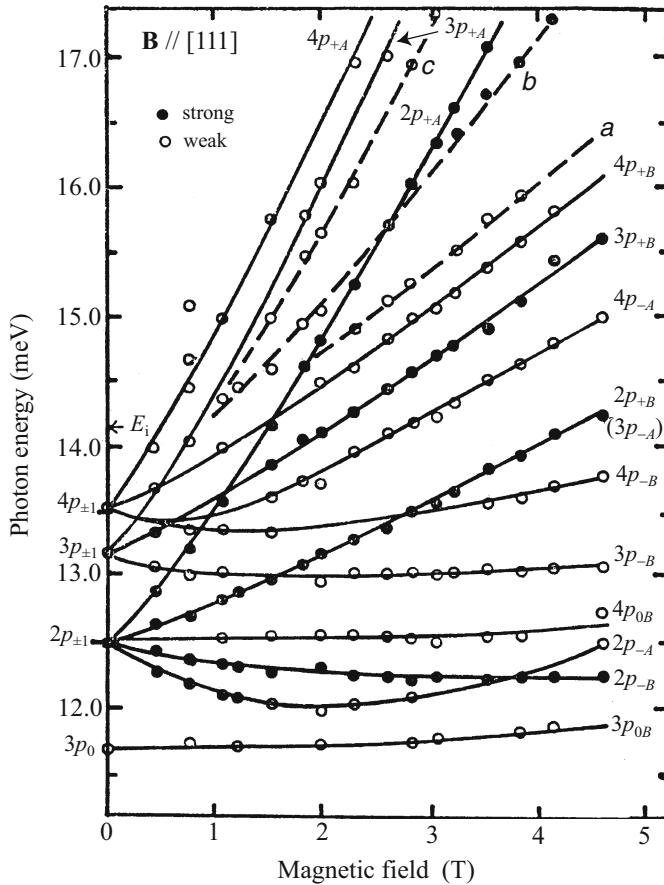


**Fig. 8.31.** Magnetic-field dependence of the Zeeman components of the As donor absorption lines in germanium for  $\mathbf{k} \parallel \mathbf{B} \parallel \langle 111 \rangle$ . Each  $np_{\pm 1}$  line gives four Zeeman components. With the notations of Table 8.14, valley 1 corresponds to  $A$  and valleys 2, 3, and 4 to  $B$ ). The energy  $E_i$  of As at zero field is indicated (after [62]). Reproduced with permission from the Physical Society of Japan

In Fig. 8.31, the split components are denoted  $np_+$  and  $np_-$  for  $np_{+1}$  and  $np_{-1}$ , followed by the valley index ( $A$  for the valley parallel to  $\mathbf{B}$ , with the largest Zeeman splitting and  $B$  for the other valleys).

Variational calculations of the eigenvalues of Hamiltonian (8.17) for donors in germanium have been made using EM wave functions to calculate the shifts of the  $1s$  and  $2p_0$  levels while the positions of the components of the  $2p_{\pm 1}$  and  $3p_{\pm 1}$  lines were calculated with harmonic-oscillator trial wave functions, taking into account the Landau levels structure [114]. These calculations, limited to the case where the magnetic field is along the main axis of the ellipsoid ( $\mathbf{B} \parallel \langle 111 \rangle$ ), were extended by Lee et al. [96] to the general case and values explicitly given for  $\mathbf{B} \parallel \langle 100 \rangle$  and  $\mathbf{B} \parallel \langle 111 \rangle$ .

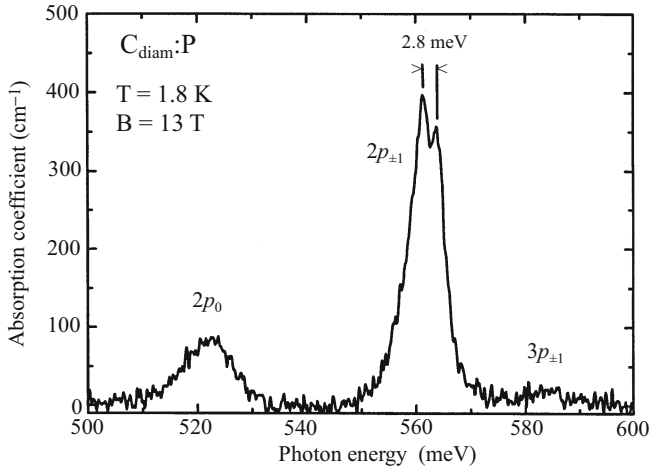


**Fig. 8.32.** Zeeman splitting of the  $2p_{\pm 1}$  line of P in diamond for  $\mathbf{B}/\langle 111 \rangle$ . [P] is  $\sim 2\text{--}3 \times 10^{18}$  at  $\text{cm}^{-3}$  (after [30]). Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission

Fine structures in the magnetic-field-tuned PTIS spectrum of P donors in germanium have been related to the spin splitting of the  $1s$  ( $A_1$ ) and  $1s$  ( $T_2$ ) levels [50]. Spin splitting is also involved in the anti-crossing of Zeeman components with opposite spin of  $1s$  ( $T_2$ ) states of As donors in germanium measured by four-wave spectroscopy, and the effect is more marked when a fixed uniaxial stress along the  $[110]$  direction is used to split the  $1s$  ( $T_2$ ) state into three sublevels ([151], and references therein).

### 8.3.1.3 Diamond

Under a magnetic field of 13 T along a  $\langle 111 \rangle$  direction, a weakly resolved splitting of 2.8 meV ( $\sim 23 \text{ cm}^{-1}$ ) of the  $2p_{\pm 1}$  line of P in diamond, shown in Fig. 8.32, has been observed by Casanova et al. [30].

The large width of the components and the small amplitude of the central dip produce an apparent reduction of the splitting, whose actual value can be estimated to be 2.9 meV, from which  $m_t = 0.31m_e$ , reported in Table 3.4, is derived using expression (8.18). Qualitatively, the splitting should be the same as the one for donors in silicon.

### 8.3.2 Shallow Acceptors

Formally, the linear Zeeman term in the EM acceptor Hamiltonian is similar to the one for free holes (expression (3.28), except that  $g_1$  and  $g_2$  are replaced by  $g'_1$  and  $g'_2$ . Calculations of the linear Zeeman splitting of the acceptor levels in germanium and silicon have been performed in the weak field limit, starting

with a study of the  $\Gamma_8^+$  ground state for deformed and non-deformed crystals by Bir et al. [16] and by Suzuki et al. [138] (the weak field limit is delimited in relation with the above-defined critical field  $B_0$ ). Perturbation calculations involving the  $\Gamma_8^+$  ground state and the  $\Gamma_8^-$ ,  $\Gamma_7^-$ , and  $\Gamma_6^-$  excited states of acceptors in germanium were also reported for  $\mathbf{B} // [001]$  by Lin Chung and Wallis [101].

A group theoretical study of the Zeeman effect of acceptors in silicon and germanium has been presented by Bhattacharjee and Rodriguez [15]. It was aimed towards the determination of the selection rules, energy splitting and relative intensities of the Zeeman components and it included the consideration of the terms quadratic in  $\mathbf{B}$ . The main assumption made in this study is that the Zeeman splitting remains small compared to the zero-field level separation. According to simple group theoretical considerations, the Zeeman part of the Hamiltonian for a  $\Gamma_6$  or  $\Gamma_7$  level can be written as:

$$H_Z^{(i)} = \mu_B g^{(i)} \mathbf{B} \cdot \boldsymbol{\sigma} + q^{(i)} B^2 \quad i = 6, 7, \quad (8.21)$$

where  $\boldsymbol{\sigma}$  is similar to the spin- $\frac{1}{2}$  matrix, and the one for a  $\Gamma_8$  level

$$H_Z^{(8)} = \mu_B (g'_1 \mathbf{B} \cdot \mathbf{J} + g'_2 (B_x J_x^3 + B_y J_y^3 + B_z J_z^3)) + q_1 \mathbf{B}^2 + q_2 (\mathbf{B} \cdot \mathbf{J})^2 + q_3 (B_x^2 J_x^2 + B_y^2 J_y^2 + B_z^2 J_z^2), \quad (8.22)$$

where  $\mathbf{J}$  is the angular momentum matrix for  $j = \frac{3}{2}$ . The  $g^{(i)}$  and  $g'_i$  are called the  $g$ -factors and the  $q^{(i)}$  and  $q_i$  the quadratic diamagnetic coefficients.

In the study by Bhattacharjee and Rodriguez, the Zeeman splitting has been explicitly calculated for the  $\Gamma_6$ ,  $\Gamma_7$ , and  $\Gamma_8$  levels as a function of the  $g^{(6)}$ ,  $g^{(7)}$ ,  $g'_1$  and  $g'_2$   $g$ -factors<sup>10</sup> for the magnetic field oriented along  $[001]$ ,  $[111]$ , and  $[110]$  crystal directions<sup>11</sup>. Except for  $\mathbf{B} // [001]$ , the  $\Gamma_8$  splitting also include quadratic terms. For  $\mathbf{B} // [001]$ ,  $[111]$  or  $[110]$ , the  $\Gamma_6$  and  $\Gamma_7$  levels ( $j = 1/2$ ) split into a doublet whose energy levels, with reference to the Zeeman Hamiltonian (8.19), are:

$$E_\mu^{(i)} = \mu \mu_B g^{(i)} \mathbf{B} + q^{(i)} \mathbf{B}^2 \quad (8.23)$$

with  $i = 6, 7$ , and  $\mu = 1/2, -1/2$ . The splitting is the same for the three orientations, given by  $\Delta E_{\pm 1/2}^{(i)} = \mu_B g^{(i)} \mathbf{B}$ .

A  $\Gamma_8$  level ( $j = 3/2$ ) splits into a quartet, where the energy of the linear part with  $\mathbf{B}$  can be expressed as:

$$E_\mu^{(8)} = \mu \mu_B g_{|\mu|} \mathbf{B}, \quad (8.24)$$

<sup>10</sup> There have been several notations for the equivalent of  $g'_1$  and  $g'_2$  for the magnetic field splitting of a  $\Gamma_8$  ground state: [19] has used parameters  $g$  and  $f$ , and [150] parameters  $K$  and  $L$ . The correspondences are  $g'_1 = g = K$  and  $g'_2 = f = L$ .

<sup>11</sup> In the expressions for the Zeeman Hamiltonian, it is assumed that for  $\mathbf{B} // \langle 100 \rangle$ ,  $\mathbf{B}$  is along the  $z$ -axis.

**Table 8.15.** Expressions of  $g_\mu$  describing the Zeeman splitting of a  $\Gamma_8$  level for the three main orientations of the magnetic field (after [23])

|            | $\mathbf{B} // [001]$ | $\mathbf{B} // [111]$              | $\mathbf{B} // [110]$                               |
|------------|-----------------------|------------------------------------|-----------------------------------------------------|
| $g_{1/2}$  | $g'_1 (1 + r)$        | $g'_1 (1 + 13r)$                   | $g'_1 \{ r [(2/r + 17)^2 + 27]^{1/2} - (1 + 7r) \}$ |
| $3g_{3/2}$ | $3g'_1 (1 + 9r)$      | $g'_1 r [(3/r + 23)^2 + 32]^{1/2}$ | $g'_1 \{ r [(2/r + 17)^2 + 27]^{1/2} + (1 + 7r) \}$ |

where the  $g$ -factor  $g_{|\mu|}$  is  $g_{1/2}$  or  $g_{3/2}$ , with an actual value depending on the orientation of  $\mathbf{B}$  with respect to the crystal axes.

For  $\mathbf{B} // [001]$ , with reference to the Zeeman Hamiltonian (8.20), the energy levels of the quadruplet are:

$$E_\mu^{(8)} = \mu\mu_B(g'_1 + g'_2\mu^2)\mathbf{B} + [q_1 + (q_2 + q_3)\mu^2]\mathbf{B}^2 \quad (8.25)$$

with  $\mu = +3/2, +1/2, -1/2, -3/2$ . Parameter  $r = g'_2/4g'_1$  is often used in the expression of the linear part of (8.23), except in Bhattacharjee and Rodriguez' paper, where  $p = g'_1/g'_2$  is used.

For  $\mathbf{B} // [111]$ , the energy levels are:

$$E_{\pm 1/2}^{(8)} = \pm 1/2\mu_B g'_1 (1 + 13r)\mathbf{B} + (q_1 + 1/4q_2 + 5/4q_3)\mathbf{B}^2, \quad (8.26a)$$

$$E_{\pm 3/2}^{(8)} = \pm 1/2\mu_B g'_1 r [(3/r + 23)^2 + 32]^{1/2} \mathbf{B} + (q_1 + 9/4q_2 + 5/4q_3)\mathbf{B}^2. \quad (8.26b)$$

The  $g$ -factors  $g_\mu$  of the  $\Gamma_8$  levels for the main orientations of the magnetic field are given in Table 8.15. The expressions for  $g'_1$ ,  $g'_2$  and  $r$  as a function of  $g_{1/2}[001]$  and  $g_{3/2}[001]$  are:

$$g'_1 = (9g_{1/2} - g_{3/2})/8, \quad (8.27a)$$

$$g'_2 = (g_{3/2} - g_{1/2})/2, \quad (8.27b)$$

$$r = \frac{g_{3/2} - g_{1/2}}{9g_{1/2} - g_{3/2}}. \quad (8.27c)$$

The separation  $\Delta E_{\pm\mu}(\mathbf{B})$  between two sublevels  $\pm\mu$  is given by  $2\mu\mu_B g_{|\mu|}\mathbf{B}$ . The value of  $g_{|\mu|}$  is thus given by  $8.638\Delta E_{\pm\mu}(\text{meV}) / (\mu_B(\text{T}))$ .

The selection rules between the Zeeman sublevels of the  $\Gamma_8$  ground state and those of the  $\Gamma_8$ ,  $\Gamma_7$ , and  $\Gamma_6$  excited states have been derived from group theory by Bhattacharjee and Rodriguez [15] for the double point group  $T_d$ . In this reference, the relative intensities of the Zeeman components of the  $\Gamma_8 \rightarrow \Gamma_6$ ,  $\Gamma_8 \rightarrow \Gamma_7$ , and  $\Gamma_8 \rightarrow \Gamma_8$  transitions for the main orientations of  $\mathbf{B}$  have also been derived.  $O_h$  point group symmetry of the acceptor Hamiltonian has been considered rather than  $T_d$  by Schmitt et al. [128] and while not modifying the physical results, it leads to some changes in the ordering of labels and in the corresponding selection rules [17]. As this later notation is

**Table 8.16.** Selection rules and polarizations for the transitions between the Zeeman sublevels of the ground state and those of the  $\Gamma_6$ ,  $\Gamma_7$ , and  $\Gamma_8$  excited states of shallow acceptors in silicon and germanium for  $\mathbf{B} // [001]$ . The point-group symmetries with the magnetic field are  $\bar{S}_4^a$  for  $\bar{T}_d$  and  $\bar{C}_{4h}$  for  $O_h$ . The first polarization is for  $\bar{S}_4$  and the second one for  $\bar{C}_{4h}$  (after [15, 128])

| $\bar{T}_d, \bar{O}_h$ |        |                           | Ground state $\Gamma_8, \Gamma_8^+$            |                                                |                                                |                                                |
|------------------------|--------|---------------------------|------------------------------------------------|------------------------------------------------|------------------------------------------------|------------------------------------------------|
|                        | $\mu$  |                           | $+3/2$                                         | $+1/2$                                         | $-1/2$                                         | $-3/2$                                         |
|                        |        | $\bar{S}_4, \bar{C}_{4h}$ | $\Gamma_6, \Gamma_8^+$                         | $\Gamma_7, \Gamma_5^+$                         | $\Gamma_8, \Gamma_6^+$                         | $\Gamma_5, \Gamma_7^+$                         |
| $\Gamma_6, \Gamma_6^-$ | $+1/2$ | $\Gamma_5, \Gamma_7^-$    | $\mathbf{E}_{\perp(-)}, \mathbf{E}_{\perp(+)}$ | $\mathbf{E}_{//}, 0$                           | $\mathbf{E}_{\perp(+)}, \mathbf{E}_{\perp(-)}$ | $0, \mathbf{E}_{//}$                           |
|                        | $-1/2$ | $\Gamma_6, \Gamma_8^-$    | $0, \mathbf{E}_{//}$                           | $\mathbf{E}_{\perp(-)}, \mathbf{E}_{\perp(+)}$ | $\mathbf{E}_{//}, 0$                           | $\mathbf{E}_{\perp(+)}, \mathbf{E}_{\perp(-)}$ |
| $\Gamma_7, \Gamma_7^-$ | $+1/2$ | $\Gamma_7, \Gamma_5^-$    | $\mathbf{E}_{\perp(+)}, \mathbf{E}_{\perp(-)}$ | $0, \mathbf{E}_{//}$                           | $\mathbf{E}_{\perp(-)}, \mathbf{E}_{\perp(+)}$ | $\mathbf{E}_{//}, 0$                           |
|                        | $-1/2$ | $\Gamma_8, \Gamma_6^-$    | $\mathbf{E}_{//}, 0$                           | $\mathbf{E}_{\perp(+)}, \mathbf{E}_{\perp(-)}$ | $0, \mathbf{E}_{//}$                           | $\mathbf{E}_{\perp(-)}, \mathbf{E}_{\perp(+)}$ |
| $\Gamma_8, \Gamma_8^-$ | $+3/2$ | $\Gamma_6, \Gamma_8^-$    | $0, \mathbf{E}_{//}$                           | $\mathbf{E}_{\perp(-)}, \mathbf{E}_{\perp(+)}$ | $\mathbf{E}_{//}, 0$                           | $\mathbf{E}_{\perp(+)}, \mathbf{E}_{\perp(-)}$ |
|                        | $+1/2$ | $\Gamma_7, \Gamma_5^-$    | $\mathbf{E}_{\perp(+)}, \mathbf{E}_{\perp(-)}$ | $0, \mathbf{E}_{//}$                           | $\mathbf{E}_{\perp(-)}, \mathbf{E}_{\perp(+)}$ | $\mathbf{E}_{//}, 0$                           |
|                        | $-1/2$ | $\Gamma_8, \Gamma_6^-$    | $\mathbf{E}_{//}, 0$                           | $\mathbf{E}_{\perp(+)}, \mathbf{E}_{\perp(-)}$ | $0, \mathbf{E}_{//}$                           | $\mathbf{E}_{\perp(-)}, \mathbf{E}_{\perp(+)}$ |
|                        | $-3/2$ | $\Gamma_5, \Gamma_7^-$    | $\mathbf{E}_{\perp(-)}, \mathbf{E}_{\perp(+)}$ | $\mathbf{E}_{//}, 0$                           | $\mathbf{E}_{\perp(+)}, \mathbf{E}_{\perp(-)}$ | $0, \mathbf{E}_{//}$                           |

<sup>a</sup> In the character table for  $\bar{S}_4$ , p. 40 of Koster et al.'s book referenced in appendix B, the characters associated with the  $\bar{S}_4$  class (last column) for the  $\Gamma_5, \Gamma_6, \Gamma_7$ , and  $\Gamma_8$  IRs should read  $\omega^3, -\omega, -\omega^3$ , and  $\omega$ , respectively, where  $\omega = \exp(\pi i/4)$

**Table 8.17.** Same as Table 8.16 for  $\mathbf{B} // [111]$  (point-group symmetry  $\bar{C}_3$ ) (after [15])

| $\bar{T}_d$ |        |             | Ground state $\Gamma_8$ |                         |                         |                         |
|-------------|--------|-------------|-------------------------|-------------------------|-------------------------|-------------------------|
|             | $\mu$  |             | $+3/2$                  | $+1/2$                  | $-1/2$                  | $-3/2$                  |
|             |        | $\bar{C}_3$ | $\Gamma_6$              | $\Gamma_4$              | $\Gamma_5$              | $\Gamma_6$              |
| $\Gamma_6$  | $+1/2$ | $\Gamma_4$  | $\mathbf{E}_{\perp(-)}$ | $\mathbf{E}_{//}$       | $\mathbf{E}_{\perp(+)}$ | $\mathbf{E}_{\perp(-)}$ |
|             | $-1/2$ | $\Gamma_5$  | $\mathbf{E}_{\perp(+)}$ | $\mathbf{E}_{\perp(-)}$ | $\mathbf{E}_{//}$       | $\mathbf{E}_{\perp(+)}$ |
| $\Gamma_7$  | $+1/2$ | $\Gamma_4$  | $\mathbf{E}_{\perp(-)}$ | $\mathbf{E}_{//}$       | $\mathbf{E}_{\perp(+)}$ | $\mathbf{E}_{\perp(-)}$ |
|             | $-1/2$ | $\Gamma_5$  | $\mathbf{E}_{\perp(+)}$ | $\mathbf{E}_{\perp(-)}$ | $\mathbf{E}_{//}$       | $\mathbf{E}_{\perp(+)}$ |
| $\Gamma_8$  | $+3/2$ | $\Gamma_6$  | $\mathbf{E}_{//}$       | $\mathbf{E}_{\perp(+)}$ | $\mathbf{E}_{\perp(-)}$ | $\mathbf{E}_{//}$       |
|             | $+1/2$ | $\Gamma_4$  | $\mathbf{E}_{\perp(-)}$ | $\mathbf{E}_{//}$       | $\mathbf{E}_{\perp(+)}$ | $\mathbf{E}_{\perp(-)}$ |
|             | $-1/2$ | $\Gamma_5$  | $\mathbf{E}_{\perp(+)}$ | $\mathbf{E}_{\perp(-)}$ | $\mathbf{E}_{//}$       | $\mathbf{E}_{\perp(+)}$ |
|             | $-3/2$ | $\Gamma_6$  | $\mathbf{E}_{//}$       | $\mathbf{E}_{\perp(+)}$ | $\mathbf{E}_{\perp(-)}$ | $\mathbf{E}_{//}$       |

used for the interpretation of some experimental results for germanium and for GaAs, the two labellings and selection rules are given in Table 8.16. For  $\mathbf{B} // [111]$  and  $\mathbf{B} // [110]$ , the two notations are the same. The right-handed coordinate system  $(x', y', z')$  is chosen with  $z'$  along  $\mathbf{B}$ . The right-handed (rcp) and left-handed circular (lcp) polarizations with respect to  $\mathbf{B}$  are denoted here by  $\mathbf{E}_+$  and  $\mathbf{E}_-$ , respectively, and the longitudinal polarization  $\mathbf{E}_{//}$  or  $\mathbf{E} // \mathbf{B}$ . Practically, as linearly polarized radiation can be decomposed into two opposite circularly polarized radiations,  $\mathbf{E}_+$  and  $\mathbf{E}_-$  correspond to  $\mathbf{E}_{\perp \mathbf{B}}$ . In the following tables,  $\mathbf{E}_+$  and  $\mathbf{E}_-$  are, therefore, denoted  $\mathbf{E}_{\perp(+)}$  and  $\mathbf{E}_{\perp(-)}$ , respectively (Table 8.17 and Table 8.18).

**Table 8.18.** Same as Table 8.16 for  $\mathbf{B} // [110]$ . The point-group symmetries with the magnetic field are  $\bar{C}_{1h}$  for  $\bar{T}_d$  and  $\bar{C}_{2h}$  for  $\bar{O}_h$ . For the orientation of  $\mathbf{B}$ , the selection rules are the same for lcp and rcv radiation and no index is added to  $\mathbf{E}_\perp$ , but they are inverted for  $\bar{O}_h$  and  $\bar{T}_d$  (after [15, 128])

| $\bar{T}_d, \bar{O}_h$ |        | Ground state $\Gamma_8$      |                                     |                                     |                                     |                                     |
|------------------------|--------|------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|
|                        | $\mu$  |                              | $+3/2$                              | $+1/2$                              | $-1/2$                              | $-3/2$                              |
|                        |        | $\bar{C}_{1h}, \bar{C}_{2h}$ | $\Gamma_3$                          | $\Gamma_4$                          | $\Gamma_3$                          | $\Gamma_4$                          |
| $\Gamma_6$             | $+1/2$ | $\Gamma_3$                   | $\mathbf{E}_\perp, \mathbf{E}_{//}$ | $\mathbf{E}_{//}, \mathbf{E}_\perp$ | $\mathbf{E}_\perp, \mathbf{E}_{//}$ | $\mathbf{E}_{//}, \mathbf{E}_\perp$ |
|                        | $-1/2$ | $\Gamma_4$                   | $\mathbf{E}_{//}, \mathbf{E}_\perp$ | $\mathbf{E}_\perp, \mathbf{E}_{//}$ | $\mathbf{E}_{//}, \mathbf{E}_\perp$ | $\mathbf{E}_\perp, \mathbf{E}_{//}$ |
| $\Gamma_7$             | $+1/2$ | $\Gamma_4$                   | $\mathbf{E}_{//}, \mathbf{E}_\perp$ | $\mathbf{E}_\perp, \mathbf{E}_{//}$ | $\mathbf{E}_{//}, \mathbf{E}_\perp$ | $\mathbf{E}_\perp, \mathbf{E}_{//}$ |
|                        | $-1/2$ | $\Gamma_3$                   | $\mathbf{E}_\perp, \mathbf{E}_{//}$ | $\mathbf{E}_{//}, \mathbf{E}_\perp$ | $\mathbf{E}_\perp, \mathbf{E}_{//}$ | $\mathbf{E}_{//}, \mathbf{E}_\perp$ |
| $\Gamma_8$             | $+3/2$ | $\Gamma_3$                   | $\mathbf{E}_\perp, \mathbf{E}_{//}$ | $\mathbf{E}_{//}, \mathbf{E}_\perp$ | $\mathbf{E}_\perp, \mathbf{E}_{//}$ | $\mathbf{E}_{//}, \mathbf{E}_\perp$ |
|                        | $+1/2$ | $\Gamma_4$                   | $\mathbf{E}_{//}, \mathbf{E}_\perp$ | $\mathbf{E}_\perp, \mathbf{E}_{//}$ | $\mathbf{E}_{//}, \mathbf{E}_\perp$ | $\mathbf{E}_\perp, \mathbf{E}_{//}$ |
|                        | $-1/2$ | $\Gamma_3$                   | $\mathbf{E}_\perp, \mathbf{E}_{//}$ | $\mathbf{E}_{//}, \mathbf{E}_\perp$ | $\mathbf{E}_\perp, \mathbf{E}_{//}$ | $\mathbf{E}_{//}, \mathbf{E}_\perp$ |
|                        | $-3/2$ | $\Gamma_4$                   | $\mathbf{E}_{//}, \mathbf{E}_\perp$ | $\mathbf{E}_\perp, \mathbf{E}_{//}$ | $\mathbf{E}_{//}, \mathbf{E}_\perp$ | $\mathbf{E}_\perp, \mathbf{E}_{//}$ |

The expression of the  $g$ -factors when considering an  $O_h$  point group symmetry for the acceptor Hamiltonian instead of  $T_d$  leads to changes in the attributions of the Zeeman sublevels and this has been used by Atzmüller et al. [7] and Schmitt et al. [128]. Its consequences for an isolated  $\Gamma_8$  level has been given by Bir et al. [17], but when one considers transitions between two  $\Gamma_8$  levels, one must keep a reference identical for the two symmetries and the choice is to keep the  $m_j$  attributions for the ground state split components unchanged, so that  $g'_1(T_d)$  and  $g'_1(O_h)$  on the one hand and  $g'_2(T_d) = g'_2(O_h)$  on the other hand are the same. With this proviso, the correspondence for the excited states are obtained by taking a ground state sublevel with a given value of  $m_j$  and considering the transitions from this state to the excited states with the same polarization characteristics for both point group symmetries (the polarization characteristics are physical properties independent of the choice between  $T_d$  and  $O_h$ ). This can be done with the help of Table 8.16, and taking for instance the  $m_j = -3/2$  ground state, it can be checked that  $m_j = +3/2, +1/2, -1/2$ , and  $-3/2$  excited state sublevels for the  $\bar{S}_4$  point group correspond to the  $m_j = -1/2, -3/2, +3/2$ , and  $+1/2$  sublevels, respectively, for the  $\bar{C}_{4h}$  point group. The relationship between the  $g$ -factors of the excited states for a line  $J$  of an acceptor spectrum for the two point group symmetries are the same. They are given below to convert the  $g$ -factors obtained with  $T_d$  symmetry into those in  $O_h$  symmetry, but the point group symmetries can be inverted as well:

$$g_1^{(J)}(T_d) = - \left[ 10g_1^{(J)}(O_h) + 91/4g_2^{(J)}(O_h) \right] / 3, \quad (8.28a)$$

$$g_2^{(J)}(T_d) = \left[ 4g_1^{(J)}(O_h) + 10g_2^{(J)}(O_h) \right] / 3. \quad (8.28b)$$



The spacing between the  $\pm 1/2$  and  $\pm 3/2$  sublevels in the  $O_h$  starting symmetry, proportional to  $g_{1/2}^{(J)}(O_h)$  and  $3g_{3/2}^{(J)}(O_h)$ , are naturally different from those in the  $T_d$  symmetry, but they are still given by the same formal expressions as those for the  $T_d$  symmetry, but with  $g_1^{(J)}(O_h)$  and  $g_2^{(J)}(O_h)$   $g$ -factor. This also holds true for the ratio  $r^{(J)}(O_h)$ , still defined by  $g_2^{(J)}(O_h)/4g_1^{(J)}(O_h)$ , but with a value different from  $r^{(J)}(T_d)$ . An application of these expressions will be given in the discussion of the Zeeman results in germanium and GaAs.

Later on, the eigenstates of the EM Hamiltonian including the magnetic field for acceptors in cubic semiconductors have been calculated by a variational method by Broeckx [22]. This Hamiltonian included the s-o split  $\Gamma_7 VB$  and the calculations were performed for  $\mathbf{B} // [001]$  and  $\mathbf{B} // [111]$  for field strengths in the 0–5 T range. In an application to acceptors in germanium, the energy levels corresponding to the 36 odd-parity Zeeman excited substates corresponding to lines  $G$ ,  $D$ ,  $C$ ,  $B$ ,  $A_4$ ,  $A_3$ ,  $A_2$ , and  $A_1$  of the acceptor Ge spectrum (see Table 7.9) were calculated, together with those of the Zeeman quadruplet ground state. These rather general calculations involved quadratic effects and they showed the interactions between substates of different lines with the same symmetry. The OS of the transitions from the ground state sublevels were also calculated and used to produce simulated spectra. The results obtained will be compared later with the experimental observations.

At about the same time, another detailed theoretical study was presented with intended applications to the acceptor spectrum in germanium and GaAs up to relatively large values of  $\mathbf{B}$  parallel to the three main crystal orientations [128]. Considering the  $VB$  s-o splitting in these crystals, the  $\Gamma_7 VB$  was disregarded so that the calculations cannot be transposed to acceptors in silicon. The numerical method (the “matrix method”) used to determine the eigenvalues in this study is non-variational and different from the finite-element method of Said et al. (ref. 51 in Chap 5). The results of these calculations will also be compared later with the experimental observations.

### 8.3.2.1 Silicon

The Zeeman effect of  $Al$  in silicon was reported by Zwerdling et al. [154]. The results of absorption measurements of  $Si:B$  were reported by Merlet et al. [104] and the Zeeman splitting of the Raman  $1\Gamma_8^+ \rightarrow 1\Gamma_7^+$  boron line by Cherlow et al. [35].

Before discussing the optical results, it seems appropriate to present the results on the acceptor ground state splitting derived from ESR measurements. The first ESR measurements were obtained under uniaxial stress [42] because of the presence in the early crystals of random internal strains due to dislocations and other imperfections, especially in the FZ crystals. These strains produced a splitting of the ground state varying with the acceptor positions, resulting in an overall broadening of the ESR lines. This broadening

prevented the observation of the ESR lines unless an external uniaxial stress which is large compared to the internal stress is applied. Later, the production of nominally dislocation-free FZ crystals allowed us to obtain useful acceptor ESR spectrum in silicon at zero external stress and values reported for  $g'_1$  and  $g'_2$  for the ground state of boron were  $-0.071 \pm 0.002$  and  $-0.031 \pm 0.001$ , respectively [110]. The negative sign corresponds to an ordering deduced from the ESR measurements under stress [16,42], and a positive sign corresponding to an ordering of  $3/2, 1/2, -1/2, -3/2$ , with energies increasing from the top of the *VB* has been adopted [138].

The magneto-Raman measurements of [35] were performed up to 9.16 T at LHeT for the three main orientations of **B** on a sample giving a relatively broad Raman line<sup>12</sup> (FWHM of 0.45 meV ( $\sim 3.6 \text{ cm}^{-1}$ )). They were interpreted by considering only the Zeeman splitting of the  $1\Gamma_8^+$  state and the values of  $g'_1$  and  $g'_2$  so obtained were  $0.84 \pm 0.09$  and  $0.13 \pm 0.08$ , respectively.

The Zeeman absorption measurements on boron-doped samples were performed in the Voigt and Faraday configurations for the main orientations of the magnetic field up to 6.4 T at a temperature  $\sim 11 \text{ K}$  [104]. The lines 1, 2, 3 and 4–5–6 of the boron spectrum were investigated at a resolution of  $\sim 0.12 \text{ meV}$  ( $1 \text{ cm}^{-1}$ ), so that only line 6 (4A) was resolved from line 4 (see Table 7.1 for the line labels and positions), but the spectra were resolution-limited. The components show a small quadratic effect, absent for lines 1 and 2. The splitting of these two lines with increasing values of **B** // [001] is shown in Fig. 8.33. The components are represented in alphabetical order indexed by the line number for increasing values of the slope *a* of the energy shift of the component with respect to the zero-field position.

While 11 of the 12 possible components are observed for line 1, only 6 are observed for line 2 because of the larger widths of the components of that line. A detailed investigation of line 3 was difficult because of its small intensity and the interpretation of the results on lines 4–6 (4–4A) flawed by ignoring line 5. Starting from the assumption that the ground state splitting  $E_{\pm 1/2}(\mathbf{B})$  and  $E_{\pm 3/2}(\mathbf{B})$  are symmetric with respect to the zero-field position of the level, the attributions of the split components of lines 1 and 2 allow one to estimate a **B**-dependent shift  $s_{\pm\mu}(I)$  of the centre of gravities of the  $\pm\mu$  components of line *I* with respect to the zero-field position  $E_{I(0)}$  of the excited state. This shift is given by:

$$s_{\pm\mu}(I) = \left\{ \left[ E_{(I)+\mu}(\mathbf{B}) - E_{(I)-\mu}(\mathbf{B}) \right] / 2 - E_I(0) \right\} / B. \quad (8.29)$$

It has been found that  $s_{\pm\mu}(I)$  was dependent on the orientation of **B**. Values of the *g*-factors of the boron  $1\Gamma_8^+$  ground state and of the excited states of line 1 ( $1\Gamma_8^-$ ) and line 2 ( $2\Gamma_8^-$ ) were deduced from this study and are given in Table 8.19.

<sup>12</sup> Raman scattering measurements require larger impurity concentrations than absorption measurements.

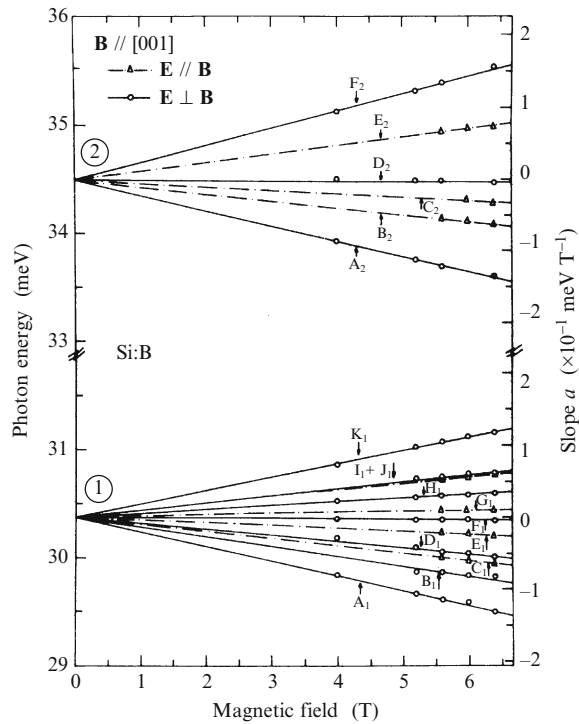


**Fig. 8.33.** Zeeman splitting of lines 1 ( $1\Gamma_8^-$ ) and 2 ( $2\Gamma_8^-$ ) of B in silicon for  $\mathbf{B} // [001]$  ([104]). Copyright 1975 by the American Physical Society

**Table 8.19.** Experimental values of factors  $g_{1/2}$  and  $g_{3/2}$  of the ground ( $1\Gamma_8^+$ ) and excited states of lines 1 and 2 of the boron acceptor in silicon as a function of the orientation of the magnetic field and values of the corresponding  $g_1$  and  $r$  parameters. The field dependence of the shift  $s_{\pm\mu}(I)$  of the centre of gravity of the  $E_{I\pm 1/2}$  and  $E_{I\pm 3/2}$  sublevels with the orientation of  $\mathbf{B}$ , expressed in units of  $10^{-2} \text{ meV T}^{-1}$  (after [104])

| Level         |                  | $\mathbf{B} // [001]$ | $\mathbf{B} // [111]$ | $\mathbf{B} // [110]$ |             |                    |
|---------------|------------------|-----------------------|-----------------------|-----------------------|-------------|--------------------|
| $1\Gamma_8^+$ | $g_{1/2}$        | $1.04 \pm 0.06$       | $1.19 \pm 0.08$       | $1.13 \pm 0.05$       | $g_1'$      | $1.03 \pm 0.06$    |
|               | $3g_{3/2}$       | $3.36 \pm 0.06$       | $3.33 \pm 0.09$       | $3.33 \pm 0.09$       | $r$         | $0.010 \pm 0.06$   |
| $1\Gamma_8^-$ | $g_{1/2}^{(1)}$  | $-1.09 \pm 0.05$      | $-0.26 \pm 0.10$      | $2.02 \pm 0.10$       | $g_1^{(1)}$ | $-1.16 \pm 0.06$   |
|               | $3g_{3/2}^{(1)}$ | $-1.71 \pm 0.12$      | $-0.26 \pm 0.10$      | $0.57 \pm 0.09$       | $r^{(1)}$   |                    |
|               | $s_{\pm 1/2}(1)$ | -0.5                  | -0.9                  | -0.3                  |             |                    |
|               | $s_{\pm 3/2}(1)$ | -1.2                  | -0.6                  | -1.7                  |             |                    |
|               |                  |                       |                       |                       |             |                    |
| $2\Gamma_8^-$ | $g_{1/2}^{(2)}$  | $-1.86 \pm 0.16$      | $1.71 \pm 0.16$       | $1.79 \pm 0.13$       | $g_1^{(2)}$ | $-2.17 \pm 0.76$   |
|               | $3g_{3/2}^{(2)}$ | $1.59 \pm 0.15$       | $1.80 \pm 0.15$       | $0.62 \pm 0.12$       | $r^{(2)}$   | $-0.137 \pm 0.008$ |
|               | $S_{\pm 1/2}(2)$ | 0.8                   | 0.8                   | 0.11                  |             |                    |
|               | $s_{\pm 3/2}(2)$ | 1.2                   | 0.11                  | 0.05                  |             |                    |

This table shows the importance of the contribution of the ground state to the Zeeman splitting of the lines, a situation which is the inverse of the one encountered in germanium, as will be seen later. It also shows that while the ground state splitting is nearly isotropic with respect to the orientation of the magnetic field, the  $1\Gamma_8^-$  and  $1\Gamma_8^-$  excited display a strong anisotropy implying a crossing of the  $E_{1/2}$  and  $E_{3/2}$  levels with the orientation changes of the magnetic field.

A study of the Zeeman effect of the PL lines of the excitons bound to group-III acceptors in silicon by Karasyuk et al. [75] has allowed us to obtain the ground-state  $g$ -factors and the quadratic coefficients  $q_2$  and  $q_3$  of these acceptors.

A comparison of the  $g$ -factors of the ground state obtained from absorption and PL measurements with those obtained from ESR, dielectric resonance absorption is shown in Table 8.20.

It is not easy to determine the values of the  $g$ -factors of free holes in silicon because in the CR experiments, one is more interested in effective masses than in the  $g$ -factors. It is usually assumed that  $g_2$  for the  $VB$  is  $\sim 0$  [16]. A value of parameter  $\kappa$  of the  $VB$  of silicon, quoted by Lawaetz (ref. 55 of Chap. 3), is  $-0.26$  and  $g_1 = 2\kappa$  should then be  $0.52$ .

### 8.3.2.2 Germanium

The splitting discussed here for germanium and in the next subsection for cubic III–V and II–VI compounds concern the ground and excited states of lines  $G$ ,  $D$ ,  $C$ , and  $B$  of the acceptor spectra.. In different references, the

**Table 8.20.** Comparison of the experimental  $g'_1$  and  $g'_2$  of the acceptor ground state in silicon obtained from different sources with calculated values. The values obtained from ESR under stress by Shimizu and Tanaka<sup>c</sup> have been converted into the zero-stress  $g$ -factors by Neubrand<sup>b</sup>. The last two columns give the quadratic coefficients of the Zeeman Hamiltonian (8.20)

|                    | $g'_1$ | $g'_2$   | $r$      | $q_2(\mu\text{eV T}^{-2})$ | $q_3(\mu\text{eV T}^{-2})$ |
|--------------------|--------|----------|----------|----------------------------|----------------------------|
| B <sup>a</sup>     | 1.03   | 0.04     | 0.010    | 0.21 <sup>e</sup>          | 0.07 <sup>e</sup>          |
| B <sup>b</sup>     | 1.071  | 0.031    | 0.007    |                            |                            |
| B <sup>c</sup>     | 1.048  | 0.061    | 0.015    |                            |                            |
| B <sup>d</sup>     | 1.070  | 0.033    | 0.008    |                            |                            |
| Al <sup>e</sup>    | 0.98   | $-0.01$  | $-0.003$ | 0.11                       | $-0.03$                    |
| Al <sup>d</sup>    | 0.997  | $-0.014$ | $-0.004$ |                            |                            |
| Ga <sup>e</sup>    | 0.96   | $-0.01$  | $-0.003$ | 0.09                       | $-0.02$                    |
| Ga <sup>d</sup>    | 0.993  | $-0.017$ | $-0.004$ |                            |                            |
| In <sup>e</sup>    | 0.86   | $-0.05$  | $-0.015$ | 0.29                       | $-0.01$                    |
| In <sup>d</sup>    | 0.885  | $-0.056$ | $-0.016$ |                            |                            |
| Tl <sup>e</sup>    | 0.60   | 0.05     | 0.021    | 0.20                       | $-0.03$                    |
| Calc. <sup>f</sup> | 0.93   | 0.13     | 0.035    |                            |                            |

<sup>a</sup> [104], <sup>b</sup> [110], <sup>c</sup> [131], <sup>d</sup> [85], <sup>e</sup> [75], <sup>f</sup> [138]

ground state can be found labelled  $1\Gamma_8^+$  or  $1S_{3/2}(\Gamma_8)$ . For germanium, the excited states of lines  $G$ ,  $D$ ,  $C$ , and  $B$  correspond to  $1\Gamma_8^-$ ,  $2\Gamma_8^-$ ,  $3\Gamma_8^+1\Gamma_7^-$  and  $4\Gamma_8^-$ , respectively (Table 7.9). For cubic compound semiconductors, the excited state of line  $G$  is denoted  $1\Gamma_8^-$  or  $2P_{3/2}(\Gamma_8)$ , the one of line  $D$ ,  $2\Gamma_8^-$  or  $2P_{5/2}(\Gamma_8)$ , and the one of line  $C$ ,  $3\Gamma_8^-$  or  $2P_{5/2}(\Gamma_7)$  (Table 7.21).

The Zeeman effect of group-III acceptors in germanium was first reported by Fisher and Fan [43] and later in more detail by Soepangkat and Fisher [133] and by Broeckx et al. [23]. Zeeman measurements of the neutral double acceptors  $\text{Zn}^0$  and  $\text{Hg}^0$  were also reported by Moore [107].

Magnetoacoustic resonance attenuation measurements in Ga-doped germanium at LHeT in the range 0–12 T have allowed [142] to measure the  $g$ -factors of the ground state of this acceptor, including two of the  $q_i$  quadratic terms of expression (8.22). The values thus obtained are:

$$g'_1 = -0.16 \pm 0.08 \quad q_2 = (4.3 \pm 1.7) \times 10^{-4} \text{ meVT}^{-2},$$

$$g'_2 = 0.08 \pm 0.04 \quad (r = -0.125) \quad q_3 = (-5.2 \pm 1.7) \times 10^{-4} \text{ meVT}^{-2}.$$

While these values have been obtained for the Ga acceptor, they should not differ markedly for the other group-III acceptors as magnetic effects are relativistic effects which are relatively insensitive to the chemical effects at and in the near vicinity of the acceptor ion [23]. Then, for the first Zeeman measurements performed for  $B \sim 2.5$  T or less, it was justified to neglect the ground state splitting as its maximum amplitude was less than  $\sim 0.06$  meV ( $0.5 \text{ cm}^{-1}$ ).

High-resolution measurements of the Zeeman splitting of  $B$ ,  $Al$ , and Ga spectra in germanium have been reported by Fisher's group [9, 44] for magnetic fields up to 7 T parallel to  $[001]$ . Assuming that the ordering of the Zeeman sublevels of lines  $G$  and  $D$  was the one predicted by the calculations, allowed a quantitative self-consistent interpretation of the Zeeman splitting of these lines. The low-field dependence of lines  $D(B)$  and  $D(Al)$  is shown in Fig. 8.34a for  $\mathbf{B} // [001]$ , compared to that of line  $B(Al)$  in Fig. 8.34b. The transitions are denoted  $(i, j)$ , where  $i$  and  $j$  correspond to the indices of the  $IRs \Gamma_i^+$  of Table 8.16 for point group  $\bar{C}_{4h}$ .

The low-field splitting of line  $D$  is similar for both acceptors and it increases monotonously with the field. Eight of the ten possible transitions are observed. It contrasts with the apparently erratic splitting of  $B(Al)$  where the 12 components allowed for both polarizations are, however observed, and a similar result is obtained for  $B(B)$  [44]. The calculations of [22] and [128] can reproduce the splitting observed. For higher values of the magnetic field, the apparently simple Zeeman splitting of  $D(Al)$  can become more intricate, as seen in Fig. 8.35.

The determination of the experimental splitting of the  $1\Gamma_8^+$  ground state for the  $B$  and  $Ga$  acceptors from the attributions of the high-resolution Zeeman spectra gives an ordering, in agreement with those calculated by Broeckx [22], but it shows that the  $\pm 1/2$  sublevels shift linearly with field with a positive  $g_{1/2}$  factor whereas the  $\pm 3/2$  sublevels show nonlinear shifts and splitting,

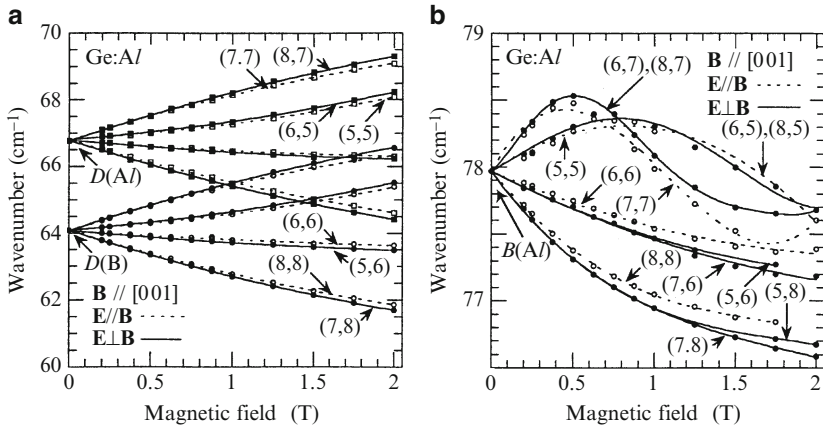


**Fig. 8.34.** (a) Field dependence of the Zeeman components of lines  $D(AI)$  and  $D(B)$  in germanium. The component denoted (7,8) corresponds to the  $\Gamma_7^+ (m - 3/2) \rightarrow \Gamma_8^+ (+3/2)$  transition of Table 8.13, observed for  $\mathbf{E} \perp \mathbf{B}$ , and so on. (b) is the same for line  $B(AI)$ . The lines are guide to the eye (after [9]). Copyright 1997, with permission from World Scientific Publishing Co. Pte. Ltd, Singapore

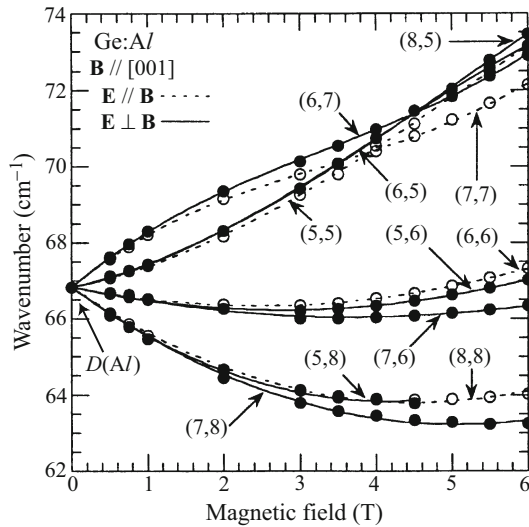


**Fig. 8.35.** Field dependence of the Zeeman components of line  $D(AI)$  in germanium showing the differences with the low-field dependence of Fig. 8.35(a) and the observation of three new components. The full curves are polynomial fits to the data and the labelling is the same as that of Fig. 8.34 (after [9]). Copyright 1997, with permission from World Scientific Publishing Co. Pte. Ltd, Singapore

**Table 8.21.** Comparison of the experimental  $g$ -factors  $g'_1$  and  $g'_2$  of the boron and aluminium ground states in germanium obtained from different sources with the calculated ones

| Ref.   | [44]               |                    | [142]            | [22]  | [128]   |
|--------|--------------------|--------------------|------------------|-------|---------|
|        | B                  | Ga                 | Ga               | Calc. | Calc.   |
| $g'_1$ | $-0.164 \pm 0.001$ | $-0.132 \pm 0.002$ | $-0.16 \pm 0.08$ | -0.45 | -0.5904 |
| $g'_2$ | $+0.091 \pm 0.001$ | $+0.084 \pm 0.002$ | $+0.08 \pm 0.04$ | +0.22 | +0.2257 |
| $r$    | -0.139             | -0.159             | -0.13            | -0.12 | -0.096  |

**Table 8.22.** Experimental and calculated  $g$ -factors of the excited states of lines  $G$ ,  $D$ , and  $B$  in germanium. ( $r^{(J)} = g_2^{(J)}/4g_1^{(J)}$ ). Schmitt et al. [128] have calculated  $g_i^{(D)}(O_h)$ , which have been converted into  $g_1^{(D)}(T_d)$  using expressions (8.28a) and (8.28b)

|             | B <sup>a</sup> | Al <sup>a</sup> | Ga <sup>b</sup> | Theory <sup>c</sup> | Theory <sup>a</sup> |
|-------------|----------------|-----------------|-----------------|---------------------|---------------------|
| $g_1^{(G)}$ |                |                 | $\pm 2.05$      |                     | -2.57               |
| $r^{(G)}$   |                |                 | -0.134          |                     | -0.122              |
| $g_1^{(D)}$ | $\pm 6.97$     | -8.4            | $\pm 7.41$      | +6.97               | -7.00               |
| $r^{(D)}$   | -0.119         | -0.121          | -0.122          | -0.217              | -0.122              |
| $g_1^{(B)}$ |                |                 |                 |                     | -8.27               |
| $r^{(B)}$   |                |                 |                 |                     | -0.122              |

<sup>a</sup> See [22], <sup>b</sup> [46], <sup>c</sup> After [128]

with a negative value of the  $g_{3/2}$  factor. The linear terms of the splitting have been used to obtain the ground-state  $g$ -factors that are compared with the calculated ones in Table 8.21.

Determination of the boron ground-state splitting have been made possible by Zeeman measurements on the boron spectrum for **B** // <110> up to 18 T, where eight components are clearly observed for line  $G$  (B) [144]. In these experiments, the Zeeman components are denoted (I,K,J,L), where I and J are the indices of the  $IR$ s (4 for  $\Gamma_4$ , 3 for  $\Gamma_3$ ) of point group  $C_{1h}$ , while K and L correspond to the sign of  $M = 3/2, 1/2, -1/2, -3/2$  (1 for positive values and 2 for negative values). The amplitude of the Zeeman splitting of  $1\Gamma_8^+$  (B) measured in germanium at 15 T is 0.46 meV, is compared with an extrapolated value of 2.9 meV in silicon. Measurements at such high fields are interesting as they go through the boundary between low and high fields, estimated at  $\sim 6$  T for acceptors in germanium.

The value of the  $g$ -factors ( $g_i^{(J)}(T_d)$ ) obtained for the excited states of the  $G$ ,  $D$  and  $B$  lines of different group-III acceptors in germanium are given in Table 8.22.

Piezo-Zeeman experiments have been reported by Freeth et al. [46] where the low-field Zeeman splitting on the  $G$  and  $D$  lines of Ga in germanium was measured for a fixed stress of  $\sim 13$  MPa along [001] combined with magnetic

fields up to 1.2 T along a [100] direction. The results of these experiments yield values  $\sim 0$  for the ground state  $g$ -factors and the values of Table 8.22 for the excited states of lines  $G$  and  $D$ .

### 8.3.2.3 Diamond

The results of a magneto-Raman study of the  $\Delta'$  transition between the  $1\Gamma_8^+$  and  $1\Gamma_7^+$  levels of boron in diamond have been reported by Kim et al. [78] for the three main orientations of the magnetic field up to 6 T. In addition to transitions between the Zeeman sublevels of the two states, other ones within the  $1\Gamma_8^+$  manifold (Raman-EPR transitions) have also been observed. It must be noted that in B-doped diamond, where the s-o coupling of both the crystal and the acceptor are small, the splitting is independent of the orientations of the magnetic field and the relation between  $g_{|\mu|}$  and  $g'_1$  and  $g'_2$  given in Table 8.15 are no longer valid. The  $g$ -factors for boron in diamond are given by ([78]):

$$g'_1 = (g_{1/2} + g_{3/2})/2, \quad (8.30a)$$

$$g'_2 = 2g_{3/2} - g_{1/2}. \quad (8.30b)$$

The measured values of  $g_{1/2}$  and  $g_{3/2}$  are 0.21 and  $-0.95$ , respectively, from which the values  $g'_1 = -0.37$  and  $g'_2 = -2.11$  are obtained. On the other hand, the relative intensities of the Raman components depend on the magnetic field orientation and their interpretation has allowed us to evaluate the ratio  $\gamma_2/\gamma_3 \sim 0.1$  of the Luttinger  $VB$  parameters of diamond [78].

### 8.3.2.4 Compound Semiconductors

The first Zeeman study in GaAs was performed up to 9 T by Kirkman et al. [81], in addition to the extensive zero-field PTIS measurements concerning mainly  $C_{As}$ . A calculation of the splitting and of the intensities of the Zeeman components was also made in this reference. Results on  $C_{As}$  and  $Zn_{Ga}$  have been published by Atzmüller et al. [7] up to 7 T for the three main orientations of the magnetic field in the Voigt geometry, and they have allowed us to obtain accurate values of the  $g$ -factors for  $C_{As}$ . Measurements on  $Be_{Ga}$  up to 7 T in the Voigt geometry were performed by Lewis et al. [98], and the field dependence of the splitting of  $C(Be)$  is shown in Fig. 8.36.

Further measurements were performed by these authors in the Faraday geometry for fields up to 30 T. The most notable result was the observation, above 25 T, of a line above the one-phonon band, whose energy increased linearly with the field. It was speculated that this feature was related to the first Landau level of the  $VB$ .

The splitting of the  $G$  line of Zn in InP has been measured up to 6.5 T in the Voigt geometry [31] and while all the Zeeman components expected



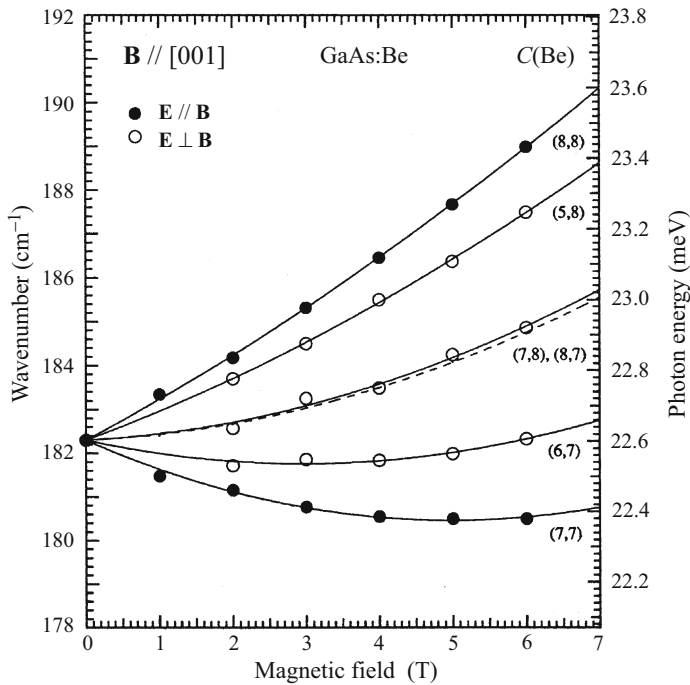


**Fig. 8.36.** Field dependence of the Zeeman components of line *C* (Be) in GaAs. The component denoted (7,8) corresponds to the  $\Gamma_7^+ (m - 3/2) \rightarrow \Gamma_8^+ (+3/2)$  transition of Table 8.11, observed for  $\mathbf{E} \perp \mathbf{B}$ , and so on. The *full lines* are a second-order polynomial fit to the data. The *dashed line* represents a fit to the average energy of the highest- and lowest-energy components [98]. Copyright 2003 by the American Physical Society

are not observed, a determination of  $g$ -factors could, however, be made by comparison with the splitting behaviour of the  $G$  line of  $\text{C}_{\text{As}}$  reported in [7].

The Zeeman effect of the Li acceptor in CdTe has also been studied by Friedrich et al. [47].

The  $g$ -factors of the acceptor ground and excited states in GaAs, InP, and CdTe derived from these Zeeman measurements are compared with those calculated for GaAs in Table 8.23. In this table, the  $g$ -factors of the Li acceptor ground and excited states of the  $G$  line in CdTe shown in Fig. 7.25 have also been included.

From this table, one can note the good agreement between the calculated and observed values for GaAs.

The aim of [47] in their Zeeman measurements of Li in CdTe was not only to determine the  $g$ -factors of this acceptor, but also values of the  $VB$  parameters of CdTe by the method proposed and used in the case of GaAs [128]. This method, which is self-consistent, is indirect and is based on the adjustment of the  $VB$  parameters of the acceptor Hamiltonian including magnetic field terms

**Table 8.23.** Values of the  $g$ -factors of the ground and first excited states ( $g_i^{(J)}(T_d)$ ) of different acceptors in compound cubic semiconductors. For some acceptors, the  $g_i^{(J)}(O_h)$  values are given in parentheses

|                            | $g'_1$      | $g'_2$      | $g_1^{(G)}$                   | $g_2^{(G)}$                    | $g_1^{(D)}$         | $g_2^{(D)}$        |
|----------------------------|-------------|-------------|-------------------------------|--------------------------------|---------------------|--------------------|
| Theory <sup>a</sup> (GaAs) | +0.2081     | +0.1147     | -2.402<br>(+0.2445)           | +1.024<br>(+0.2093)            | -3.642<br>(-1.7068) | +1.826<br>(1.2305) |
| C (GaAs) <sup>b</sup>      | +0.30       | +0.09       | -2.38<br>(+0.27)              | +1.01<br>(+0.19)               | -3.15<br>(-1.41)    | +1.57<br>(+1.035)  |
| Be (GaAs) <sup>c</sup>     | +0.30       | +0.09       | -1.63                         | +0.64                          | -2.88               | +1.47              |
| Zn (InP) <sup>d</sup>      | +0.96       | -0.18       | -2.28                         | +0.98                          |                     |                    |
| Li (CdTe) <sup>e</sup>     | $\pm 0.483$ | $\pm 0.001$ | $\pm 2.07$<br>( $\pm 0.311$ ) | $\pm 0.870$<br>( $\pm 0.137$ ) |                     |                    |

<sup>a</sup> [128], <sup>b</sup> [7], <sup>c</sup> [98], <sup>d</sup> [31], <sup>e</sup> [47]

to calculate the Zeeman splitting matching the experimental ones. Putting aside the technical difficulties of an accurate calculation, for spectra in the vicinity of the one-phonon absorption, where the dielectric constant presents non-negligible dispersion, the final results depend critically on the choice of this quantity, which also determines the actual value of the effective Rydberg.

## 8.4 Effect of Electric Fields

The effects of electric fields on neutral shallow EM impurities at low temperature in insulating samples are discussed here. In the absence of electrical compensation of the samples, a homogeneous electric field can be produced in a sample by voltage biasing through appropriate electrical contacts. In a compensated sample, the presence of statistically distributed anions and cations produces a permanent random electric field whose importance depends, in a first approximation, on the compensation ratio. We consider first the effect of the homogeneous electric fields. This situation has known a renewed interest with the proposal of the control of the charge state and the spin of individual dopant atoms, including application to quantum computing by Kane [71].

### 8.4.1 Homogeneous Electric Fields

There is an essential difference between the application of a homogeneous electric field to an insulating semiconductor sample at low temperature, compared to that of a magnetic field. While there seems to be no limit to the maximum magnetic field which can be applied to a sample, the maximum electric field is limited by the dielectric strength of the crystal. This strength is characterized by a breakdown electric field  $E_{\text{break}}$  above which the crystal becomes electrically conducting (in standard air,  $E_{\text{break}} \sim 3.6 \times 10^6 \text{ V m}^{-1}$ ). In semiconductors, made insulating at low temperature by the trapping of electrons or holes by ionized impurities, there are two main mechanisms by which

free carriers can be generated by the electric field. The first one is an impact ionization of the bound electrons or holes by injected or stray free carriers and the second one is field ionization by which the electrons (holes) tunnel from the neutral donor (acceptor) to the  $CB(VB)$ . To be precise, there is no abrupt breakdown of the field as field ionization is progressive and the field region where ionization takes place is loosely defined. It has been measured at LHeT for P in silicon by Dargys et al. [39] and for shallow donors in germanium by Žurauskas et al. [153]. It was found that, in the nanosecond time scale, the tunnelling from the ground state occurred for fields in the  $17\text{--}26\text{ kV cm}^{-1}$  and  $1.1\text{--}1.9\text{ kV cm}^{-1}$  ranges for silicon and germanium, respectively.

There has been recent calculations of the Stark effect of the  $1s$  donor triplet levels of P in silicon, based on EMA taking into account the valley-orbit splitting in different ways [40, 48, 132]. The study by Debernardini et al. [40] compares the electric field dependence of the energies of the first donor levels with the energy dependence with field of the ionization threshold. It indicates that for the  $2p_0$  level, field ionization takes place for  $\sim 3\text{ kV cm}^{-1}$ , but that for the  $1s(A_1)$  ground state, it is only reached in the  $25\text{ kV cm}^{-1}$  region, in qualitative agreement with the experimental determination. Within the EMA, an increase with the field of  $E(2p_0)$  is predicted while  $E(1sA_1)$  remains practically unchanged and this leads to an interaction between the two levels for fields  $\sim 24.5\text{ kV cm}^{-1}$ . The calculations also show that the difference between the EM-like  $1s(E)$  and  $1s(T_2)$  levels and the  $1s(A_1)$  level decreases with increasing electric fields [40, 48]. These calculations have been extended to the ground state donor level of the  $4H$  SiC polytype by Ivanov and Janzén [65].

The splitting of the impurity levels by a homogeneous electric field has been studied by Kohn [84]. For shallow donors, electron described by Hamiltonian (5.4) submitted to an external electric field  $\mathbf{E}$  along a  $z$  axis, the perturbation Hamiltonian is:

$$H_{St} = -eEz. \quad (8.31)$$

The EM Hamiltonian is invariant under inversion and the matrix elements of  $H_{St}$  between two eigenstates  $\psi^{(i)} = \sum_i F^{(i)}(r) \varphi_{k(i)}(r)$  of this Hamiltonian vanish in the absence of accidental degeneracies such as the  $(2s, 2p)$  degeneracy in the case of hydrogen atom. There is, therefore, no linear Stark effect within this approximation. The second-order Stark shift of a non-degenerate level  $m$ , quadratic with the electric field, is due to the contribution of the interaction of this level with other levels mediated by the electric field and is given by:

$$\Delta E_{St(m)} = \sum_{n \neq m} |\langle m | H_{St} | n \rangle|^2 / (E_m - E_n).$$

Estimation of this shift [147] for the  $2p$  level in silicon for an electric field of  $1\text{ kV cm}^{-1}$  gives  $\Delta E_{St} \sim 60\text{ }\mu\text{eV}$  ( $0.5\text{ cm}^{-1}$ ).

In a first approximation, a  $\Gamma_8$  acceptor state is neither split nor shifted by an external electric field when considering a Hamiltonian with inversion symmetry ( $O_h$ ). However, it becomes possible when considering a local symmetry

$T_d$  for the central cell [17, 84]. When keeping  $O_h$  symmetry, to second order, the field-induced perturbation combines the contributions from the neighbouring states and the  $\Gamma_8$  state considered can display a quadratic shift, and as in the case of a uniaxial stress, a splitting into two Kramers doublets. From the spectroscopic viewpoint, these calculations predict that except for the  $2p_0$  line, other odd-parity transitions should be impossible to observe above  $\sim 1 \text{ kV cm}^{-1}$ .

Practically, the production of an electric field in a crystal necessitates the fabrication of ohmic contacts to the crystal and this is not an obvious task because of the possibility to create rectifying contacts resulting from the accidental production of diode structures with the insulating medium. Electrical contacts have been obtained by first implanting and annealing a dopant of the same type as the one in the bulk of the sample to produce a  $p^+pp^+$  or a  $n^+nn^+$  structure before soldering wires to the highly doped  $p^+$  or  $n^+$  region. Metal electroplating and formation of a metal/semiconductor eutectic has also been used for p-type silicon [147]. Inversely, the depletion region of diode structures has been used as a medium in which relatively high electric fields could be produced.

A decrease with the electric field of the ionization energy of P in silicon has been measured by Guichar et al. [52] from a photoconductivity study of the photoionization spectrum of P at LHeT. This decrease was found to be maximum ( $-3 \text{ meV}$ ) for  $E \sim 400 \text{ V cm}^{-1}$  for  $[P] \sim 2 \times 10^{17} \text{ cm}^{-3}$ , and it was interpreted as a first-order Stark effect due to a coupling between two P atoms, which is the largest when the P atoms are neither tightly nor loosely coupled. A study of the Stark effect of the first transitions of  $\text{Se}^0$  in silicon at 35 K has been reported by Larsson and Grimmeiss [91] using a  $p^+n$  diode structure, with the measurements performed in the depletion region of the diode. They observed an increase of the intensity of the  $1s(T_2)$  line with field and were able to follow a quadratic shift of the  $1s(T_2)$  state of  $2.1 \times 10^{-3} \text{ meV cm}^2 \text{ kV}^2$  for fields up to  $\sim 17 \text{ kV cm}^{-1}$ . For the  $2p_0$  state, the quadratic shift is  $3.0 \times 10^{-2} \text{ meV cm}^2 \text{ kV}^{-2}$  for fields up to  $\sim 6 \text{ kV cm}^{-1}$ . These shifts are both negative and this is in qualitative agreement with the calculations of [40]. Electroabsorption measurements of the  $\text{Sp}$  donor spectrum in GaP were performed at 20 K by Kopylov et al. [86]. They revealed an inversion splitting of  $2p_{\pm 1}$  line related to the camel's back structure of the  $CB$  minimum of GaP and an analysis was made of a model suitable for the calculation of the inversion splitting associated with the camel's back structure. These measurements also allowed us to measure the Stark shifts and broadening of the lines investigated.

A shift and a broadening of the absorption of lines 1, 2, 3, and 4 of boron in silicon have been reported by White [147] from absorption measurements<sup>13</sup>

<sup>13</sup> The spectral resolution and the fact that the compensation ratio of the sample used was  $\sim 2$  resulted in a superposition of lines 4 and 5 of Table 7.2, with  $1\Gamma_6$  and  $1\Gamma_7$  excited states, in peak 4 observed in this reference.

under a DC electric field performed at LHeT. The apparent peak shift could be fitted to a quadratic field-dependence, as shown in Fig. 8.37.

The observed broadening of the same lines, taken as the difference  $h_{1/2}^{(J)}(E)$  between the FWHM( $E$ ) and the FWHM at zero field, appeared to follow a quadratic field dependence. It was fitted to  $h_{1/2}^{(J)}(E) = t_{(J)}E^2$  for line  $J$ , and the values of  $t_{(J)}$  for lines 1, 2, 3, and 4 are 2.0, 1.2, 30.0, and 10.2, respectively, in units of  $10^{-5} \mu\text{eV cm}^2 \text{V}^{-2}$ . This broadening was attributed to an unresolved Stark splitting of the acceptor states due to a second order partial removal of the degeneracies by the field. Since all the FWHMs of the absorption lines increased with field, some ground-state splitting may be present and an upper limit of this splitting was estimated as  $12 \mu\text{eV}$  at  $1 \text{ kV cm}^{-1}$  [147]. Theoretical estimates of the first- and second-order Stark splitting of the  $1\Gamma_8$  ground state [17] are well within this upper limit.

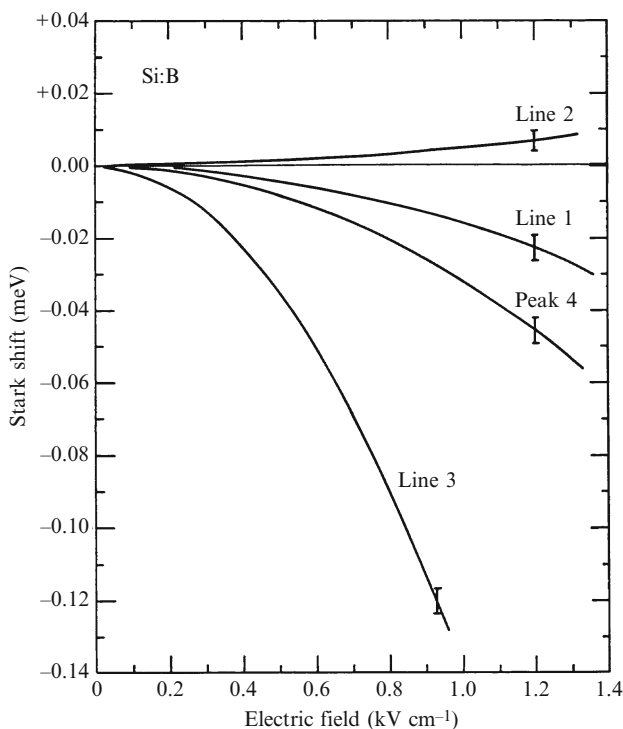


**Fig. 8.37.** Quadratic fit to the shift of the first lines of the B acceptor in silicon under an applied electric field. The excited states of lines 1, 2, and 3 are  $1\Gamma_8$ ,  $2\Gamma_8$ , and  $3\Gamma_8$ , respectively. Peak 4 corresponds to lines 4 and 5 of Table 7.2. The bars are the standard error estimates (after [147]). Reproduced with permission of the NRC (Canada)

### 8.4.2 Internal Electric Fields

In electrically neutral semiconductor samples, random internal electric fields can be present at low temperature because of the compensation and/or of the simultaneous presence of the electrically-charged deep centres. The following estimation of the effect of random internal electric fields on shallow impurity levels is taken from [123] who used it for a qualitative explanation of the broadening of some donor lines in NTD silicon [67], and from [64], who presented it in a more general form.

In a semiconductor with dielectric constant  $\epsilon$ , skipping the factor  $(4\pi\epsilon_0)^{-1}$ , the potential energy  $V(r)$  due to the ionized centres evaluated at a distance  $r$  close from a neutral impurity atom can be written as [66]:

$$V(r) = \sum_i \frac{e_i}{\epsilon |R_i - \mathbf{r}|} = 4\pi \sum_i \frac{e_i}{\epsilon R_i} \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{1}{2l+1} \left( \frac{r}{R_i} \right)^l Y_{lm}^*(\theta_i, \varphi_i) Y_{lm}(\theta, \varphi), \quad (8.32)$$

where  $e_i$  denotes the electric charge (positive or negative) on the  $i$ th centre with spherical coordinates  $R_i, \theta_i, \varphi_i$ , and  $r, \theta, \varphi$  the spherical coordinates of  $r$ . For  $l = 0$ , expression (8.32) reduces to  $\sum_i e_i / \epsilon R_i$ , which is the potential evaluated at the neutral centre ( $\mathbf{r} = 0$ ). This term shifts all the levels of the neutral impurity by the same amount and leaves, therefore, the transition energies unchanged. The  $l = 1$  terms reduce to  $-\mathbf{E}(0) \cdot \mathbf{r}$  where  $\mathbf{E}(0)$  is the electric field associated with the potential, evaluated at  $r = 0$ . This term produces the Stark effect and for weak electric fields, the level  $E_n$  of a hydrogen atom with principal quantum number  $n$  expressed in Rydberg units [88] is:

$$E_n(\mathbf{E}) = -1/2n^2 + 3/2n (n_1 - n_2) \mathbf{E} - 1/16n^4 \left[ 17n^2 - 3(n_1 - n_2)^2 - 9m^2 + 19 \right] \mathbf{E}^2 + \dots, \quad (8.33)$$

where  $m$  is the magnetic quantum number for the orbital angular momentum along the direction of the electric field, and the integers  $n_1$  and  $n_2$ , which can be positive or equal to zero, obey  $n = n_1 + n_2 + |m| + 1$ . This perturbation produces a shift of the energy levels which depends on  $E_n$  and the energy distribution of these shifts results in a broadening of the lines due to an inhomogeneous Stark effect.

An estimate of the value of the average electric field  $\langle \mathbf{E} \rangle$  produced by an ion at a neutral donor site has been given [123] as

$$\langle \mathbf{E} \rangle \sim \frac{e}{\epsilon} (N_I)^{2/3},$$

where  $N_I$  is the concentration of ions. For  $n = 3$  in expression (8.33), it is found that the contribution of the linear Stark effect is larger than that of the quadratic Stark effect. Linear Stark effect can be present for QHD-like shallow donors in direct-gap III-V or II-VI compounds with degenerate  $np$  states, but the situation is different for donors in silicon where levels with different values

of  $l$  are not degenerate. This is the reason why for shallow donors in silicon and germanium, the linear Stark effect is assumed to be zero, as mentioned in Sect. 8.4.1. This implies that from expression (8.33), the contribution of the inhomogeneous (quadratic) Stark effect to the donor spectra in silicon and germanium is negative, producing an asymmetric broadening of the lines, with a tail towards the low-energy side.

The  $l = 2$  terms in the multi-pole expansion (8.32), which are linear in the electric field gradient  $(\partial E/\partial z)_{r=0}$ , are known as the quadrupole terms [89, 90] and they produce a broadening of the shallow impurity lines known as the quadrupole broadening. At a difference with the quadratic Stark broadening, the quadrupole broadening results in a more symmetric profile of the perturbed line [90].

In the early studies of the inhomogeneous line broadening by internal electric fields, it has been assumed that the distribution of ionized impurities was random. While this is likely to be the case for the atomic distribution, the situation can be different when considering the charge state of the compensated majority impurities. In the case of strongly compensated semiconductors, a correlated distribution of the electrons (holes) occurs at LHeT on the majority donor (acceptor) impurities in such a way that the distribution of ionized majority impurities is frozen in a configuration of minimum energy. In the general case, [70] found that this correlated distribution reduced the average distance between the neutral and ionized impurities of the same kind because neutral and ionized impurities tend to form pairs. In these pairs, the mean distance  $R_p$  between the neutral and charged impurities, which is of the order of the mean distance  $R_r = N_I^{-1/3}$  in the absence of correlation ( $N_I$  is the concentration of ionized impurities), becomes  $R_p = (N_0/N_I^2)^{-1/3}$  when correlation is present ( $N_0$  is the concentration of neutral impurities), and it is smaller than  $R_r$ . As a consequence, in the case of correlation, there is an *increase* of the line width compared to the random distribution in the case of high compensation. It is pointed out that a temperature increase or background illumination should restore a random distribution and lead to a decrease of the line width. Inversely, in the case of lightly doped compensated semiconductors where quadrupole effects dominate, considering a correlated distribution results in a decrease of the low-temperature line width compared to the random distribution [83].

Extensive theoretical studies of donor and acceptor spectra have shown that in semiconductors with a concentration of neutral impurities  $N_0$  and a concentration of ionized centres  $N_I$ , the increase of the line widths is proportional to  $(N_I/N_0)^{2/3}$  when linear Stark effect is present, to  $(N_I/N_0)^{4/3}$  when the quadratic Stark effect dominates, and to  $N_I/N_0$  when the quadrupole effect dominates [70, 90].

Figure 8.38b gives an experimental display of the consequence of the quadratic Stark effect of the profile of the  $3p_{\pm 1}$  (P) line in a partially annealed NTD silicon sample.

In (a), where the FWHM of the line is  $\sim 0.1$  meV ( $0.8 \text{ cm}^{-1}$ ), the line shape and the broadening can be accounted for by a quadratic Stark effect due to a

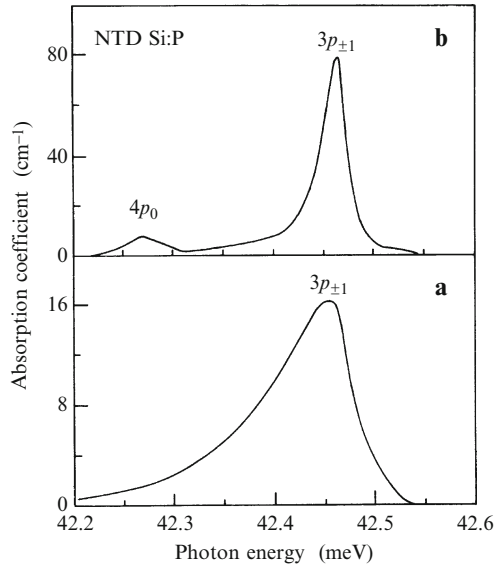


**Fig. 8.38.** Comparison of the profiles of the  $3p_{\pm 1}$  P line at LHeT in a NTD  $^{\text{nat}}\text{Si}$  sample with  $[\text{P}] \sim 2 \times 10^{15} \text{ cm}^{-3}$  after (a) a post-irradiation 2-h annealing at  $650^\circ \text{C}$  and (b) a complementary annealing at  $800^\circ \text{C}$ , showing the effect of quadratic Stark effect in (a). The spectral range is  $340.37\text{--}343.59 \text{ cm}^{-1}$  and the resolution  $0.06 \text{ cm}^{-1}$  ( $7 \mu\text{eV}$ ) (after [67]). Copyright 1981 by the American Physical Society

charged defect concentration estimated at  $\sim 10^{15} \text{ cm}^{-3}$  after the first annealing (before annealing, no P line is observed because of the total donor compensation by the irradiation defects produced by the fast-neutron component). The FWHM in (b) is  $\sim 0.03 \text{ meV}$  ( $0.24 \text{ cm}^{-1}$ ) [67].

The effect of the internal electric field on the line widths of the Ga acceptor lines has been studied as a function of compensation in isotopically controlled germanium samples with different  $^{70}\text{Ge}/^{74}\text{Ge}$  ratios, where the Ga and As dopant was introduced by NTD [64]. The absorption of  $D(\text{Ga})$  and  $C(\text{Ga})$  lines for the same neutral Ga concentration  $N_0$ , but different compensation ratios  $K = N_{\text{As}}/N_{\text{Ga}}$  is shown in Fig. 8.39.

The FWHM of the  $D(\text{Ga})$  line was found to be roughly proportional to the ratio  $N_{\text{I}}/N_0$  where  $N_{\text{I}}$  is  $2[\text{As}]$  and  $N_0$  is  $[\text{Ga}] - [\text{As}]$ , indicating the dominant contribution of a quadrupole interaction between the acceptor atoms and the electric field gradient. Estimations of the compensation dependence of the FWHM of  $D(\text{Ga})$  for correlated and random distributions of ionized impurities showed that the experimental dependence could be explained by a correlated distribution (with the random model, the dependence of the FWHM on  $N_{\text{I}}$  was overestimated by a factor of 4–5). The comparison of the correlated distribution fit with the experimental dependence also showed that the domain of validity of the fit determined by Kogan and Lien [83] extended beyond the compensation limit where the fit was supposed to be valid. By



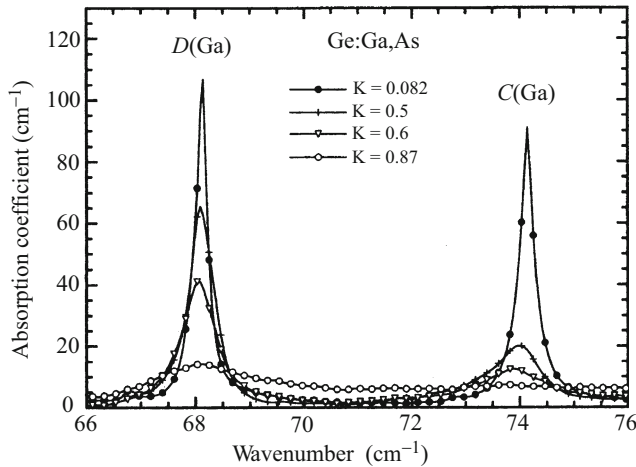


**Fig. 8.39.** Absorption (8.18 – 9.42 meV) of the  $D(\text{Ga})$  and  $C(\text{Ga})$  lines in germanium at 4.6 K for different compensation ratios  $K$ .  $[\text{Ga}^0]$  is  $\sim 5 \times 10^{15} \text{ cm}^{-3}$  for all the spectra. The resolution is  $0.2 \text{ cm}^{-1}$  or  $25 \mu\text{eV}$  (after [64]). Copyright 1996 by the American Physical Society

measuring the FWHMs for increasing temperatures, no sign of a transition from correlated-to-random distribution was observed around the temperature predicted by theory [64].

The inverse experiment was carried out by Kato et al. [76] who measured the FWHM of  $2p_{\pm 1}(\text{As})$  in germanium samples with different Ga compensation ratios, in the low-concentration regime where concentration broadening can be ignored. They found that for low compensation ratios, the dependence of the FWHM of  $2p_{\pm 1}(\text{As})$  on  $K$  is consistent with a random distribution of ionized impurities. In this region, the FWHM increases from  $\sim 0.07$  to  $\sim 0.6 \text{ cm}^{-1}$  ( $9\text{--}70 \mu\text{eV}$ ) from negligible compensation to  $K \sim 0.4$ . For higher values of  $K$ , the increase of the FWHM is comparatively smaller due to the transition into the correlated distribution regime and it is only  $\sim 0.8 \text{ cm}^{-1}$  ( $0.1 \text{ meV}$ ) for  $K \sim 0.98$ .

## 8.5 Line Widths and Lifetimes

In the preceding chapters and in the present one, values of the FWHMs of the EM electronic transitions have been considered, either as intrinsic characteristics of the transitions or in connection with the broadening mechanisms which depend on concentration, compensation ratio, or inhomogeneous impurity distribution. In Chaps. 6 and 7, examples of resonant broadening with lattice phonons, which depend on the difference between the phonons and electronic frequencies, have also been given and they are not considered here. The broadening due to the inhomogeneous Stark effect has been discussed in

the preceding section and the reader is referred to this section for more details. In the EM spectra considered under TEC in compensated samples (all samples are compensated to some extent), this broadening is present and hence, when the observation of sharp lines is the main objective, the compensated samples are illuminated with above-band-gap light to suppress this effect, but with the addition of the lines of the compensating impurity.

In an ideal crystal, the FWHMs of the lines of a H-like centre should be determined by its interaction with the lattice phonon. This so-called phonon broadening is discussed in the next subsection.

### 8.5.1 Phonon Broadening

Phonon broadening is due to the interaction of the H-like centre with lattice phonons and possibly to the isotopic distribution of atoms of the lattice, and this broadening should determine the FWHMs of the donor and acceptor lines in high-purity uncompensated crystals in the absence of residual strains. The interaction between lattice phonons and electronic transitions of shallow impurities has been considered early by Lax and Burstein [94], who proposed that the widths of the ground and excited states were proportional to the mean square amplitude of the nuclear vibrations of the lattice atoms. In this model, the acoustical phonons of importance are those with a wavelength of the order or larger than  $a/2$ , where  $a$  is the effective Bohr radius for a given state. One of the features of this model is that, when comparing the excited states with the  $1s$  ground state, the number of modes with wavelength  $> a/2$  is inversely proportional to  $(a/2)^3$ , the broadening of the  $2p$ ,  $3p$ , or  $4p$  states are reduced roughly by factors  $1/8$ ,  $1/27$  or  $1/64$ , respectively, with respect to that of the ground state, so that the contribution of this state to the width of the line is predominant. Considering the zero-point vibration of the lattice, simple estimations of this model yielded 0 K values of the width  $\sim 3.6$  meV for shallow impurities in silicon, and this seemed adequate to explain the line widths of the order of the meV observed at that time for donor and acceptor electronic lines in silicon. In a phonon-based description, this broadening process corresponded to the simultaneous emission or absorption of acoustical phonons accompanying the electronic transition. In view of the weakness of the electron to phonon interaction, Kane [72] suggested that the electron to phonon interaction contributed only a broad background to the spectrum and that the widths observed were purely instrumental. To account for a finite line width, he proposed that the broadening is due to the lifetime of the excited state, mediated by its de-excitation with the emission of one phonon, and he estimated a 0 K value of  $\sim 50$   $\mu$ eV for the width of the lowest excited state. A more detailed study based on Kane's premise was carried out by Nishikawa and Barrie [113] with an application to shallow impurity lines in silicon [13]. In this theory, it was shown that the lifetime broadening of a given excited state resulted from the electron-phonon interaction through the other excited states.

Experimentally, the phonon broadening has mainly been investigated in silicon for the group-III acceptors and the group-V and -VI donors in a concentration range where concentration broadening could be ignored. To get rid of residual strains, the sample is cut from FZ material where the residual strain due to the presence of a large concentration of  $O_i$  is minimized. A few studies on group-III acceptors and group-V donors have also been performed in germanium.

In germanium, the FWHMs of the shallow donor and acceptor lines look roughly independent from the transition considered, probably because the line energies lie below the phonon energy spectrum. For silicon, if the FWHMs of the donor lines seem also to be independent of the transition considered, this is different for the lowest energy transitions of boron and indium, corresponding to the deepest states, which are larger than the other ones, probably because of a stronger coupling with the two-phonon and three-phonon background (see Table 7.5). In  $^{nat}Si$ , the sharpest FWHMs of the acceptor lines are  $\sim 0.2 \text{ cm}^{-1}$  ( $25 \mu\text{eV}$ ). The FWHMs of the lines of the donor spectra are more uniform and for the P donor they are  $\sim 0.08 \text{ cm}^{-1}$  ( $10 \mu\text{eV}$ ). The FWHMs of the neutral chalcogen and chalcogen complexes have been measured in  $^{nat}Si$ , and the sharpest ones ( $\sim 0.2 \text{ cm}^{-1}$  or  $25 \mu\text{eV}$ ) are observed for the highly excited states of the sulphur-related spectra.

A substantial decrease of the FWHMs has been observed in silicon between the values measured in natural and qmi materials. This is illustrated for donors in Table 6.1, where the FWHM of  $2p_0$  (P) is seen to decrease by a factor of  $\sim 2.6$  in qmi  $^{28}Si$  as compared with  $^{nat}Si$ . For boron, the decrease is not uniform, and the broadest lines in  $^{nat}Si$  remain broad in  $^{qmi}Si$ , but for line 15(B), the decrease is by a factor 6.6 in qmi  $^{28}Si$  (compare Figs. 7.2 and 7.6).

Presently, the most dramatic effect occurs for component  $\Gamma_7$  of  $1s(T_2)$  ( $Se^+$ ). This component is shown in Fig. 6.18 in  $^{nat}Si$  doped with  $^{nat}Se$ , and its FWHM is  $\sim 0.5 \text{ cm}^{-1}$  ( $60 \mu\text{eV}$ ). In  $^{nat}Si$  doped with  $^{77}Se$ , the FWHM of the line is reduced to  $0.18 \text{ cm}^{-1}$  ( $22 \mu\text{eV}$ ) because of the absence of contribution of isotopes other than  $^{77}Se$ , but in qmi  $^{28}Si$ , the FWHM of  $1s(T_2)$  ( $^{77}Se^+$ ) shrinks to  $0.008 \text{ cm}^{-1}$  ( $1 \mu\text{eV}$ ) and the decrease comes with a factor  $\sim 22$  [141]. This demonstrates the existence of a broadening mechanism due to the random isotopic distribution of lattice atoms and one can wonder the energy dependence of this isotope effect.

The sharpest donor lines reported in  $^{nat}Ge$  are  $4p_{\pm 1}$  ( $D(H, O)$ ) and  $4f_{\pm 1}$  ( $D(H, O)$ ), with FWHMs  $\sim 6.4 \mu\text{eV}$  ( $0.05 \text{ cm}^{-1}$ ). The model of Nishikawa and Barrie [113] has been used by Navarro et al. [109] to compare with the calculated line width the residual width of the  $2p_{\pm 1}$  line of the  $D(H, O)$  donor in ultrapure  $^{nat}Ge$ , measured by Zeeman tuning of the energier frequencies. The broadening calculated by taking into account the interaction of the  $2p_{\pm 1}$  level with the four nearest levels ( $2p_0$ ,  $2s$ ,  $3p_0$ , and  $3s$ ) was  $\sim 2.5 \mu\text{eV}$ , compared to an experimental value of  $8.6 \mu\text{eV}$  for the FWHM of the  $2p_{\pm 1}$  line, but the calculated value was found to be sensitive to the value of the effective Bohr radius used in the calculation. For the acceptors, the sharpest line reported

in  $^{\text{nat}}\text{Ge}$  seems to be  $C(\text{Al})$ , with a FWHM<sup>14</sup> of  $0.038\text{ cm}^{-1}$  ( $4.7\mu\text{eV}$ ). One should also expect to observe an isotopic sharpening of the lines of the H-like centres in germanium, for which qmi crystals with different isotopes have been prepared, but no information on high-resolution shallow impurity spectra in qmi germanium seems to be presently available.

Line widths limited by electron–phonon interaction have also been measured in QHD spectra in GaAs under a magnetic field (see Fig. 6.41b) and the FWHMs of  $1s \rightarrow 2p_m = -1$  transitions for Te, S, and Sn or Se are  $0.06$ ,  $0.045$ , and  $0.02\text{ cm}^{-1}$  ( $7$ ,  $5.6$ , and  $2.5\mu\text{eV}$ ), respectively, for a magnetic field of  $6.3\text{ T}$ .

When temperature increases above LHeT, shallow impurity spectra are usually observed as long as the ground state is populated, but the FWHMs of the line increases as the phonon broadening is temperature-dependent. The increase for line 2(Al) in silicon has, for instance, been followed up to  $90\text{ K}$  and for  $[\text{Al}] = 4.4 \times 10^{14}\text{ cm}^{-3}$ , the FWHM is  $\sim 0.75\text{ meV}$  ( $6.0\text{ cm}^{-1}$ ) at this temperature [61] compared to  $\sim 0.2\text{ meV}$  ( $1.7\text{ cm}^{-1}$ ) at LHeT in the spectrum of Fig. 7.4.

Information on the broadening of donor and acceptor lines in FZ silicon between  $5$  and  $60\text{ K}$  is given in a concise report by Agladze et al. [3], where the spectra were obtained when necessary under high resolution. Representative examples are given in Fig. 8.40. In the original figure, the lines considered were not indicated and tentative attributions have been made here.

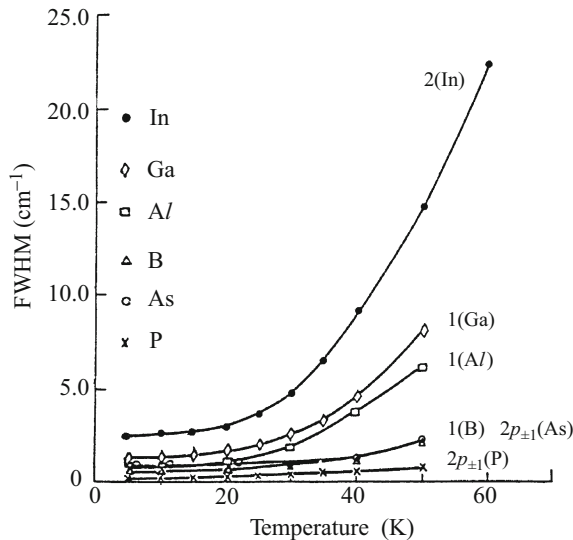


**Fig. 8.40.** Temperature dependence of the FWHMs of representative absorption lines of group-III acceptors and group-V donors in  $^{\text{nat}}\text{Si}$  (after [3])

<sup>14</sup> The value is given first in the unit used in the original publication.

Within experimental error, the very small increase of the FWHM of  $2p_{\pm 1}$  (P) between 5 and  $\sim 15$  K is consistent with the absence of broadening deduced from the FWHM values at 16 K reported by Shen et al. [130]. For In, line 2 must be chosen because, while slightly sharper than line 1, it is about one order of magnitude more intense.

It is clear that the thermal broadening of the acceptor lines is stronger than those of the donor lines, and for the acceptor lines, the larger the central-cell effect, the larger is the broadening observed.

### 8.5.2 Concentration Broadening

Extreme examples of concentration broadening are visible in Figs. 6.7 and 6.8. This effect is due, above some critical concentration, to an overlap of the envelope functions of the excited states, and it was investigated by [111]. Spectroscopic data obtained in the 1960s showed that for B in silicon, concentration broadening of the doublet 4–5 (unresolved at that time) was already present for a neutral [B] value of  $1.2 \times 10^{15} \text{ cm}^{-3}$  [37], while a crude calculation by Baltensperger [10] predicts a corrected onset of  $3 \times 10^{15} \text{ cm}^{-3}$ . The onset should be proportional to  $(a_0^*)^{-3}$ , where  $a_0^*$  is the effective Bohr radius of the impurity, and is correlated with the EM parameters of the semiconductors: it is smaller for shallow donors and acceptors in germanium than in silicon, with no reference, however, to diamond. At the inverse, for donors in GaAs, interaction between donors is observed in the standard samples, explaining why a magnetic field is needed in this material to obtain sharp lines (see Fig. 6.41). There has, however, been no recent systematic study of concentration broadening of impurities in silicon or germanium.

### 8.5.3 Lifetimes

A lower limit of the lifetimes of the excited states can be estimated from these FWHMs if one assumes no broadening of the ground state. For a Lorentzian line shape, the lifetime  $\tau_e$  of the excited state is given by

$$\tau_e (\text{s}) = (2\pi c \text{FWHM} (\text{cm}^{-1}))^{-1}. \quad (8.34)$$

When expressed in picosecond,  $\tau_e$  is given as  $5.31 \times (\text{FWHM} (\text{cm}^{-1}))^{-1}$ , or  $658 \times (\text{FWHM} (\mu\text{eV}))^{-1}$ .

With the demonstration of the stimulated emission associated with these states [119], and also with the requirement of quantum computing, a keen interest has developed on the actual lifetimes of the donor excited states in silicon. Population inversion of donor electrons has been achieved by non-resonant pumping with a CO<sub>2</sub> laser with discrete energies tunable in the  $\sim 124$  meV range, and by resonant pumping at the energies of the donor absorption lines with a FEL [118]. These experiments have shown the importance

of the  $2p_0$  level, with a relatively long lifetime, because it is separated from the  $1s(E)$  and  $1s(T_2)$  levels by a relatively high energy, and of the  $1s(E)$  level, with a relatively short lifetime due to an efficient de-excitation to the ground state mediated by the emission of a  $g-$  TA inter-valley phonon. Such experiments have been performed at LHeT with  $^{nat}Si:P$ ,  $^{nat}Si:As$ , and  $^{nat}Si:Sb$  with donor concentrations in the  $3 \times 10^{15} \text{ cm}^{-3}$  range, and the laser transitions observed were  $2p_0 \rightarrow 1s(E)$ ,  $2p_{\pm 1} \rightarrow 1s(E)$ , and  $2p_{\pm 1} \rightarrow 1s(T_2)$ .

The lifetime of the excited state of the  $2p_0(P)$  line at 34.1 meV was measured at 10 K by a pump-probe experiment with a FEL in a  $^{nat}Si$  FZ sample with  $[P] \sim 2 \times 10^{15} \text{ cm}^{-3}$ . This was done by following the transient decay of the transmission dip at 34.1 meV as a function of the time delay between the pump and probe pulses (the pulse duration was 10 ps and pump powers were between  $\sim 0.1$  and  $1.67 \text{ kW cm}^{-2}$ ). A simple exponential decay gave a value of  $\tau_{\text{exc}}$  of  $(205 \pm 18)$  ps [145]. This lifetime is much larger than the one ( $\sim 65$  ps) derived from the FWHM of  $2p_0(P)$  measured at 1.6 K in a  $^{nat}Si$  FZ sample with  $[P] \sim 3 \times 10^{12} \text{ cm}^{-3}$ , but comparable to the one ( $\sim 170$  ps) derived from the FWHM of  $2p_0(P)$  in a qmi  $^{28}Si$  sample (see Table 6.1). This shows that the lower limits of the lifetimes deduced from the FWHMs of the lines do not represent generally the actual lifetimes of the excited states, and this could be due to the neglected ground state contribution to the FWHM and to residual inhomogeneous broadening. The LHeT lifetimes of the excited states of the  $np_{\pm 1}(P)$  lines have also been measured by the transient decay method and the values are near 160 ps. By comparison, the lifetimes for  $2p_0(As)$  and  $2p_{\pm 1}(As)$  in  $^{nat}Si$  are near 120 ps (for  $2p_0(As)$  the lifetime deduced from the FWHM of Table 6.1 is  $\sim 28$  ps). The transient decay results are summarized in Fig. 8.41.

In the same study, the temperature dependence of the apparent lifetime of the donor electron in  $2p_0(P)$  and  $2p_{\pm 1}(P)$  before being re-trapped in the ground state has been investigated up to 110 K. It is found that up to  $\sim 50$  K, this lifetime increases (to a value of  $\sim 200$  ps for  $2p_{\pm 1}(P)$ ). This increase can be attributed to the contribution of thermal ionization from the excited state to the bottom of the  $CB$ , followed by some kind of cascade recombination to the ground state. At higher temperature, the electron is excited higher in the  $CB$  and it recombines directly to the ground state with TO phonon emission and this reduces the lifetime [145].

By analogy with the donor states, an order of magnitude of the lifetimes of some boron excited states in silicon can be obtained from the FWHMs measured in qmi samples. In qmi  $^{28}Si$ , the FWHM of the  $^{11}B$  component of lines 21 ( $353.33 \text{ cm}^{-1}$  in  $^{nat}Si$ ) and 23 ( $354.55 \text{ cm}^{-1}$  in  $^{nat}Si$ ) is  $0.022 \text{ cm}^{-1}$  at 1.4 K, corresponding to lifetime of  $\sim 240$  ps.

In germanium, the lifetimes of the first excited states of the Sb donor and of the  $1\Gamma_8^-$  acceptor state<sup>15</sup> of boron have been determined by careful

<sup>15</sup> In this reference, the germanium acceptor states are noted following [103], where the (8-01) and (7-0) states correspond in this book to  $1\Gamma_8^-$  and  $1\Gamma_7^-$ , respectively.

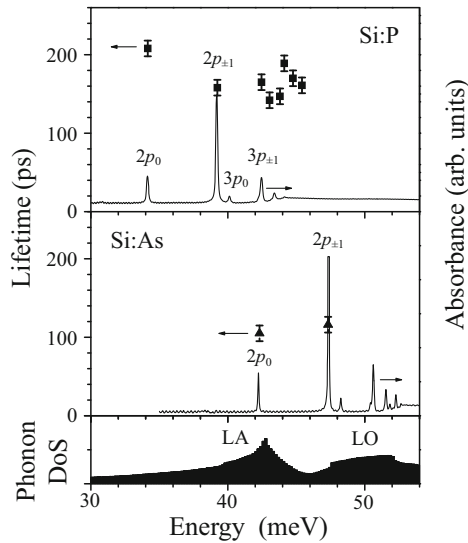


**Fig. 8.41.** Transient decay lifetimes of the electrons in the excited states of P and As lines in  $^{\text{nat}}\text{Si}$  at 10 K, indicated above the transitions considered. The one-phonon DoS in silicon including LA and LO phonons, which determines the phonon emission decay rate at low temperature is shown at the *bottom* [145]. Copyright 2008 National Academy of Sciences, U.S.A

measurements of transitions between the excited states detected by PTIS as a function of the background radiation and of temperature [49]. These LHeT lifetime values for  $2p_0$  (Sb),  $3p_0$  (Sb), and  $2p_{\pm 1}$  (Sb) are 400, 100, and 600 ps, respectively, slightly larger than the ones for P in silicon, and they are concentration-independent up to about  $10^{14} \text{ cm}^{-3}$ . The LHeT lifetime reported for the hole in the  $1\Gamma_8^-$  (B) state is very large ( $6 \times 10^4$  ps) compared to the donor values, and independent of the acceptor concentration up to  $5 \times 10^{15} \text{ cm}^{-3}$ . For comparison, the lower limit of the lifetime of the hole in the  $1\Gamma_7^-$  (Al) state deduced from the FWHM of  $C$  (Al) is 173 ps. All these results confirm that the frequency-domain spectroscopy with  $^{\text{nat}}\text{Si}$  and  $^{\text{nat}}\text{Ge}$  samples can provide only a lower limit of the lifetimes of the excited states. It would be interesting to know if the measurement with qmi Ge samples would produce the same sharpening of the donor and acceptor lines as the one observed in silicon, considering that this sharpening could depend on the isotopic purity of the samples.

## References

1. A. Abragam, M.H.L. Pryce, Proc. R. Soc. Lond. A **205**, 135 (1951)
2. R.L. Aggarwal, A.K. Ramdas, Phys. Rev. **137**, A602 (1965)

3. N.I. Agladze, A.S. Kaminskii, A.N. Safonov, *Defects Diff. Forum* **103–105**, 299 (1993)
4. B.A. Andreev, T.M. Lifshits, *High Purity Subst. (Russia)* **5**, 7 (1990)
5. T.R. Anthony, A.D. Alvarenga, M. Grimditch, H. Kim, A.K. Ramdas, S. Rodriguez, R. Vogelgesang, *Curr. Sci.* **4**, 317 (1998)
6. S.N. Artemenko, A.A. Kal'fa, Sh.M. Kogan, V.I. Sidorov, *Sov. Phys. Semicond.* **8**, 1405 (1975)
7. R. Atzmüller, M. Dahl, J. Kraus, G. Schaack, J. Schubert, *J. Phys. C* **3**, 6775 (1991)
8. R.J. Baker, P. Fisher, *Solid State Commun.* **99**, 679 (1996)
9. R.J. Baker, P. Fisher, R.E.M. Vickers, E.E. Haller, W.L. Hansen, in *Proceedings of 7<sup>th</sup> International Conference on Shallow-Level Centers, Amsterdam 17–19 July 1996*, (eds). C.A.J. Ammerlaan, B. Pajot (World Scientific, Singapore, 1997) pp. 357–362
10. W. Baltensperger, *Philos. Mag.* **44**, 1355 (1953)
11. P.I. Baranskii, V.V. Kolomoets, *Phys. Stat. Sol. B* **45**, K55 (1971)
12. J. Bardeen, W. Shockley, *Phys. Rev.* **80**, 72 (1950)
13. R. Barrie, K. Nishikawa, *Can. J. Phys.* **41**, 1823 (1963)
14. K. Bergman, G. Grossmann, H.G. Grimmeiss, M. Stavola, R.E. McMurray, *Phys. Rev. B* **39**, 1104 (1989)
15. A.K. Bhattacharjee, S. Rodriguez, *Phys. Rev. B* **6**, 3836 (1972)
16. G.L. Bir, E.I. Butikov, G.E. Pikus, *J. Phys. Chem. Solids* **24**, 1467 (1963)
17. G.L. Bir, E.I. Butikov, G.E. Pikus, *J. Phys. Chem. Solids* **24**, 1475 (1963)
18. G.L. Bir, G.E. Pikus, *Symmetry and Strain-Induced Effects in Semiconductors* (Wiley, New York, 1974)
19. B. Bleaney, *Proc. Phys. Soc.* **73**, 939–942. *Corrig. ibid.* **74**, 493 (1959)
20. W.S. Boyle, *J. Phys. Chem. Solids* **8**, 321 (1959)
21. W.S. Boyle, R.E. Howard, *J. Phys. Chem. Solids* **19**, 181 (1961)
22. J. Broeckx, *Phys. Rev. B* **43**, 9643 (1991)
23. J. Broeckx, P. Clauws, K. Van den Steen, J. Vennik, *J. Phys. C* **12**, 4061 (1979)
24. J. Broeckx, J. Vennik, *Phys. Rev. B* **35**, 6165 (1987)
25. J. Broeckx, P. Clauws, J. Vennik, *J. Phys. C* **19**, 511 (1986)
26. H. Brooks, *Theory of the Electrical Properties of Germanium and Silicon*. In: L. Marton (ed) *Advances in Electronics and Electron Physics*, vol. 7 (Academic, New York, 1955) pp. 85–182
27. R. Buczko, *Nuovo Cimento* **9D**, 669 (1987)
28. A. Burenkov Yu, S.P. Nikanorov, A.V. Stepanov, *Sov. Phys. Solid State* **12**, 1940 (1971)
29. N.R. Butler, P. Fisher, A.K. Ramdas, *Phys. Rev. B* **12**, 3200 (1975)
30. N. Casanova, E. Gheeraert, E. Bustarret, S. Koizumi, T. Teraji, H. Kanda, J. Zeman, *Phys. Stat. Sol. A* **186**, 291 (2001)
31. R.L. Causley, R.A. Lewis, *Physica B* **302–303**, 327 (2001)
32. H.R. Chandrasekhar, P. Fisher, A.K. Ramdas, S. Rodriguez, *Phys. Rev. B* **8**, 3836 (1973)
33. H.R. Chandrasekhar, A.K. Ramdas, S. Rodriguez, *Phys. Rev. B* **12**, 5780 (1975)
34. H.R. Chandrasekhar, A.K. Ramdas, S. Rodriguez, *Phys. Rev. B* **14**, 2417 (1976)
35. J.M. Cherlow, R.L. Aggarwal, B. Lax, *Phys. Rev. B* **7**, 4547 (1973)



36. Y.S. Choi, J.S. Lim, T. Numata, T. Nishida, S.E. Thompson, J. Appl. Phys. **102**, 104507/1–5 (2007)
37. K. Colbow, Can. J. Phys. **41**, 1801 (1963)
38. R.A. Cooke, R.J. Nicholas, R.A. Stradling, J.C. Portal, S. Askenazy, Solid State Commun. **26**, 11 (1978)
39. A. Dargys, S. Žurauskas, S. Žurauskienė, Appl. Phys. A **52**, 13 (1991)
40. A. Debernardi, A. Baldereschi, M. Fanciulli, Phys. Rev. B **74**, 035202 (2006)
41. H.Y. Fan, P. Fisher, J. Phys. Chem. Solids **8**, 270 (1959)
42. G. Feher, J.C. Hensel, E.A. Gere, Phys. Rev. Lett. **5**, 309 (1960)
43. P. Fisher, H.Y. Fan, Phys. Rev. Lett. **2**, 456 (1959)
44. P. Fisher, G.J. Takacs, R.E.M. Vickers, A.D. Warner, Phys. Rev. B **47**, 12 999 (1993)
45. P. Fisher, R.E.M. Vickers, D.C. Lau, Surface Rev. Lett. **10**, 277 (2003)
46. C.A. Freeth, P. Fisher, P.E. Simmonds, Solid State Commun. **60**, 175 (1986)
47. T. Friedrich, J. Kraus, M. Meininger, G. Schaack, W.O.G. Schmitt, J. Phys. Cond. Matter. **6**, 4307 (1994)
48. M. Friesen, Phys. Rev. Lett. **94**, 186403/1–4 (2005)
49. E.M. Gershenzon, G.N. Gol'tsman, N.G. Ptitsina, Sov. Phys. JETP **49**, 355 (1979)
50. V.G. Golubev, V.I. Ivanov-Omsky, G.I. Kropotov, Solid State Commun. **42**, 869 (1982)
51. X. Goncharov, Sov. Phys. Semicond. **11**, 556 (1977)
52. G.M. Guichar, C. Sebenne, F. Proix, M. Balkanski, Phys. Rev. B **5**, 422 (1972)
53. R.R. Haering, Can. J. Phys. **36**, 1161 (1958)
54. J.J. Hall, Phys. Rev. **128**, 68 (1962)
55. J.J. Hall, Phys. Rev. **161**, 756 (1967)
56. S.M. Harris, E.W. Prohofskey, Phys. Rev. **170**, 749 (1968)
57. H. Hasegawa, Phys. Rev. **129**, 1029 (1963)
58. J.C. Hensel, G. Feher, Phys. Rev. **129**, 1041 (1963)
59. J.C. Hensel, K. Suzuki, Phys. Rev. B **9**, 4219 (1974)
60. C. Herring, E. Vogt, Phys. Rev. **101**, 944 (1956)
61. L.T. Ho, Chin. J. Phys. **16**, 87 (1978)
62. K. Horii, Y. Nisida, J. Phys. Soc. Jpn. **31**, 783 (1971)
63. A.E. Hughes, W.A. Runciman, Proc. Phys. Soc. **90**, 827 (1967)
64. K.M. Itoh, J. Muto, W. Walukiewicz, J.W. Beeman, E.E. Haller, H. Kim, A.J. Mayur, M.D. Sciacca, A.K. Ramdas, R. Buczko, J.W. Farmer, V.I. Ozhogin, Phys. Rev. B **53**, 7797 (1996)
65. I.G. Ivanov, E. Janzén, in *Silicon Carbide and Related Materials 2006*, (eds). N. Wright, C.M. Johnson, K. Vassilevski, I. Nikitina, A. Horsfall, Trans Tech. Mater. Sci. Forum **556–557**, 435 (2007)
66. J.D. Jackson, *Classical Electrodynamics*, 2nd edn. (Wiley, New York, 1975) p. 102
67. C. Jagannath, Z.W. Grabowski, A.K. Ramdas, Phys. Rev. B **23**, 2082 (1981)
68. C. Jagannath, A.K. Ramdas, Phys. Rev. B **23**, 4426 (1981)
69. J.M. Kahn, R.E. McMurray, E.E. Haller, L.M. Falicov, Phys. Rev. B **36**, 8001 (1987)
70. A.A. Kal'fa, Sh.M. Kogan, Sov. Phys. Semicond. **6**, 1839 (1973)
71. B.E. Kane, Nature (London) **393**, 133 (1998)
72. E.O. Kane, Phys. Rev. **119**, 40 (1960)

73. A.A. Kaplyanskii, Opt. Spectrosc. (USSR) **16**, 329 (1967); J. Phys. Colloque C4, suppl. no 8-9 **28**, C4 (1964)
74. A.A. Kaplyanskii, Opt. Spectrosc. (USSR) **16**, 557 (1964)
75. V.A. Karasyuk, M.L.W. Thewalt, S. An, E.C. Lightowers, A.S. Kaminskii, Phys. Rev. B **54**, 10543 (1996)
76. J. Kato, K.M. Itoh, E.E. Haller, Physica B **302-303**, 1 (2001)
77. A.G. Kazanskii, P.L. Richards, E.E. Haller, Solid State Commun. **24**, 603 (1977)
78. H. Kim, Z. Barticevic, A.K. Ramdas, S. Rodriguez, M. Grimsditch, T.R. Anthony, Phys. Rev. B **62**, 8038 (2000)
79. L.C. Kimerling, in *Oxygen, Carbon, Hydrogen and Nitrogen in Crystalline Silicon*, (eds). J.C. Mikkelsen, Jr, S.J. Pearton, J.W. Corbett, S.J. Pennycook, Mater. Res. Soc. Symp. Proc. **59**, 83 (1986)
80. L.C. Kimerling, J.L. Benton, Appl. Phys. Lett. **39**, 410 (1981)
81. R.F. Kirkman, R.A. Stradling, P.J. Lin-Chung, J. Phys. C **11**, 419 (1978)
82. W.H. Kleiner, L.M. Roth, Phys. Rev. Lett. **2**, 334 (1959)
83. Sh.M. Kogan, N.V. Lien, Sov. Phys. Semicond. **15**, 26 (1981)
84. W. Kohn, in *Solid State Physics Advances in Research and Applications*, vol. 5 (eds). F. Seitz, D. Turnbull (Academic, London, 1957), pp. 257-320
85. A. Köpf, K. Lassmann, Phys. Rev. Lett. **69**, 1580 (1992)
86. A.A. Kopylov, S.P. Medvedev, A.N. Pikhtin, Sov. Phys. Semicond. **13**, 924 (1979)
87. W.E. Krag, W.H. Kleiner, H.J. Zeiger, Phys. Rev. B **33**, 8304 (1986)
88. L.D. Landau, E.M. Lifshitz, *Quantum Mechanics Non Relativistic Theory*, 3rd edn. (Pergamon, Oxford, 1962) p. 251
89. D.M. Larsen, Phys. Rev. B **8**, 535 (1973)
90. D.M. Larsen, Phys. Rev. B **13**, 1681 (1976)
91. K. Larsson, H.G. Grimmeiss, J. Appl. Phys. **63**, 4524 (1988)
92. L.D. Laude, F.H. Pollack, M. Cardona, Phys. Rev. B **3**, 2623 (1971)
93. B. Lax, L.M. Roth, S. Zwerdling, J. Phys. Chem. Solids **8**, 311 (1959)
94. M. Lax, E. Burstein, Phys. Rev. **100**, 592 (1955)
95. K.M. Lee, J. Trombetta, G.D. Watkins, *Microscopic Identification of Electronic Defects in Semiconductors*, (ed). N.M. Johnson, G.D. Watkins, Mater. Res. Soc. Symp. Proc. **46**, 263 (1985)
96. N. Lee, D.M. Larsen, B. Lax, J. Phys. Chem. Solids **35**, 401 (1974)
97. R.A. Lewis, P. Fisher, N.A. McLean, Aust. J. Phys. **47**, 329 (1994)
98. R.A. Lewis, Y.J. Wang, M. Henini, Phys. Rev. B **67**, 235204 (2003)
99. M. Li, J. Chen, X. Zhao, Y. Li, in *Defects in Semiconductors 14*, (ed). H.J. von Bardeleben, Trans Tech. Mater. Sci. Forum **10-12**, 469 (1986)
100. J.S. Lim, X. Yang, T. Nishida, S.E. Thomson, Appl. Phys. Lett. **89**, 073509 (2006)
101. P.J. Lin-Chung, R.F. Wallis, J. Phys. Chem. Solids **30**, 1453 (1969)
102. J.S. Lomont, *Application of Finite Groups* (Academic, New York, 1959)
103. Mendelson and James, J. Phys. Chem. Solids **25**, 729 (1964)
104. F. Merlet, B. Pajot, Ph. Arcas, A.M. Jean-Louis, Phys. Rev. B **12**, 3297 (1975)
105. J. Michel, J.R. Niklas, J.M. Spaeth, Phys. Rev. B **40**, 1732 (1989)
106. L.V. Mizrukhin, L.I. Khirunenko, V.I. Shakhovtsov, V.K. Shinkarenko, V.I. Yashnick, Sov. Phys. Semicond. **23**, 441 (1989)
107. W.J. Moore, J. Phys. Chem. Solids **32**, 93 (1971)

108. Y.M. Mu, J.P. Peng, P.L. Liu, S.C. Shen, J.B. Zhu, Phys. Rev. B **48**, 10864 (1993)
109. H. Navarro, E.E. Haller, F. Keilman, Phys. Rev. B **37**, 10822 (1988)
110. H. Neubrand, Phys. Stat. Sol. B **86**, 269 (1978)
111. R. Newman, Phys. Rev. **103**, 103 (1956)
112. S.P. Nikanorov, A. Burenkov Yu, A.V. Stepanov, Sov. Phys. Sol. State **13**, 2516 (1971)
113. K. Nishikawa, R. Barrie, Can. J. Phys. **41**, 1135 (1963)
114. Y. Nisida, K. Horii, J. Phys. Soc. Jpn. **31**, 776 (1971)
115. A. Onton, P. Fisher, A.K. Ramdas, Phys. Rev. **163**, 686 (1967)
116. B. Pajot, F. Merlet, G. Taravella, Can. J. Phys. **50**, 2186 (1972)
117. B. Pajot, F. Merlet, G. Taravella, Ph. Arcas, Can. J. Phys. **50**, 1106 (1972)
118. S.G. Pavlov, H.W. Hübers, P.M. Haas, J.N. Hovenier, T.O. Klaassen, R.Kh. Zhukavin, V.N. Shastin, D.A. Carder, B. Redlich, Phys. Rev. B **78**, 165201 (2008)
119. S.G. Pavlov, R.Kh. Zhukavin, E.E. Orlova, V.N. Shastin, V.N. Kirsanov, H.W. Hübers, K. Auen, H. Riemann, Phys. Rev. Lett. **84**, 5220 (2000)
120. R.E. Peale, K. Muro, A.J. Sievers, F.S. Ham, Phys. Rev. B **37**:10829 (1988)
121. R.E. Peale, R.M. Hart, A.J. Sievers, F.S. Ham, *Shallow Impurities in Semiconductors 1988*, (ed). B. Monemar, Inst. Phys. Conf. Ser. 95, Bristol, 1989, pp. 89–94
122. A.K. Ramdas, P.M. Lee, P. Fisher, Phys. Lett. **7**, 99 (1963)
123. A.K. Ramdas, S. Rodriguez, Rep. Progr. Phys. **44**, 1297 (1981)
124. A.K. Ramdas, S. Rodriguez, in *The Spectroscopy of Semiconductors*, (eds). D.G. Seiler, C.L. Littler, vol. 36 of the Series Semiconductors and Semimetals (Academic, San Diego, 1992), pp. 137–221
125. J.H. Reuszer, P. Fisher, Phys. Rev. **140**, A245 (1965)
126. S. Rodriguez, P. Fisher, F. Barra, Phys. Rev. B **5**, 2219 (1972)
127. S. Rodriguez, T.D. Schultz, Phys. Rev. **178**, 1252 (1969)
128. W.O.G. Schmitt, E. Bangert, G. Landwehr, J. Phys. Cond. Matter **3**, 6789 (1991)
129. S.C. Shen, Solid State Commun. **93**, 357 (1995)
130. S.C. Shen, Z.Y. Yu, Y.X. Huang, Int. J. Infrared Millim. Waves **11**, 595 (1990)
131. T. Shimizu, N. Tanaka, Phys. Lett. A **45**, 5 (1973)
132. G.D.J. Smit, S. Rogge, J. Caro, T.M. Klapwijk, Phys. Rev. B **70**, 035206 (2004)
133. H.P. Soepangkat, P. Fisher, Phys. Rev. B **8**, 870 (1973)
134. M. Stavola, Physica **146B**, 187 (1987)
135. M. Stavola, in *Proc. NATO Advanced Workshop on the Early Stages of Oxygen Precipitation in Silicon*, (ed). R. Jones, NATO ASI Series 3, vol. 17, High Technology (Kluwer, Dordrecht, 1996) pp. 223–242
136. M. Stavola, K.M. Lee, Mater. Res. Soc. Symp. Proc. **59**, 95 (1986)
137. M. Stavola, K.M. Lee, J.C. Nabity, P.E. Freeland, L.C. Kimerling, Phys. Rev. Lett. **54**, 2639 (1985)
138. K. Suzuki, M. Okazaki, H. Hasegawa, J. Phys. Soc. Jpn. **19**, 930 (1964)
139. G. Taravella, Ph. Arcas, B. Pajot, Solid State Commun. **13**, 353 (1973)
140. V.H. Tekippe, H.R. Chandrasekhar, P. Fisher, A. Ramdas, Phys. Rev. B **6**, 2348 (1972)
141. M.L.W. Thewalt, M. Steger, A. Yang, N. Stavrias, M. Cardona, H. Riemann, N.V. Abrosimov, M.F. Churbanov, A.V. Gusev, A.D. Bulanov, I.D. Kovalev, A.K. Kaliteevskii, O.N. Godisov, P. Becker, H.J. Pohl, J.W. Ager, E.E. Haller, Physica B **401–402**, 587 (2007)

- 142. H. Tokumoto, T. Ishiguro, Phys. Rev. B **15**, 2099 (1977)
- 143. R.E.M. Vickers, P. Fisher, C.A. Freeth, Solid State Commun. **65**, 271 (1988)
- 144. R.E.M. Vickers, R.A. Lewis, P. Fisher, Y.J. Wang, Phys. Rev. B **77**, 115212 (2008)
- 145. N.Q. Vinh, P.T. Greenland, K. Litvinenko, B. Redlich, A.F.G. van der Meer, S.A. Lynch, M. Warner, A.M. Stoneham, G. Aeppli, D.J. Paul, C.R. Pidgeon, B.N. Murdin, Proc. Natl. Acad. Sci. (USA) **105**, 10649 (2008)
- 146. P. Wagner, H. Gottschalk, J. Trombetta, G.D. Watkins, J. Appl. Phys. **61**, 346 (1987)
- 147. J.J. White, Can. J. Phys. **45**, 2695 (1967)
- 148. D.K. Wilson, G. Feher, Phys. Rev. B **124**, 1068 (1961)
- 149. D.J. Wolford, J.A. Bradley, Solid State Commun. **53**, 1069 (1985)
- 150. Y. Yafet, D.G. Thomas, Phys. Rev. **131**, 2405 (1963)
- 151. E.R. Youngdale, R.L. Aggarwal, Phys. Rev. B **37**, 2514 (1988)
- 152. P. Zeeman, Philos. Mag. **45**, 197 (1898)
- 153. S. Žurauskas, A. Dargys, N. Žurauskienė, Phys. Stat. Sol. B **173**, 647 (1992)
- 154. S. Zwerdling, K.J. Button, B. Lax, Phys. Rev. **118**, 975 (1960)

## Appendix A

---

### Energy Units Used in Spectroscopy and Solid-State Physics

The energy of an electron accelerated by a potential of 1 volt is 1 electron volt (eV), a quantity of the order of magnitude of the energies at the atomic scale. The infrared spectroscopists prefer the wavenumber (the number of wavelengths  $\lambda$  per unit length, usually noted  $\tilde{\nu}$ ), specially when dealing with vibrational energies. It is commonly expressed in reciprocal centimeter ( $\text{cm}^{-1}$ ). The phonon frequencies are often evaluated in Terahertz. The absolute temperature is often used to measure energy in statistical mechanics. The correspondence with macroscopic energies is provided by multiplying the energies in eV by the Avogadro constant  $N_A$  and evaluating the result in kJ per mole ( $1 \text{ J} = 6.24151 \times 10^{18} \text{ eV}$ ).

The correspondences between the eV and these units is given below. It is derived from  $E = eV = hc\tilde{\nu} = h\nu = k_B T = hc/\lambda$  (the Boltzmann constant is noted  $k_B$  instead of  $k$ ).

| $E$ (eV)                  | $\tilde{\nu}$ ( $\text{cm}^{-1}$ ) | $\nu$ (THz) | K (Kelvin) | kJ mole $^{-1}$ | $\lambda$ ( $\mu\text{m}$ ) |
|---------------------------|------------------------------------|-------------|------------|-----------------|-----------------------------|
| 1                         | 8065.545                           | 241.7992    | 11,604.50  | 96.48534        | 1.239842                    |
| $1.239842 \times 10^{-4}$ | 1                                  | 0.0299792   | 1.438781   | 0.0119627       | 10,000                      |
| 0.004135667               | 33.35641                           | 1           | 47.99237   | 0.399030        | 299.792                     |
| $8.61734 \times 10^{-5}$  | 0.695036                           | 0.0208366   | 1          | 0.00831444      | 14,387.8                    |
| 0.0103643                 | 83.5935                            | 2.50608     | 120.273    | 1               | 119.627                     |
| 1.239842                  | 10,000                             | 299.792     | 14,387.81  | 119.627         | 1                           |

In the book,  $1 \text{ cm}^{-1}$  is taken as  $0.1239842 \text{ meV}$ . In the visible and UV regions of the spectrum, the nanometre (nm) wavelength unit is used ( $1 \text{ \AA} = 0.1 \text{ nm}$ ). In the IR region of the spectrum, the  $\mu\text{m}$  wavelength unit is mostly used above  $2500 \text{ nm}$  and below  $1 \text{ mm}$ .

## Values of Selected Physical Constants Recommended by CODATA (2006)

Except for the value for  $c$ ,  $\mu_0 = 4\pi \times 10^{-7}$ , and  $\varepsilon_0$ , taken as exact, all the physical constants are rounded.

|                                                                                                    |                                       |
|----------------------------------------------------------------------------------------------------|---------------------------------------|
| Speed $c$ of light in vacuum ( $\text{m s}^{-1}$ ):                                                | 299,792,458                           |
| Magnetic constant $\mu_0$ ( $\text{N A}^{-2}$ )<br>(permeability of vacuum):                       | $12.566,370,614 \dots \times 10^{-7}$ |
| Electric constant $\varepsilon_0 = 1/\mu_0 c^2$ ( $\text{F m}^{-1}$ )<br>(permittivity of vacuum): | $8.854187817 \dots \times 10^{-12}$   |
| Electron charge $e$ (C):                                                                           | $1.602176487(10) \times 10^{-19}$     |
| Planck constant $h$ (J s):                                                                         | $6.62606896(33) \times 10^{-34}$      |
| Planck constant $h$ (eV s):                                                                        | $4.13566733(10) \times 10^{-15}$      |
| Planck constant over $2\pi$ $\hbar$ (J s):                                                         | $1.054571628(53) \times 10^{-34}$     |
| Planck constant over $2\pi$ $\hbar$ (eV s):                                                        | $6.58211899(16) \times 10^{-16}$      |
| Boltzmann constant $k_B$ ( $\text{J K}^{-1}$ ):                                                    | $1.3806505(24) \times 10^{-23}$       |
| " ( $\text{eV K}^{-1}$ ):                                                                          | $8.617343(15) \times 10^{-5}$         |
| Bohr radius $a_0$ (m) $= \varepsilon_0 h^2 / \pi m_e e^2$                                          | $0.529177208(59) \times 10^{-10}$     |
| Rydberg constant $R_\infty$ ( $\text{m}^{-1}$ )<br>$= m_e e^4 / (8\varepsilon_0^2 h^3 c)$          | 10 973731.568527(73)                  |
| Rydberg constant converted in eV:                                                                  | 13.60569193(34)                       |
| Avogadro constant $N_A$ (atom per mole):                                                           | $6.02214179(30) \times 10^{23}$       |
| Electron mass $m_e$ (kg)                                                                           | $9.10938215(45) \times 10^{-31}$      |
| Atomic mass constant<br>$m_u = \frac{1}{12} m(^{12}\text{C})$ (kg)                                 | $1.660538782 \times 10^{-27}$         |
| Bohr magneton $\mu_B = e\hbar/2m_e$ ( $\text{JT}^{-1}$ )                                           | $927.400915(23) \times 10^{-26}$      |
| " ( $\text{eV T}^{-1}$ )                                                                           | $5.7883817555 \times 10^{-5}$         |

In the atomic units (a.u.) system, the permittivity of vacuum is dimensionless and set equal to  $(4\pi)^{-1}$ , while  $a_0$ ,  $e^2$ ,  $m_e$ , and  $\hbar$  are set equal to unity. The atomic unit of energy, the Hartree, is equal to two times the Rydberg constant.

## Appendix B

---

### Bravais Lattices, Symmetry and Crystals

3D space can be filled without voids or overlapping by identical prismatic cells with well-defined symmetries, and their types are limited to seven. These units cells can be defined by the lengths of three nonplanar primitive vectors  $\mathbf{a}_1$ ,  $\mathbf{a}_2$  and  $\mathbf{a}_3$  and by the angles  $\alpha$ ,  $\beta$  and  $\gamma$  between these vectors. They generate the seven simple crystal systems or classes, defined by the sets of all points taken from a given origin of these cells, that are defined by vectors

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3 \quad (\text{B.1})$$

where  $n_1$ ,  $n_2$  and  $n_3$  are integers. Table B.1 enumerates these crystal systems and their geometric characteristics.

The other crystal lattices can be generated by adding to some of the above-defined cells extra high-symmetry points by the so-called centering method. Table B.2 shows the new systems added to the simple crystal lattices (noted s, or  $P$ , for primitive) and the numbers of lattice points in each conventional unit cell. The body-centred lattices are noted bc or  $I$  (for German *Innenzentrierte*), the face-centred, fc or  $F$ , and the side-centred or base-centred lattices are noted  $C$  (an extra atom at the Centre of the base). These 14 lattice systems are known as the Bravais lattices (noted here  $BL$ s). A representation of their unit cells can be found in the textbook by Kittel [7].

A primitive cell of a  $BL$  is a cell of minimum volume that contains only one lattice point, so that the whole lattice can be generated by all the translations of this cell. This definition allows for different primitive cells for the same  $BL$ , but their volumes must be the same. The parallelepiped defined by the three primitive vectors  $\mathbf{a}_1$ ,  $\mathbf{a}_2$ , and  $\mathbf{a}_3$  of a simple  $BL$  is a primitive cell of this lattice.

The conventional unit cell showing the symmetry of the hexagonal system is that of a right prism, whose height is usually noted  $c$ , with a regular hexagon as a base. This cell contains three lattice points, hence three primitive cells consisting in a right prism with a base made of a rhomb with one  $120^\circ$  angle.

The unit cells of the simple  $P$  systems are primitive cells. Primitive cells are not unique and most don't have the  $BL$  symmetry, but it is possible

**Table B.1.** The seven 3D simple crystal systems. The conditions on the primitive vectors of the unit cells and on their orientations are indicated. Angle  $\gamma$  is taken as the one between  $\mathbf{a}_1$  and  $\mathbf{a}_2$

| System                  | Restrictions for vectors lengths and angles                                                          |
|-------------------------|------------------------------------------------------------------------------------------------------|
| Triclinic               | $\mathbf{a}_1 \neq \mathbf{a}_2 \neq \mathbf{a}_3$<br>$\alpha \neq \beta \neq \gamma$                |
| Monoclinic              | $\mathbf{a}_1 \neq \mathbf{a}_2 \neq \mathbf{a}_3$<br>$\alpha = \gamma = 90^\circ \neq \beta$        |
| Orthorhombic or rhombic | $\mathbf{a}_1 \neq \mathbf{a}_2 \neq \mathbf{a}_3$<br>$\alpha = \beta = \gamma = 90^\circ$           |
| Tetragonal              | $\mathbf{a}_1 = \mathbf{a}_2 \neq \mathbf{a}_3$<br>$\alpha = \beta = \gamma = 90^\circ$              |
| Hexagonal               | $\mathbf{a}_1 = \mathbf{a}_2 \neq \mathbf{a}_3$<br>$\alpha = \beta = 90^\circ, \gamma = 120^\circ$   |
| Trigonal                | $\mathbf{a}_1 = \mathbf{a}_2 = \mathbf{a}_3$<br>$\alpha = \beta = \gamma \neq 90^\circ, < 120^\circ$ |
| Cubic (isometric)       | $\mathbf{a}_1 = \mathbf{a}_2 = \mathbf{a}_3$<br>$\alpha = \beta = \gamma = 90^\circ$                 |

**Table B.2.** Number of lattice points in the unit cells of the 14 3D Bravais lattices

| System       | Simple ( $P$ ) | Body-centred | Face-centred | Base-centred |
|--------------|----------------|--------------|--------------|--------------|
| Triclinic    | 1              | —            | —            | —            |
| Monoclinic   | 1              | —            | —            | 2            |
| Orthorhombic | 1              | 2            | 4            | 2            |
| Tetragonal   | 1              | 2            | —            | —            |
| Hexagonal    | 1              | —            | —            | —            |
| Trigonal     | 1              | —            | —            | —            |
| Cubic (c)    | 1 (sc)         | 2 (bcc)      | 4 (fcc)      | —            |

to construct a primitive cell with the symmetry of the  $BL$ . The recipe is to connect a given lattice point to its nearest neighbours by straight lines and to intersect these lines at mid-point by perpendicular planes. The inner volume defined by these planes is the volume of the primitive cell known as the Wigner-Seitz cell. In particular, the Wigner-Seitz cell for the hexagonal system is an hexagonal prism whose volume is that of the hexagonal unit cell.

Real crystal lattices are made from atoms, atomic or molecular entities associated with lattice points of the  $BL$ s or of their combinations. For instance, when they are centred at the lattice points of a fcc  $BL$ , entities of two same atoms lying along the diagonal of the unit cell of this  $BL$  and separated by one quarter of this diagonal generate the diamond structure (when the two atoms are different, the structure generated is that of sphalerite, also called zinc-blende).



## B.1 The Reciprocal Lattice

When dealing with the interactions of crystals with particles that can display wave-like properties, like photons, phonons or electrons, it is useful to introduce a reciprocal lattice associated with the real (or direct) crystal lattice. Let us consider a set of vectors  $\mathbf{R}$  constituting a given 3D *BL* and a plane wave  $e^{i\mathbf{k}\cdot\mathbf{r}}$ . For special choices of  $\mathbf{k}$ , it can be shown that  $\mathbf{k}$  can also display the periodicity of a *BL*, known as the reciprocal lattice of the direct *BL*. For all  $\mathbf{R}$  of the direct *BL*, the set of all wave vectors  $\mathbf{G}$  belonging to the reciprocal lattice verify the relation

$$e^{i\mathbf{G}\cdot(\mathbf{r}+\mathbf{R})} = e^{i\mathbf{G}\cdot\mathbf{r}} \quad (\text{B.2})$$

for any  $\mathbf{r}$ . The reciprocal lattice can thus be defined as the set of wave vectors  $\mathbf{G}$  satisfying

$$e^{i\mathbf{G}\cdot\mathbf{R}} = 1 \quad (\text{B.3})$$

The reciprocal lattice of a *BL* whose primitive unit cell is defined by three vectors  $\mathbf{a}_1$ ,  $\mathbf{a}_2$  and  $\mathbf{a}_3$  is generated by three primitive vectors

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \wedge \mathbf{a}_3}{v}, \mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \wedge \mathbf{a}_1}{v}, \mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \wedge \mathbf{a}_2}{v} \quad (\text{B.4})$$

where  $v = \mathbf{a}_1 \cdot (\mathbf{a}_2 \wedge \mathbf{a}_3)$  is the volume of the primitive unit cell of the direct lattice (the notation  $\mathbf{u} \wedge \mathbf{v}$  denotes the vector product of vectors  $\mathbf{u}$  and  $\mathbf{v}$ ).

It is clear that the  $\mathbf{a}_i$  and  $\mathbf{b}_j$  satisfy condition B.3 as  $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$  where  $\delta_{ij}$  is the Kronecker symbol (0 if  $i \neq j$ , 1 if  $i = j$ ). Similarly, it can be checked that for any vector  $\mathbf{G} = m_1\mathbf{b}_1 + m_2\mathbf{b}_2 + m_3\mathbf{b}_3$  ( $m_1$ ,  $m_2$  and  $m_3$  being integers) of the lattice generated by the  $\mathbf{b}_j$ , condition B.3 is met when  $\mathbf{R}$  is a vector of the direct lattice.

It can be also checked by using expressions B.4 that the reciprocal lattice of the reciprocal lattice is the original direct lattice and that the volume of the primitive unit cell of the reciprocal lattice is  $(2\pi)^3/v$ . The Wigner-Seitz primitive cell of the reciprocal lattice is known as the first Brillouin zone (BZ) of the reciprocal lattice. As an example, the reciprocal lattice of the fcc *BL* with conventional cubic unit cell of side  $a$  is the corresponding bcc *BL* with a conventional cubic unit cell of side  $4\pi/a$ , and by applying twice the construction of a reciprocal lattice, it is seen that the reciprocal lattice of the bcc *BL* is the corresponding fcc *BL*. The angular correspondence is not a general rule, however, and the reciprocal lattice of the hexagonal *BL* is another hexagonal *BL* rotated through  $30^\circ$  about the  $c$  axis of the direct lattice. A general account on the symmetries of the Wigner-Seitz cells for the different *BL*s can be found in the review by Koster [8] and be easily extrapolated to the first BZs.

## B.2 Lattice Planes and Miller Indices

Let us start with a few definitions. A lattice plane of a given 3D  $BL$  contains at least three noncollinear lattice points and this plane forms a 2D  $BL$ . A family of lattice planes of a 3D  $BL$  is a set of parallel equally-spaced lattice planes separated by the minimum distance  $d$  between planes and this set contains all the points of the  $BL$ . The resolution of a given 3D  $BL$  into a family of lattice planes is not unique, but for any family of lattice planes of a direct  $BL$ , there are vectors of the reciprocal lattice that are perpendicular to the direct lattice planes. Inversely, for any reciprocal lattice vector  $\mathbf{G}$ , there is a family of planes of the direct lattice normal to  $\mathbf{G}$  and separated by a distance  $d$ , where  $2\pi/d$  is the length of the shortest reciprocal lattice vector parallel to  $\mathbf{G}$ . A proof of these two assertions can be found in Ashcroft and Mermin [1].

As one generally uses a vector normal to a lattice plane to specify its orientation, one can as well use a reciprocal lattice vector. This allows to define the Miller indices of a lattice plane as the coordinates of the shortest reciprocal lattice vector normal to that plane, with respect to a specified set of direct lattice vectors. These indices are integers with no common factor other than 1. A plane with Miller indices  $h, k, l$  is thus normal to the reciprocal lattice vector  $\mathbf{G} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$ , and it is contained in a continuous plane  $\mathbf{G} \cdot \mathbf{r} = \text{constant}$ . This plane intersects the primitive vectors  $\mathbf{a}_i$  of the direct lattice at the points of coordinates  $x_1\mathbf{a}_1$ ,  $x_2\mathbf{a}_2$  and  $x_3\mathbf{a}_3$ , where the  $x_i$  must satisfy separately  $\mathbf{G} \cdot x_i\mathbf{a}_i = \text{constant}$ . Since  $\mathbf{G} \cdot \mathbf{a}_1$ ,  $\mathbf{G} \cdot \mathbf{a}_2$  and  $\mathbf{G} \cdot \mathbf{a}_3$  are equal to  $h, k$  and  $l$ , respectively, the  $x_i$  are inversely proportional to the Miller indices of the plane. When the plane is parallel to a given axis, the corresponding  $x$  value is taken for infinity and the corresponding Miller index taken equal to zero.

Lattice planes are specified by giving their Miller indices in parentheses:  $(h \ k \ l)$ . For instance, in the cubic system, the Miller indices of a plane intersecting the  $\mathbf{a}_1$ ,  $\mathbf{a}_2$  and  $\mathbf{a}_3$  axes at 3,  $-1$  and 2, respectively will be  $(2 \ -6 \ 3)$  and the plane will be noted  $(2\bar{6}3)$ . The corresponding normal direction in the direct lattice is noted  $[2\bar{6}3]$ . The body diagonal of the unit cell of the cubic lattice lies in a  $[111]$  direction and more generally, the lattice point  $n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$  lies in the direction  $[n_1 \ n_2 \ n_3]$  from the origin. For symmetry reasons, there exists equivalent families of planes in non triclinic crystals and the equivalent planes are noted collectively  $\{uvw\}$ . For instance, in the cubic lattice, the  $(100)$ ,  $(010)$  and  $(001)$  planes are noted  $\{100\}$ . Similarly, the  $[100]$ ,  $[010]$ ,  $[001]$ ,  $[\bar{1}00]$ ,  $[0\bar{1}0]$  and  $[00\bar{1}]$  directions are collectively noted  $\langle 100 \rangle$ .

In fcc and bcc lattices, there are no cubic primitive cells whereas in simple cubic system, the reciprocal lattice is also simple cubic and the Miller indices of a family of lattice planes represent the coordinates of a vector normal to the planes in the usual Cartesian coordinates. As the lattice planes of a fcc cubic lattice or a bcc cubic lattice are parallel to those of a sc lattice, it has then been fixed as a rule to define the lattice planes of the fcc and bcc cubic lattices as if they were sc lattices with orthogonal primitive vectors of the reciprocal lattice.

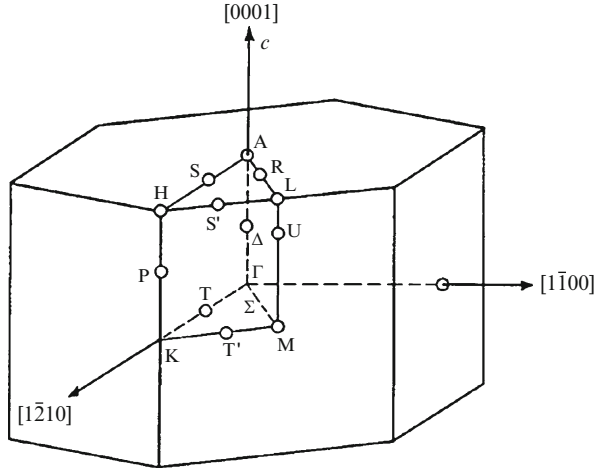


**Fig. B.1.** First Brillouin zone of the hexagonal *BL*

The lattice planes of the hexagonal structures can be defined by three coplanar basis vectors  $\mathbf{a}_1$ ,  $\mathbf{a}_2$  and  $\mathbf{a}_3$  at  $120^\circ$  from one another and such as  $\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3 = 0$  and by axis  $c$  perpendicular to these vectors. The Miller indices of a plane for these structures is written  $(h\ k\ i\ l)$  where  $h$ ,  $k$  and  $i$  are the reciprocals of the intercept of the plane with  $\mathbf{a}_1$ ,  $\mathbf{a}_2$  and  $\mathbf{a}_3$  and  $l$  the reciprocal of the intercept in the  $c$  direction. The indices  $h$ ,  $k$  and  $i$  are not linearly independent and their sum must be zero. The first BZ of the hexagonal *BL* is shown in Fig. B.1.

## B.3 A Toolbox for Symmetry Groups

### B.3.1 The Abstract Groups

A presentation of the optical spectroscopy of impurity centres in crystals requires some understanding of group theory and we provide here basic definitions. Specific answers to many questions on group theory and to its applications in solid state physics and spectroscopy can be found in [5]. Among other properties (see Heine [6]), the abstract finite groups are characterized by (1) their order, i.e., the number of elements they contain; (2) a closed combination law within the group such that the application of this law to any two elements of the group still yields an element of the group. The order of application is important because for any two group elements  $G$  and  $P$ , the element resulting from  $GP$  is usually different from that resulting from  $PG$ , where multiplication is used as the combination law. When  $GP$  gives the same result as  $PG$  whatever  $G$  and  $P$ , the group is said to be abelian; (3) the existence of an identity element (noted  $E$ ) such as, for any  $G$  belonging to the group,

$GE$  or  $EG$  yields  $G$ ; and (4) the existence for any element  $G$  of an inverse element  $G^{-1}$  belonging to the group and such that  $GG^{-1} = G^{-1}G = E$ . Two elements  $A$  and  $B$  of a group are said to be conjugate if  $A = GBG^{-1}$ , from which  $B = G^{-1}AG$  is readily derived. A set of mutually conjugate elements of a group constitutes a class of the group and any element of the group appears only in one class ( $E$  is a class by itself). A subset of a given group displaying general group properties with the same multiplication law as the initial group is called a subgroup of this group.

### B.3.2 The Symmetry Point Groups

The 3D symmetry point groups are a particular category of finite groups whose elements are spatial symmetry operations and 32 of them, derived from the symmetries of the *BLs*, are known as the crystallographic point groups. A *BL* or any entity left invariant under all the symmetry operations of a given point group is said to belong to this point group. Two or three of these point groups can sometimes show a one to one correspondence between their elements, with the same formal multiplication tables, despite the fact that the symmetry operations are spatially different. Such groups, which correspond to the same abstract group, are said to be isomorphous. There are two notations for the point groups: the international one, also known as the Hermann-Mauguin notation, mainly used by cristallographers, and the one based on the Schönflies notation (used here), mainly used in molecular and semiconductor physics. The correspondence between the two notations is given in Tables 7.2 and 7.3 of [1], pp. 121 and 122.

A short description of the 32 crystallographic point groups is given below. They are:

- The pure rotation groups  $C_n$  ( $n = 1, 2, 3, 4, 6$ ) containing only rotations  $2\pi k/n$  about an axis ( $k$  is an integer between 1 and  $n$ ). The rotations made clockwise are noted  $C_n$ , and those made counter-clockwise  $C_n^{-1}$  (they are obviously the inverse of each other), except for  $n = 2$  where the two rotations yield the same result. For the  $C_n$  groups, these two rotations are unilateral (not equivalent) and they form two distinct classes. When  $k$  differs from  $n$  and from  $n/2$  ( $C_n^{n/2} = C_2$ ), the rotations  $C_n^k$  belong to different classes. For instance, the different classes of the  $C_6$  group are  $E$ ,  $C_6$ ,  $C_6^2 = C_3$ ,  $C_6^3 = C_2$ ,  $C_6^4 \equiv C_3^{-1}$  and  $C_6^5 \equiv C_6^{-1}$ . The  $C_n$  groups are called cyclic as the  $C_n$  operation repeated  $n$  times ( $C_n^n$ ) gives  $E$ . The only element of group  $C_1$  is  $E$ . Other point groups derived from  $C_n$  are:
- The  $S_{2n}$  groups ( $n = 1, 2, 3$ ), with additional rotations  $\pi/n$  about the main axis, followed by a reflection through a plane perpendicular to the main axis ( $S_{2n}$  or  $S_{2n}^{-1}$  rotation-reflections). For  $n = 1$ , this corresponds to inversion  $I$ . The  $S_n$  operations are called improper rotations, by comparison with the proper rotations  $C_n$ . The only element of group  $S_2$  (besides  $E$ ) is  $I$  so that this group is also noted  $C_i$ .

- The  $C_{nh}$  groups ( $n = 1, 2, 3, 4, 6$ ), with additional  $S_n$  rotation-reflections and a symmetry reflection  $\sigma_h$  through a plane perpendicular to the main axis, plus  $I$  for  $n$  even. A symmetry reflection is another kind of improper rotation (rotation-inversion) resulting from a rotation  $C_2$  followed by inversion ( $IC_2$ );
- The  $C_{nv}$  groups ( $n = 2, 3, 4, 6$ ), with additional reflections through  $n$  symmetry planes containing the main axis (one kind,  $\sigma_v$ , for  $n = 3$ , two kinds,  $\sigma_v$  and  $\sigma'_v$ , for  $n$  even);
- The  $D_n$  groups ( $n = 2, 3, 4, 6$ ), with additional rotations of an angle  $\pi$  through  $n$  axes perpendicular to the main axis (one kind,  $C'_2$ , for  $n = 3$ , two kinds,  $C'_2$  and  $C''_2$  for  $n$  even). For the groups including these additional rotations, the  $C_n$  and  $C_n^{-1}$  rotations about the main axis are equivalent (bilateral) and they belong to the same class of symmetry operations.
- The  $D_{nh}$  groups ( $n = 2, 3, 4, 6$ ), derived from the  $D_n$  groups by adding reflections through  $n$  symmetry planes containing the main axis and the  $C'_2$  axes (one kind,  $\sigma_v$ , for  $n = 3$ , two kinds,  $\sigma_v$  and  $\sigma'_v$ , for  $n$  even), a reflection  $\sigma_h$  through a plane containing the  $C'_2$  axes, plus  $I$  for  $n$  even;
- The  $D_{nd}$  groups ( $n = 2, 3$ ), derived from the  $D_n$  groups by adding reflections through  $n$  symmetry planes containing the main axis and midway of the  $C'_2$  axes (one kind,  $\sigma_v$ , for  $D_{3d}$ , two kinds,  $\sigma_v$  and  $\sigma'_v$ , for  $D_{2d}$ ), plus  $I$  for  $D_{3d}$ .

The five other point groups are known as the cubic point groups. They are groups  $T$  and  $O$ , including all the proper rotational symmetries of the tetrahedron and of the cube, respectively, group  $T_h$ , derived from  $T$  by adding a centre of symmetry, and finally groups  $T_d$  and  $O_h$ , including all the rotational symmetry transformations of the tetrahedron and of the cube, respectively.

As already said, the above point groups are derived from the symmetries of the *BLs*. They cannot therefore include groups with  $C_5$  rotational symmetry, like the  $C_5$  group and the groups derived from it. The icosahedral point group, sometimes noted  $Y$ , contains fifteen  $C_2$ , ten  $C_3$ , and six  $C_5$  axes. It displays the rotational symmetries of the regular icosahedron and dodecahedron, the two other regular polyhedra (platonic solids) besides the tetrahedron, the cube and the octahedron. The  $I_h$  point group, also often referred to as the icosahedral point group, is derived from  $Y$  by the addition of a centre of symmetry and it is the point group with the largest number of symmetry elements (120).  $I_h$  is the symmetry point group attributed to fullerene ( $C_{60}$ ), whose structure possess regular hexagonal and pentagonal faces.  $C_5$  rotational symmetry can also be found in some quasicrystals (for a review, see [4]).

### B.3.3 Representations and Basis Functions

A set of matrices transforming under the multiplication laws of a group constitutes a representation of this group. When this set is in the diagonal form and that it can be reduced into subsets that cannot be further reduced

(we assume the reader is familiar with matrix algebra), these subsets form irreducible representations (*IRs*) of this group. When the initial set cannot be reduced, it is already an *IR* of the group. There are as many *IRs* of a group as the number of classes of this group. The sums of the diagonal elements of the diagonalized matrices are the characters of the *IRs* and they are the same for all the elements of a given class. As the identity  $E$  is a class by itself, the characters of the *IRs* corresponding to  $E$  are simply the dimensions of the *IRs*. Most of the group characters are real numbers, but some of them can also be imaginary (for instance in group  $C_4$ ) or complex (for instance in group  $C_3$ ). The character tables of the 32 crystallographic point groups can be found in [6, 8, 9]. A function or a set of functions that transforms under the symmetry operations  $R$  of a group through the set of matrices corresponding to a given representation forms a basis for this representation (actually, the basis functions are used to determine the representations). Among the *IRs*, there is always a unit representation, 1D, whose characters are 1, whatever the class.

In the notation of [11], the *IRs* are noted by capital letters eventually with indices and/or primes, the convention being to label by A or B the 1D *IRs*, by E (not to be confused with the identity operation  $E$ ), the 2D ones and by T the 3D ones. In the notation of Bethe [2] used by Koster [9], the *IRs* are simply noted  $\Gamma_i$  ( $i = 1, 2, 3$ , etc), eventually with indices and primes.

The symmetry operations considered up to now are supposed to apply on components  $x, y, z$  of polar vectors (like those of a force or of an electric field), that change sign under inversion symmetry, or on components  $S_x, S_y, S_z$  of axial vectors, or pseudo-vectors, (like the angular momentum or the magnetic field) that do not change sign under inversion. It is possible to calculate the characters of the 3D matrix representations associated with the components of polar and axial vectors for the different symmetry operations of the 32 point groups and the corresponding list [10] is given in Table B.3.

This table can be used to determine the representation for a polar or axial vector in a given symmetry group. In some cases, these representations are irreducible, as for the  $T_d$  group, but for the others, they are reducible and the character table of the *IRs* of the group must be used for the reductions into *IRs*.

Now, to go further and to provide conceptual tools that will be used in the interpretation of the electronic spectra of impurities in crystals, a new group has to be introduced, the 3D rotation group, noted here  $R^+(3)$ , which is the

**Table B.3.** Characters of the representations spanned by polar and axial vectors for the different symmetry operations of the crystallographic point groups

| Symmetry operation | $E$ | $C_2$ | $C_3$ | $C_4$ | $C_6$ | $I$ | $\sigma$ | $S_3$ | $S_4$ | $S_6$ |
|--------------------|-----|-------|-------|-------|-------|-----|----------|-------|-------|-------|
| Polar vector       | 3   | -1    | 0     | 1     | 2     | -3  | 1        | -2    | -1    | 0     |
| Axial vector       | 3   | -1    | 0     | 1     | 2     | 3   | -1       | 2     | 1     | 0     |

group of all the rotations through any angle about any axis.  $R^+(3)$  is an infinite group and its *IRs* and their basis functions are intimately related to the quantum-mechanical properties of the total angular momentum of an electron in a free atom. In the one-electron approximation, quantum mechanics tells us that the energy level of an electron whose eigenvalue of angular momentum is  $j$  is  $(2j + 1)$ -fold degenerate. This level is associated with  $(2j + 1)$  eigenfunctions differing in the value  $m$  of the  $z$ -component of the angular momentum, running from  $j$  to  $-j$ . For integral values of  $j$ , these eigenfunctions are the spherical harmonics

$$Y_{lm} = N_{lm} P_{l|m|}(\cos \theta) e^{im\phi}$$

where  $\theta$  and  $\phi$  are the spherical polar coordinates,  $P_{l|m|}$  an associated Legendre polynomial and  $N_{lm}$  a normalizing factor. When the electron spin is included,  $j$  can take integral and half-integral values so that the degeneracy is 1, 2, 3, etc. . . . From the quantum-mechanical analogy between the operators of an infinitely small rotation and angular momentum, it can be shown that the value of  $j$  can be used to label the  $(2j + 1)$ -dimensional *IRs* of  $R^+(3)$ , noted  $D^{(j)}$ . The unit representation of  $R^+(3)$  is  $D^{(0)}$  and the components of an axial vector transform as *IR*  $D^{(1)}$  of  $R^+(3)$ . Under rotation by angle  $\phi$  about a given axis, the basis functions of *IR*  $j$  are multiplied by  $e^{im\phi}$ . For half-integral values of  $j$ , it is seen that the rotation of  $2\pi$  about an arbitrary axis does not correspond to the unit element  $E$  for  $R^+(3)$  as the basis functions change sign, but to a new element of the group, usually noted  $\bar{E}$  (notations  $\hat{E}$  and  $Q$  are also found) and such that  $\bar{E}\bar{E} = E$ . This can be translated to point groups when studying the symmetry properties of electronic systems with half-integral values of the angular momentum in crystals. In that case, besides  $\bar{E}$ , one has to introduce for the point group new classes of symmetry operations, noted here generically  $\bar{R}$  with respect to the usual ones, such that  $R\bar{E} = \bar{R}$ , and they lead to a two-valued representation of the group, sometimes referred to as the double group in this particular case. For instance, a  $\bar{C}_n$  class corresponds to  $C_n\bar{E}$ . The number of classes of the double group is larger than that of the original group, but not always twice as large.

The tables of characters of a point group are very useful to determine the splitting of a degenerate electronic energy level in a crystal field of a given symmetry. They also allow to determine if a transition between two levels associated with different *IRs* is IR-allowed or Raman-allowed. For the double groups, the characters of the *IRs* not involving spin are the same for the  $R$  and  $\bar{R}$  symmetry operations. For those involving spin, the characters are different, unless the  $R$  and  $\bar{R}$  operations belong to the same class. As an example, the full double group character table of the  $T_d$  symmetry point group is given in Table B.4. The double groups and their symmetry operations keep the notation of the standard point groups with an upper bar ( $\bar{T}_d$ ).

For the double representations, the basis functions that are eigenfunctions of angular momentum  $j$  and projection  $m$  on the  $z$  axis are noted  $\phi(j, m)$ . For  $\Gamma_7$ , the basis functions transform like the products  $\phi(j, m)$  of the basis functions of  $\Gamma_6$  and those of  $\Gamma_2$  and they are noted  $\Gamma_6 \times \Gamma_2$ .

**Table B.4.** Double group characters table for the  $T_d$  point group. The numbers before the symmetry operations correspond to the number of geometrically different axes or symmetry planes. Some of the operations of the double group belong to the same class as those of the original group. When more than one  $IR$  is indicated, the first one corresponds to the notation of Mulliken [11], the second one to Koster et al. [9] and the one in parentheses to [3]

| Symmetry<br>classes: $IRs$      | $E$ | $\bar{E}$ | $8C_3$ | $8\bar{C}_3$ | $3C'_2$<br>$3\bar{C}_2$ | $6S_4$      | $6\bar{S}_4$ | $6\sigma_d$<br>$6\bar{\sigma}_d$ | Basis<br>functions                                                                |
|---------------------------------|-----|-----------|--------|--------------|-------------------------|-------------|--------------|----------------------------------|-----------------------------------------------------------------------------------|
| $A_1, \Gamma_1$                 | 1   | 1         | 1      | 1            | 1                       | 1           | 1            | 1                                | $xyz$                                                                             |
| $A_2, \Gamma_2$                 | 1   | 1         | 1      | 1            | 1                       | -1          | -1           | -1                               | $S_x S_y S_z$                                                                     |
| $E, \Gamma_3 (\Gamma_{12})$     | 2   | 2         | -1     | -1           | 2                       | 0           | 0            | 0                                | $(2z^2 - x^2 - y^2)$<br>$\sqrt{3}(x^2 - y^2)$                                     |
| $T_2, \Gamma_5 (\Gamma_{15})^a$ | 3   | 3         | 0      | 0            | -1                      | -1          | -1           | 1                                | $x, y, z$                                                                         |
| $T_1, \Gamma_4 (\Gamma_{25})$   | 3   | 3         | 0      | 0            | -1                      | 1           | 1            | -1                               | $S_x, S_y, S_z$                                                                   |
| $\Gamma_6$                      | 2   | -2        | 1      | -1           | 0                       | $\sqrt{2}$  | $-\sqrt{2}$  | 0                                | $\phi(1/2, 1/2),$<br>$\phi(1/2, -1/2)$                                            |
| $\Gamma_7$                      | 2   | -2        | 1      | -1           | 0                       | $-\sqrt{2}$ | $\sqrt{2}$   | 0                                | $\Gamma_6 \times \Gamma_2$                                                        |
| $\Gamma_8$                      | 4   | -4        | -1     | 1            | 0                       | 0           | 0            | 0                                | $\phi(3/2, 3/2),$<br>$\phi(3/2, 1/2),$<br>$\phi(3/2, -1/2),$<br>$\phi(3/2, -3/2)$ |

### B.3.4 The Symmetry Space Groups

The global symmetry of a crystal is specified not only by a spatial invariance with respect to the proper and improper rotations defined by the elements of its point group, but also by the translation operations<sup>1</sup> by vectors  $\mathbf{t}_n$  defined by B.1. The primitive translation vectors are defined by the lattice points of the primitive cells of the different  $BLs$  and they constitute an invariant symmetry group. The symmetry space group of a crystal contains elements combining the operations of the point (or rotation) group and of the translation group of the crystal. The number of symmetry space groups is finite and equal to 230 in 3D. The translation group of operations is a subgroup of the space group of the crystal. When this group contains only the primitive translations of the  $BL$ , the rotation group is also a subgroup of the space group of the crystal, which is then called symmorphic or simple space group. There are 73 such space groups in 3D. The translation groups of the other space groups (157 in 3D) contain vectors that are not primitive vectors of the  $BLs$  and the rotation groups associated with these space groups are not subgroups of these space groups [8].

We consider here a few particular space groups. The fcc  $BL$  is generated by three primitive translation vectors making equal angles with one another.

<sup>1</sup> For a crystal of finite size, translation symmetry necessitates proper consideration of boundary conditions (Heine [6]).



The unit cell contains four lattice points. If one lattice point is at the corner of the cube, the three primitive translations extend from this point to the centre of the faces of the cube adjacent to this corner. They can be taken as:

$$\begin{aligned} \mathbf{t}_1 &= \left( t / \sqrt{2} \right) (\mathbf{i} + \mathbf{j}) \\ \mathbf{t}_2 &= \left( t / \sqrt{2} \right) (\mathbf{i} + \mathbf{k}) \\ \mathbf{t}_3 &= \left( t / \sqrt{2} \right) (\mathbf{j} + \mathbf{k}) \end{aligned} \quad (\text{B.5})$$

where  $\mathbf{i}$ ,  $\mathbf{j}$ , and  $\mathbf{k}$  are unit vectors along the edges of the cube and  $t$  the length of the translations. The combinations of these primitive translations with the  $T_d$  and  $O_h$  point groups result in the symmorphic  $T_d^2$  and  $O_h^5$  space groups<sup>2</sup> (noted  $F\bar{4}3m$  and  $Fm\bar{3}m$ , respectively in the international notation).  $T_d^2$  is the space groups of sphalerite (cubic ZnS), a crystal structure shared by several III-V and II-VI compounds, and  $O_h^5$  the space group of sodium chloride and calcium fluoride. When adding to the fcc primitive translations (B.5) the nonprimitive translation  $\frac{1}{4}(\mathbf{t}_1 + \mathbf{t}_2 + \mathbf{t}_3)$  and combining with  $O_h$ , the space group generated is  $O_h^7$  ( $Fd\bar{3}m$ ). By construction, this space group is not symmorphic and it generates the diamond structure.

The BZ of the fcc  $BL$ , associated with space group  $O_h^5$  is shown in Fig. B.2, where the Miller indices of the main symmetry axes are indicated. The critical points  $\Delta$ ,  $\Lambda$ , and  $\Sigma$  are general points inside the BZ on the indicated axes.

The BZ of the  $O_h^7$  and  $T_d^2$  space groups have the same geometry, but the point group symmetries associated with the critical points can differ. These symmetries are given in Table B.5.

The combination of the primitive translation vectors of the hexagonal  $BL$  and of a nonprimitive translation vector to be defined later with the  $C_{6v}$  rotation group results in the  $C_{6v}^4$  space group ( $P6_3mc$ ). This space group is the one of wurtzite (hexagonal ZnS) to which belong the III-V nitrides and several II-VI compounds. The BZ of the hexagonal  $BL$  is shown in Fig. B.1. The point groups along the  $\Gamma$ - $\Delta$ - $A$ ,  $K$ - $P$ - $H$ , and  $M$ - $U$ - $L$  axes of the BZ for the wurtzite structure are  $C_{6v}$ ,  $C_{3v}$ , and  $C_{2v}$ , respectively [12].

**Table B.5.** Point group symmetries associated with the critical points of the BZ of the fcc  $BL$  for different space groups

| Space group         | $\Gamma$ | $\Delta$ | $\Lambda$ | $\Sigma$ | X        | L        | K        | W        |
|---------------------|----------|----------|-----------|----------|----------|----------|----------|----------|
| $O_h^5$ and $O_h^7$ | $O_h$    | $C_{4v}$ | $C_{3v}$  | $C_{2v}$ | $D_{4h}$ | $D_{3d}$ | $C_{2v}$ | $D_{2d}$ |
| $T_d^2$             | $T_d$    | $C_{2v}$ | $C_{3v}$  | $C_{2v}$ | $D_{2d}$ | $C_{3v}$ | $C_{2v}$ | $S_4$    |

<sup>2</sup> These notations simply mean that  $T_d^2$  was the second space group including  $T_d$  and  $O_h^5$  the fifth space group including  $O_h$  derived by Schönflies.

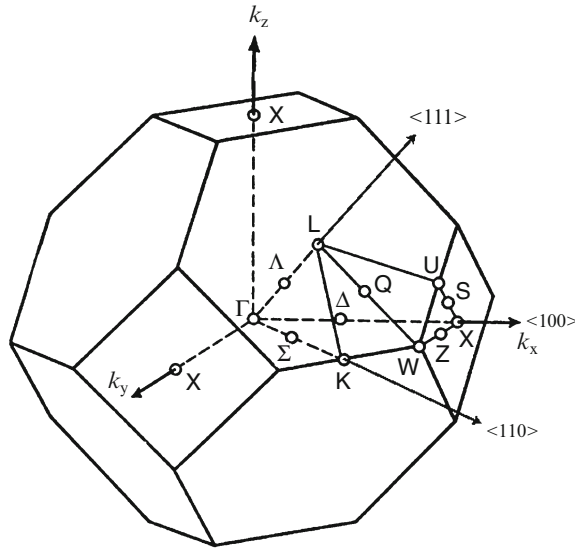


**Fig. B.2.** First Brillouin zone of the fcc  $BL$ , showing the critical points. Its geometry is the same as that of the Wigner-Seitz primitive cell of the bcc  $BL$

## B.4 Some Crystal Structures

### B.4.1 Cubic Structures

The cubic structure is found in many crystals, but with different arrangements of the atoms. The simplest ones are the  $\text{NaCl}$  and the  $\text{CsCl}$  structures. The  $\text{NaCl}$  structure is the superposition of two identical fcc Bravais sublattices shifted by  $1/2$  of the edges of their unit cell; one  $\text{Na}^+$  ( $\text{Cl}^-$ ) ion has 6  $\text{Cl}^-$  ( $\text{Na}^+$ ) *nns* along  $\langle 100 \rangle$  directions. The  $\text{CsCl}$  structure is the superposition of two identical simple cubic (sc) sublattices translated by  $1/2$  of the diagonal of their unit cell; one  $\text{Cs}^+$  ( $\text{Cl}^-$ ) ion has 8  $\text{Cl}^-$  ( $\text{Cs}^+$ ) *nns* of the other sublattice along  $\langle 111 \rangle$  directions. The symmorphic space group of  $\text{CsCl}$  is  $O_h^1$  ( $\text{Pm}3m$ ).

The fluorite ( $\text{CaF}_2$ ) lattice is the superposition of a fcc sublattice of  $\text{Ca}^{++}$  ions with a sc sublattice of  $\text{F}^-$  ions. The lengths of the edges of the unit cells of the  $\text{Ca}^{++}$  and  $\text{F}^-$  sublattices are in the ratio of 2 to 1, respectively and the  $\text{F}^-$  unit cell is shifted by  $1/4$  along the diagonal of the  $\text{Ca}^{++}$  cubic cell. The  $\text{CaF}_2$  lattice is thus made of unit cells containing each four  $\text{Ca}^{++}$  ions and eight  $\text{F}^-$  ions. Crystals with the same atomic arrangement as fluorite, but where the more electronegative element is exchanged with the more positive one of fluorite, like  $\text{Mg}_2\text{Si}$ , are said to have the antifluorite structure. This Mg-based family of crystals has semiconductor properties.

The diamond structure and the cubic  $\text{ZnS}$  (sphalerite or zinc-blende) structure can be seen as the superposition of two identical fcc Bravais sublattices translated by one quarter of the diagonal of their unit cell. In these structures,

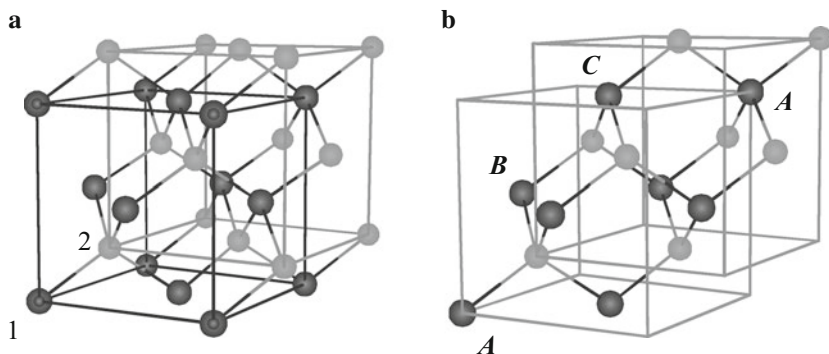


**Fig. B.3.** (a) Ball and sticks model of the sphalerite structure showing the two interpenetrating fcc unit cells. Each cell contains only one type of atom. The displacement between the two cells is materialized by the bond between atoms 1 and 2. (b) Same cells as in (a) showing atoms bonding along a privileged  $\langle 111 \rangle$  axis of the crystal. Along this axis, the period of the crystal is the diagonal of one unit cell and it contains three stacks of atoms of one type (the **ABC** stacking period of sphalerite). The atoms not involved in the bonding have been omitted for clarity

each atom is bonded to its four *nns* in a regular tetrahedral configuration (see Fig. B.3 (a) and (b)). In the diamond structure, the atoms of the two sublattices are the same and the associated rotational symmetry is the one of the fcc structure,  $O_h$ , or  $m\bar{3}m$  in the international notation, which includes inversion symmetry. In the sphalerite structure, as the two atoms are different, there is no more inversion symmetry and the point group symmetry is  $T_d$  or  $\bar{4}3m$ . There must be no confusion with the site symmetry of a substitutional impurity, which is  $T_d$  for both structures. A partial list of crystals with these structures is given in Appendix C.

The perovskite structure is shared by many oxides and other compounds of generic formula  $AMX_3$  where A is a group IIA atom, M, a metal atom and X is a group VI atom. The unit cell is the exact superposition of two identical bcc and fcc lattices. Atom A with coordinates 0,0,0 is common to both lattices, atom M is at the centre of the cube and the X atoms are at the centres of the faces of cube. An A atom has 12 nearest neighbours (*nn*) X atoms, an M atom has 6 *nn* X atoms and 8 *nn* A atoms while an X atom has two M *nn* and four A *nn*. In some compounds including  $CaTiO_3$  (perovskite), this cubic structure is distorted and the structure is no longer cubic, but orthorhombic.

### B.4.2 Hexagonal Structures

The hexagonal closed-packed (hcp) structure can be viewed as two interpenetrating hexagonal *BLs* where one is shifted vertically along the *c*-axis by half of the height *c* of the hexagonal unit cell and horizontally so that the points of one hexagonal lattice lie directly above the centres of the triangles formed

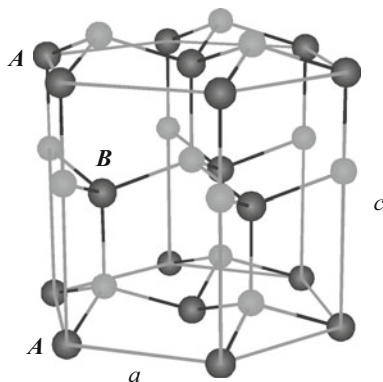


**Fig. B.4.** Ball and sticks model of the wurtzite structure. Along the  $c$  direction, the period of the crystal is equal to the height  $c$  of the cell and it contains two stacks of atoms of one type (the **AB** stacking period of wurtzite). To better appreciate the symmetry, the limits of one hexagonal subunit have been outlined. The minimum distance between superposed non-bonded atoms along the  $c$ -axis is  $\sim 0.625c$ .

by the points of the other one. The hcp structure is the same as that of a close-packed stack of identical spheres. If the radius of these spheres is  $a$ , the distance  $c/2$  between the first and second layers is  $\sqrt{2/3}a$  and this packing condition determines the ratio 1.633 between the side  $a$  of the hexagon and the height  $c$  of the unit in the hcp structure. The wurtzite structure (so called after the hexagonal allotropic form of ZnS) is the superposition of two hcp sublattices whose unit cells are shifted by  $5c/8$  along the height of the cell (the  $c$ -axis) and it is shown in Fig. B.4.

The symmetry point group associated with this structure is  $C_{6v}$  (6 mm) and it is derived from the corresponding space group. The symmetry difference between wurtzite and sphalerite leads naturally to environment differences: in sphalerite, an atom has 24 closer 3<sup>rd</sup>  $nn$  atoms and 12 more distant 3<sup>rd</sup>  $nn$  atoms. In wurtzite there are four categories of 3<sup>rd</sup>  $nn$  atoms: only one 3<sup>rd</sup>  $nn$  atom is at a distance only slightly larger than the  $nn$ , along the same  $c$ -axis as the reference atom. The three other categories contain 6, 6 and 12 atoms. The real crystals with wurtzite structure do show a small crystal distortion along the  $c$  axis so that the ratio  $c/a$  between the height of the unit cell and the side of the regular hexagonal base differs from the ideal value 1.6333. This produces a small increase of the  $nn$  and  $nnn$  distances for orientations along or predominantly along the  $c$ -axis.

Many IIA-sulphides and -oxides as well as IIIA-nitrides crystallize in the wurtzite form, but some of them (ZnS, of course, but also CdS, GaN and others) can also be found in the sphalerite form. SiC can adopt the wurtzite form (2H-SiC) or less frequently the sphalerite form (3C-SiC), with a notable difference in the band gap (3.3 or 2.3 eV, respectively), but when grown by vapour-phase epitaxy, SiC is usually obtained in the form of polytypes with

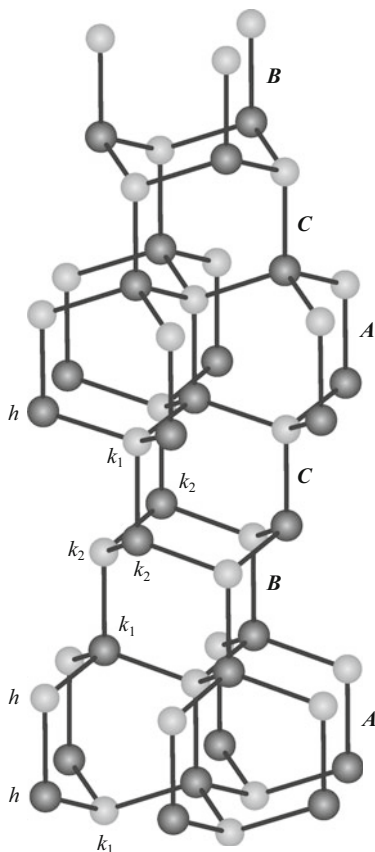


**Fig. B.5.** Unit cell of the  $6H$ -SiC polytype showing the  $ABCACB$  stacking sequence and the different sites (see text)

stacking periods different from those of  $3C$ -SiC and  $2H$ -SiC. One of the most common variety is  $6H$ -SiC, whose stacking period along the  $c$ -axis is  $ABCACB$ . Its unit cell is shown in Fig. B.5.

In the  $6H$ -SiC polytype, there are three different sites: an hexagonal one noted  $h$ , and two cubic ones noted  $k_1$  and  $k_2$ . As shown in Fig. B.5, an  $h$  site is surrounded by three  $k_1$  and one  $h$   $nn$  sites, a  $k_1$  site by three  $h$  and one  $k_2$   $nn$  sites, and a  $k_2$  site by three  $k_2$  and one  $k_1$   $nn$  sites.

Very small carbon crystals with the hexagonal structure of Fig. B.4 have been found in some meteorites, and this form of carbon is called lonsdaleite.

### B.4.3 Other Crystal Structures

Corundum ( $\alpha$ - $Al_2O_3$ ) structure displays trigonal (or rhombohedral) symmetry. When considering an ionic configuration  $(Al^{3+})_2 (O^{2-})_3$ , the point group

symmetry of this crystal is  $C_{3v}$  or  $3/m$ . Instead of considering the trigonal unit cell containing two  $Al_2O_3$  units, it is usual to consider an hexagonal cell with axis  $c$  along the longest diagonal of the trigonal unit cell. The side  $a$  of the hexagon is the projection of  $a_0$  in a plane perpendicular to the  $c$  axis and the height  $c$  of the cell is the length of the longest diagonal of the trigonal unit cell. For corundum,  $a$  and  $c$  are 0.47489 and 1.29912 nm, respectively, and each  $Al^{3+}$  cation is surrounded by 6  $nn$   $O^{2-}$  anions at the corners of a nearly regular octahedron. 3 among these 6  $nns$  are slightly closer to  $Al^{3+}$  than the others (0.1856 and 0.1969 nm).

Besides the 3D crystalline structures, 2D crystalline structures can also form 3D solids. In these solids, the bonding between the layers is weak and an archetype of these solids is graphite. Graphite, a semimetal, has a simple 2D hexagonal  $BL$  with C atomic layers separated by about 2.4 times the  $nn$  separation in the layer plane. Such a structure can also be considered as a 3D crystal with space group  $D_{6h}^4$  ( $P63/mmc$ ). It is actually the stable structure of crystalline carbon while diamond and lonsdaleite are metastable phases. Similarly, the stable form of BN is a 2D hexagonal form ( $h$ -BN), but at a difference with graphite, where half of the C atoms of one layer projects onto the empty centre of hexagons of the adjacent layers and the other half on C atoms, a B atom of a  $h$ -BN layer always projects onto a N atom of the adjacent layers. In these 2D crystals, the axis perpendicular to the plane of the layers is noted as the  $c$ -axis. Layered structures made of composite layers of several atoms are found for instance in many III-VI compounds like GaSe, often termed as lamellar. In this latter structure, the “unit” layer is made of a four-layer structure in which two inner bonded layers of Ga atoms are each bonded to an external layer of Se atoms.

## References

1. N.W. Ashcroft, N.D. Mermin, *Solid State Physics* (Saunders College, Philadelphia, 1976)
2. H. Bethe, Ann. Der Phys. **3**, 133 (1933)
3. L.B. Bouckaert, R. Smoluchowski, E. Wigner, Phys. Rev. **50**, 58 (1936)
4. J.W. Cahn, J. Res. Natl. Inst. Stand. Tech. **106**, 975 (2001)
5. M.S. Dresselhaus, G. Dresselhaus, A. Jorio, *Group Theory: Application to the Physics of Condensed Matter* (Springer, New York, 2008)
6. V. Heine, *Group Theory in Quantum Mechanics* (Pergamon Press, Oxford, 1964)
7. C. Kittel, *Introduction to Solid State Physics*, 7<sup>th</sup> edn. (Wiley, New York, (1996)
8. G.F. Koster, in *Solid State Physics Advances in Research and Application*, vol. 5, ed. by F. Seitz, D. Turnbull (Academic, New York, 1957), p. 173
9. G.F. Koster, J.O. Dimmock, R.G. Wheeler, H. Statz, *Properties of the Thirty-Two Point Groups*, (MIT, Cambridge, MA, 1963)
10. M. Lax, *Symmetry Principles in Solid State and Molecular Physics* (Dover Publications, Mineola, NY, 1974)
11. R.S. Mulliken, Phys. Rev. **43**, 279 (1933)
12. L. Patrick, D.R. Hamilton, W.J. Choyke, Phys. Rev. **143**, 526 (1966)

## Appendix C

### Optical Band Gaps and Crystal Structures of Some Insulators and Semiconductors

Band-gap energies  $E_g$  (eV) at RT and, when known, at LHeT of some insulators and semiconductors with direct (D) or indirect (I) band gaps. For the uniaxial crystals, the band gaps for  $\mathbf{E}/c$  and  $\mathbf{E}\perp c$  slightly differ and the value given is an average. The equivalent of the RT value of  $E_g$  is expressed in wavelength ( $\lambda$ ) in the last column. It is close to the high-frequency limit of transparency for pure and nondiffusing materials. The visible range extends from 400 to about 750 nm.

For the crystal structures, c, h, and hcp stand for cubic, hexagonal, and hexagonal close-packed, respectively. The name of the crystals used as references are bold-faced.

| Material                                            | Crystal structure           | $E_g$ (RT)   | $E_g$ (LHeT)       | $\lambda$ (nm) |
|-----------------------------------------------------|-----------------------------|--------------|--------------------|----------------|
| MgF <sub>2</sub> (sellaite)                         | Tetragonal                  | 11.3         |                    | 110            |
| SiO <sub>2</sub> ( $\alpha$ -cristobalite)          | Tetragonal                  | $\sim 10$    |                    | $\sim 124$     |
| <b>CaF<sub>2</sub> (fluorite)</b>                   | <b>fluorite (c)</b>         | $\sim 9.5$   |                    | 130            |
| SiO <sub>2</sub> ( $\alpha$ -quartz)                | h                           | $\sim 9$     |                    | $\sim 140$     |
| $\alpha$ -Al <sub>2</sub> O <sub>3</sub> (corundum) | Trigonal                    | $\sim 9$     |                    | $\sim 140$     |
| <b>NaCl (halite)</b>                                | <b>NaCl (c)</b>             | 9.0 D        |                    | 138            |
| CdF <sub>2</sub>                                    | c (fluorite)                | 7.8          |                    | 159            |
| MgO (periclase)                                     | c (NaCl)                    | 7.6 D        |                    | 163            |
| c-BN                                                | c (sphalerite)              | 6.4 I        |                    | 194            |
| AlN                                                 | hcp (wurtzite)              | 6.2 D        |                    | 200            |
| C (lonsdaleite)                                     | hcp                         | $\sim 5.5$   |                    | $\sim 220$     |
| <b>C<sup>diam</sup> (diamond)</b>                   | <b>C<sup>diam</sup> (c)</b> | 5.475 I      | 5.487 <sup>a</sup> | 226            |
| h-BN                                                | h 2D                        | 5.2 I        |                    | 238            |
| <b>ZnS (wurtzite)</b>                               | <b>wurtzite (hcp)</b>       | 3.8 D        |                    | 325            |
| <b>ZnS (sphalerite)</b>                             | <b>sphalerite (c)</b>       | 3.68 D       | 3.78               | 335            |
| w-GaN or $\alpha$ -GaN                              | hcp (wurtzite)              | $\sim 3.4$ D | 3.50               | 365            |
| ZnO (zincite)                                       | hcp (wurtzite)              | 3.4 D        | 3.44               | 365            |

(continued)

| Material                      | Crystal structure            | $E_g$ (RT)                    | $E_g$ (LHeT)       | $\lambda$ (nm) |
|-------------------------------|------------------------------|-------------------------------|--------------------|----------------|
| <i>c</i> -GaN or $\beta$ -GaN | c (sphalerite)               | 3.30 D                        | 3.41               | 376            |
| 2 <i>H</i> -SiC (moissanite)  | hcp (wurtzite)               | 3.3 I                         | 3.33               | 376            |
| CuCl (nantokite)              | c (sphalerite)               | 3.26 D                        | 3.399              | 381            |
| 4 <i>H</i> -SiC               | polytype                     | 3.23 I                        | 3.27               | 384            |
| 6 <i>H</i> -SiC               | polytype                     | 2.86 I                        | 3.03               | 434            |
| ZnSe (stilleite)              | c (sphalerite)               | 2.67 D                        | 2.82               | 460            |
| CdS (hawleyite)               | c (sphalerite)               | 2.50 D                        |                    | 496            |
| CdS (greenockite)             | hcp (wurtzite)               | 2.49 D                        |                    | 498            |
| AlP                           | c (sphalerite)               | 2.45 I                        | 2.505              | 506            |
| 3 <i>C</i> -SiC               | c (sphalerite)               | $\sim 2.3$ I                  | 2.41               | $\sim 540$     |
| ZnTe                          | c (sphalerite)               | 2.28 D                        | 2.394              | 544            |
| GaP                           | c (sphalerite)               | 2.272 I                       | 2.350              | 546            |
| Cu <sub>2</sub> O (cuprite)   | c                            | $\sim 2.2$ D                  |                    | $\sim 560$     |
| AlAs                          | c (sphalerite)               | 2.15 I                        | 2.229              | 577            |
| HgI <sub>2</sub>              | tetragonal                   | 2.13 D                        | 2.37               | 582            |
| $\alpha$ -HgS (cinnabar)      | trigonal                     | 2.10 I                        | 2.275              | 590            |
| GaSe                          | quasi-2D                     | $\sim 2$ D                    |                    | $\sim 620$     |
| CdSe (cadmoselite)            | hcp (wurtzite)               | 1.714 D                       | 1.829 <sup>a</sup> | 709            |
| AlSb                          | c (sphalerite)               | 1.62 I                        | 1.686              | 765            |
| CdTe                          | c (sphalerite)               | 1.526 D                       | 1.607              | 812            |
| GaAs                          | c (sphalerite)               | 1.424 D                       | 1.519              | 873            |
| InP                           | c (sphalerite)               | 1.344 D                       | 1.424              | 923            |
| <i>H</i> -MnTe                | h (NiAs)                     | 1.27                          |                    | 976            |
| B                             | $\beta$ -rhombohedral        | $\sim 1.6$ I                  |                    | $\sim 1000$    |
| Si                            | c (C <sub>diam</sub> )       | 1.124 I                       | 1.1700             | 1101           |
| CuInSe <sub>2</sub>           | Tetragonal<br>(chalcopyrite) | $\sim 1$                      |                    | $\sim 1240$    |
| $\beta$ -FeSi <sub>2</sub>    | Orthorhombic                 | 0.87 D                        | 0.93               | 1425           |
| CdO (monteponite)             | c (NaCl)                     | 0.84 I                        |                    | 1476           |
| InN                           | hcp (wurtzite)               | $\sim 0.8$ D                  |                    | $\sim 1550$    |
| GaSb                          | c (sphalerite)               | 0.727 D                       | 0.811              | 1705           |
| Ge                            | c (C <sub>diam</sub> )       | 0.670 I                       | 0.7447             | 1851           |
| Mg <sub>2</sub> Si            | c (antifluorite)             | $\sim 0.6$ I                  | 0.77               | $\sim 2070$    |
| Mg <sub>2</sub> Ge            | c (antifluorite)             | 0.54 I                        | 0.74               | $\sim 2480$    |
| PbS (galena)                  | c (NaCl)                     | 0.41 D                        | 0.29               | $\sim 3350$    |
| InAs                          | c (sphalerite)               | 0.354 D                       | 0.418              | $\sim 3440$    |
| Te (native)                   | trigonal                     | 0.32 (//)<br>0.37 ( $\perp$ ) |                    | $\sim 3440$    |
| PbTe (clausthalite)           | c (NaCl)                     | 0.29 D                        | 0.190              | $\sim 4280$    |
| PbSe (altaite)                | c (NaCl)                     | 0.26 D                        | 0.165              | $\sim 4770$    |
| SnTe                          | c (NaCl)                     | 0.19 D                        |                    | $\sim 6320$    |
| Mg <sub>2</sub> Sn            | c (antifluorite)             | 0.18 I                        |                    | $\sim 6900$    |
| InSb                          | c (sphalerite)               | 0.18 D                        | 0.2344             | $\sim 6900$    |

<sup>a</sup> At LNT



# Appendix D

## Table of Isotopes

An asterisk denotes a radioactive isotope whose lifetime is indicated in the column Natural abundance. When a stable element has several radioactive isotopes, a few ones have been chosen for their interest in different applications. For the radioactive elements, only the isotopes with the longest lifetimes and at least one with a nonzero nuclear spin **I** are indicated. The electronic configuration of an element with atomic number **Z** is given in italics in the Name and symbol column. When relevant, the old Group label notation of the periodic table is indicated in brackets in this same column. The radioactive elements francium, radium, and actinium ( $Z = 87, 88,$  and  $89,$  respectively) have been omitted.

| Name and symbol                                    | Z        | Number of<br>nucleons | Natural<br>abundance (%) | Average<br>mass (amu) | I   |
|----------------------------------------------------|----------|-----------------------|--------------------------|-----------------------|-----|
| Hydrogen (H or $^1\text{H}$ )                      | <b>1</b> | 1                     | (99.985)                 | 1.008                 | 1/2 |
| Deuterium (D or $^2\text{H}$ )                     |          | 2                     | (0.0148)                 |                       | 1   |
| Tritium* (T or $^3\text{H}$ )                      |          | 3*                    | 12.32 y                  |                       | 1/2 |
| <i>1s</i>                                          |          |                       |                          |                       |     |
| Helium (He)                                        | <b>2</b> | 3                     | (0.000138)               | 4.003                 | 1/2 |
| <i>1s</i> <sup>2</sup>                             |          | 4                     | (99.999862)              |                       | 0   |
| Lithium (Li) [IA]                                  | <b>3</b> | 6                     | (7.6)                    | 6.941                 | 1   |
| [He] <i>2s</i>                                     |          | 7                     | (92.4)                   |                       | 3/2 |
| Beryllium (Be) [IIA]                               | <b>4</b> | 9                     | (100)                    | 9.012                 | 3/2 |
| [He] <i>2s</i> <sup>2</sup>                        |          | 10*                   | $1.52 \times 10^6$ y     |                       | 0   |
| Boron (B) [IIIB]                                   | <b>5</b> | 10                    | (19.8)                   | 10.81                 | 3   |
| [He] <i>2s</i> <sup>2</sup> <i>2p</i>              |          | 11                    | (80.2)                   |                       | 3/2 |
| Carbon (C) [IVB]                                   | <b>6</b> | 12                    | (98.93)                  | 12.01                 | 0   |
| [He] <i>2s</i> <sup>2</sup> <i>2p</i> <sup>2</sup> |          | 13                    | (1.07)                   |                       | 1/2 |
|                                                    |          | 14*                   | 5,715 y                  |                       | 0   |
| Nitrogen (N) [VB]                                  | <b>7</b> | 14                    | (99.632)                 | 14.01                 | 1   |
| [He] <i>2s</i> <sup>2</sup> <i>2p</i> <sup>3</sup> |          | 15                    | (0.368)                  |                       | 1/2 |

(continued)

| Name and symbol       | Z         | Number of<br>nucleons | Natural<br>abundance (%) | Average<br>mass (amu) | I   |
|-----------------------|-----------|-----------------------|--------------------------|-----------------------|-----|
| Oxygen (O) [VIB]      | <b>8</b>  | 16                    | (99.757)                 | 16.00                 | 0   |
| [He] $2s^2 2p^4$      |           | 17                    | (0.038)                  |                       | 5/2 |
|                       |           | 18                    | (0.205)                  |                       | 0   |
| Fluorine (F) [VIIB]   | <b>9</b>  | 18*                   | 1.83 h                   | 19.00                 | 1   |
| [He] $2s^2 2p^5$      |           | 19                    | (100)                    |                       | 1/2 |
| Neon (Ne)             | <b>10</b> | 20                    | (90.48)                  | 20.18                 | 0   |
| [He] $2s^2 2p^6$      |           | 21                    | (0.27)                   |                       | 3/2 |
|                       |           | 22                    | (9.25)                   |                       | 0   |
| Sodium (Na) [IA]      | <b>11</b> | 22*                   | 2.605 y                  | 22.99                 | 3   |
| [Ne] $3s$             |           | 23                    | (100)                    |                       | 3/2 |
| Magnesium (Mg) [IIA]  | <b>12</b> | 24                    | (78.99)                  | 24.31                 | 0   |
| [Ne] $3s^2$           |           | 25                    | (10.00)                  |                       | 5/2 |
|                       |           | 26                    | (11.01)                  |                       | 0   |
| Aluminium (Al) [IIIB] | <b>13</b> | 26*                   | $7.1 \times 10^5$ y      | 26.98                 | 5   |
| [Ne] $3s^2 3p$        |           | 27                    | (100)                    |                       | 5/2 |
| Silicon (Si) [IVB]    | <b>14</b> | 28                    | (92.23)                  | 28.086                | 0   |
| [Ne] $3s^2 3p^2$      |           | 29                    | (4.67)                   |                       | 1/2 |
|                       |           | 30                    | (3.10)                   |                       | 0   |
|                       |           | 31*                   | 2.62 h                   |                       | 0   |
| Phosphorus (P) [VB]   | <b>15</b> | 31                    | (100)                    | 30.97                 | 1/2 |
| [Ne] $3s^2 3p^3$      |           | 32*                   | 14.28 d                  |                       | 1   |
| Sulphur (S) [VIB]     | <b>16</b> | 32                    | (94.93)                  | 32.07                 | 0   |
| [Ne] $3s^2 3p^4$      |           | 33                    | (0.76)                   |                       | 3/2 |
|                       |           | 34                    | (4.29)                   |                       | 0   |
|                       |           | 36                    | (0.02)                   |                       | 0   |
| Chlorine (Cl) [VIIB]  | <b>17</b> | 35                    | (75.78)                  | 35.45                 | 3/2 |
| [Ne] $3s^2 3p^5$      |           | 36*                   | 301,000 y                |                       | 0   |
|                       |           | 37                    | (24.22)                  |                       | 3/2 |
| Argon (Ar)            | <b>18</b> | 36                    | (0.337)                  | 39.95                 | 0   |
| [Ne] $3s^2 3p^6$      |           | 38                    | (0.063)                  |                       | 0   |
|                       |           | 39*                   | 268 y                    |                       | 7/2 |
|                       |           | 40                    | (99.600)                 |                       | 0   |
| Potassium (K) [IA]    | <b>19</b> | 39                    | (93.26)                  | 39.10                 | 3/2 |
| [Ar] $4s$             |           | 40*                   | (0.012)                  |                       | 4   |
|                       |           |                       | $1.28 \times 10^9$ y     |                       |     |
|                       |           | 41                    | (6.73)                   |                       | 3/2 |
|                       |           | 40                    | (96.941)                 |                       | 0   |
| Calcium (Ca) [IIA]    | <b>20</b> | 41*                   | 102,000 y                | 40.08                 | 7/2 |
| [Ar] $4s^2$           |           | 42                    | (0.647)                  |                       | 0   |
|                       |           | 43                    | (0.135)                  |                       | 7/2 |
|                       |           | 44                    | (2.086)                  |                       | 0   |

(continued)

| Name and symbol                        | Z  | Number of<br>nucleons | Natural<br>abundance (%) | Average<br>mass (amu) | I   |
|----------------------------------------|----|-----------------------|--------------------------|-----------------------|-----|
|                                        |    | 46                    | (0.004)                  |                       | 0   |
|                                        |    | 48                    | (0.187)                  |                       | 0   |
| Scandium (Sc)                          | 21 | 45                    | (100)                    | 44.96                 | 7/2 |
| [Ar] 3d 4s <sup>2</sup>                |    | 46*                   | 83.81 d                  |                       | 4   |
| Titanium (Ti)                          | 22 | 44*                   | 67 y                     |                       | 0   |
| [Ar] 3d <sup>2</sup> 4s <sup>2</sup>   |    | 46                    | (8.25)                   | 47.87                 | 0   |
|                                        |    | 47                    | (7.44)                   |                       | 5/2 |
|                                        |    | 48                    | (73.72)                  |                       | 0   |
|                                        |    | 49                    | (5.41)                   |                       | 7/2 |
|                                        |    | 50                    | (5.18)                   |                       | 0   |
| Vanadium (V)                           | 23 | 50                    | (0.25)                   | 50.94                 | 6   |
| [Ar] 3d <sup>3</sup> 4s <sup>2</sup>   |    | 52                    | (99.75)                  |                       | 7/2 |
| Chromium (Cr)                          | 24 | 50                    | (4.35)                   | 52.00                 | 0   |
| [Ar] 3d <sup>5</sup> 4s                |    | 51*                   | 27.7 d                   |                       | 7/2 |
|                                        |    | 52                    | (83.79)                  |                       | 0   |
|                                        |    | 53                    | (9.50)                   |                       | 3/2 |
|                                        |    | 54                    | (2.36)                   |                       | 0   |
| Manganese (Mn)                         | 25 | 53*                   | 3.7 × 10 <sup>6</sup> y  |                       | 7/2 |
| [Ar] 3d <sup>5</sup> 4s <sup>2</sup>   |    | 55                    | (100)                    | 54.94                 | 5/2 |
| Iron (Fe)                              | 26 | 54                    | (5.85)                   | 55.85                 | 0   |
| [Ar] 3d <sup>6</sup> 4s <sup>2</sup>   |    | 56                    | (91.75)                  |                       | 0   |
|                                        |    | 57                    | (2.12)                   |                       | 1/2 |
|                                        |    | 58                    | (0.28)                   |                       | 0   |
|                                        |    | 60*                   | 1.5 × 10 <sup>6</sup> y  |                       | 0   |
| Cobalt (Co)                            | 27 | 58*                   | 70.9 d                   |                       | 2   |
| [Ar] 3d <sup>7</sup> 4s <sup>2</sup>   |    | 59                    | (100)                    | 58.93                 | 7/2 |
|                                        |    | 60*                   | 5.271 y                  |                       | 5   |
| Nickel (Ni)                            | 28 | 58                    | (68.08)                  | 58.69                 | 0   |
| [Ar] 3d <sup>8</sup> 4s <sup>2</sup>   |    | 59*                   | 76,000 y                 |                       | 3/2 |
|                                        |    | 60                    | (26.22)                  |                       | 0   |
|                                        |    | 61                    | (1.14)                   |                       | 3/2 |
|                                        |    | 62                    | (3.63)                   |                       | 0   |
|                                        |    | 64                    | (0.93)                   |                       | 0   |
| Copper (Cu) [IB]                       | 29 | 63                    | (69.17)                  | 63.55                 | 3/2 |
| [Ar] 3d <sup>10</sup> 4s               |    | 64*                   | 12.701 h                 |                       | 1   |
|                                        |    | 65                    | (30.83)                  |                       | 3/2 |
|                                        |    | 66*                   | 5.09 m                   |                       | 1   |
| Zinc (Zn) [IIB]                        | 30 | 64                    | (48.63)                  | 65.41                 | 0   |
| [Ar] 3d <sup>10</sup> 4 s <sup>2</sup> |    | 65*                   | 243.8 d                  |                       | 5/2 |
|                                        |    | 66                    | (27.90)                  |                       | 0   |
|                                        |    | 67                    | (4.10)                   |                       | 5/2 |

(continued)

| Name and symbol                                                               | Z         | Number of<br>nucleons | Natural<br>abundance (%)  | Average<br>mass (amu) | I   |
|-------------------------------------------------------------------------------|-----------|-----------------------|---------------------------|-----------------------|-----|
| Gallium (Ga) [IIIB]<br>[Ar] 3d <sup>10</sup> 4s <sup>2</sup> 4p               | <b>31</b> | 68                    | (18.75)                   | 69.72                 | 0   |
|                                                                               |           | 70                    | (0.62)                    |                       | 0   |
|                                                                               |           | 69                    | (60.11)                   |                       | 3/2 |
|                                                                               |           | 70*                   | 21.1 m                    |                       | 1   |
|                                                                               |           | 71                    | (39.89)                   |                       | 3/2 |
| Germanium (Ge) [IVB]<br>[Ar] 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>2</sup> | <b>32</b> | 72*                   | 14.10 h                   | 72.64                 | 3   |
|                                                                               |           | 70                    | (20.84)                   |                       | 0   |
|                                                                               |           | 71*                   | 11.2 d                    |                       | 1/2 |
|                                                                               |           | 72                    | (27.54)                   |                       | 0   |
|                                                                               |           | 73                    | (7.73)                    |                       | 9/2 |
|                                                                               |           | 74                    | (36.28)                   |                       | 0   |
|                                                                               |           | 75*                   | 1.38 h                    |                       | 1/2 |
|                                                                               |           | 76                    | (7.61)                    |                       | 0   |
| Arsenic (As) [VB]<br>[Ar] 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>3</sup>    | <b>33</b> | 77*                   | 11.30 d                   | 74.92                 | 7/2 |
|                                                                               |           | 75                    | (100)                     |                       | 3/2 |
|                                                                               |           | 76*                   | 26.3 h                    |                       | 2   |
| Selenium (Se) [VIB]<br>[Ar] 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>4</sup>  | <b>34</b> | 74                    | (0.89)                    | 78.96                 | 0   |
|                                                                               |           | 76                    | (9.37)                    |                       | 0   |
|                                                                               |           | 77                    | (7.63)                    |                       | 1/2 |
|                                                                               |           | 78                    | (23.77)                   |                       | 0   |
|                                                                               |           | 79*                   | 65,000 y                  |                       | 7/2 |
|                                                                               |           | 80                    | (49.61)                   |                       | 0   |
|                                                                               |           | 82                    | (8.73)                    |                       | 0   |
|                                                                               |           | 77*                   | 2.376 d                   |                       | 3/2 |
| Bromine (Br) [VIIB]<br>[Ar] 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>5</sup>  | <b>35</b> | 79                    | (50.69)                   | 79.90                 | 3/2 |
|                                                                               |           | 81                    | (49.31)                   |                       | 3/2 |
|                                                                               |           | 78                    | (0.35)                    | 83.80                 | 0   |
| Krypton (Kr)<br>[Ar] 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>6</sup>         | <b>36</b> | 80                    | (2.28)                    |                       | 0   |
|                                                                               |           | 82                    | (11.58)                   |                       | 0   |
|                                                                               |           | 83                    | (11.49)                   |                       | 9/2 |
|                                                                               |           | 84                    | (57.00)                   |                       | 0   |
|                                                                               |           | 85*                   | 10.73 y                   |                       | 9/2 |
|                                                                               |           | 86                    | (17.30)                   |                       | 0   |
|                                                                               |           | 83*                   | 86.2 d                    |                       | 5/5 |
|                                                                               |           | 85                    | (72.17)                   | 85.47                 | 5/2 |
| Rubidium (Rb) [IA]<br>[Kr] 5s                                                 | <b>37</b> | 87*                   | (27.83)                   |                       | 3/2 |
|                                                                               |           |                       | 4.75 × 10 <sup>10</sup> y |                       |     |
|                                                                               |           | 84                    | (0.56)                    | 87.62                 | 0   |
| Strontium (Sr) [IIA]<br>[Kr] 5s <sup>2</sup>                                  | <b>38</b> | 86                    | (9.86)                    |                       | 0   |
|                                                                               |           | 87                    | (7.0)                     |                       | 9/2 |

(continued)

| Name and symbol                      | Z  | Number of<br>nucleons | Natural<br>abundance (%) | Average<br>mass (amu) | I   |
|--------------------------------------|----|-----------------------|--------------------------|-----------------------|-----|
|                                      |    | 88                    | (82.58)                  |                       | 0   |
|                                      |    | 90*                   | 29.1 y                   |                       | 0   |
| Yttrium (Y)                          | 39 | 89                    | (100)                    | 88.91                 | 1/2 |
| [Kr] 4d 5s <sup>2</sup>              |    |                       |                          |                       |     |
| Zirconium (Zr)                       | 40 | 90                    | (51.45)                  | 91.22                 | 0   |
| [Kr] 4d <sup>2</sup> 5s <sup>2</sup> |    | 91                    | (11.22)                  |                       | 5/2 |
|                                      |    | 92                    | (17.15)                  |                       | 0   |
|                                      |    | 94                    | (17.38)                  |                       | 0   |
|                                      |    | 96*                   | (2.80)                   |                       | 0   |
|                                      |    |                       | 3.9 × 10 <sup>19</sup> y |                       |     |
| Niobium (Nb)                         | 41 | 92*                   | 3.7 × 10 <sup>7</sup> y  |                       | 7   |
| [Kr] 4d <sup>4</sup> 5s              |    | 93                    | (100)                    | 92.91                 | 9/2 |
|                                      |    | 94*                   | 24,000 y                 |                       | 6   |
| Molybdenum (Mo)                      | 42 | 92                    | (14.84)                  | 95.94                 | 0   |
| [Kr] 4d <sup>5</sup> 5s              |    | 93*                   | 3,500 y                  |                       | 5/2 |
|                                      |    | 94                    | (9.25)                   |                       | 0   |
|                                      |    | 95                    | (15.92)                  |                       | 5/2 |
|                                      |    | 96                    | (16.68)                  |                       | 0   |
|                                      |    | 97                    | (9.55)                   |                       | 5/2 |
|                                      |    | 98                    | (24.13)                  |                       | 0   |
|                                      |    | 100                   | (9.63)                   |                       | 0   |
| Technetium* (Tc)                     | 43 | 97*                   | 2.6 × 10 <sup>6</sup> y  |                       | 9/2 |
| [Kr] 4d <sup>5</sup> 5s <sup>2</sup> |    | 98*                   | 4.2 × 10 <sup>6</sup> y  |                       | 6   |
|                                      |    | 99*                   | 213,000 y                |                       | 9/2 |
| Ruthenium (Ru)                       | 44 | 96                    | (5.52)                   | 101.1                 | 5/2 |
| [Kr] 4d <sup>7</sup> 5s              |    | 98                    | (1.88)                   |                       | 0   |
|                                      |    | 99                    | (12.70)                  |                       | 0   |
|                                      |    | 100                   | (12.60)                  |                       | 0   |
|                                      |    | 101                   | (17.00)                  |                       | 5/2 |
|                                      |    | 102                   | (31.60)                  |                       | 0   |
|                                      |    | 104                   | (18.70)                  |                       | 0   |
| Rhodium (Rh)                         | 45 | 101*                  | 3.5 y                    |                       | 1/2 |
| [Kr] 4d <sup>8</sup> 5s              |    | 102*                  | 2.9 y                    |                       | 6   |
|                                      |    | 103                   | (100)                    | 102.9                 | 1/2 |
| Palladium (Pd)                       | 46 | 102                   | (1.02)                   | 106.4                 | 0   |
| [Kr] 4d <sup>10</sup>                |    | 104                   | (11.14)                  |                       | 0   |
|                                      |    | 105                   | (22.33)                  |                       | 5/2 |
|                                      |    | 106                   | (27.33)                  |                       | 0   |
|                                      |    | 107*                  | 6.5 × 10 <sup>6</sup> y  |                       | 5/2 |
|                                      |    | 108                   | (26.46)                  |                       | 0   |
|                                      |    | 110                   | (11.72)                  |                       | 0   |

(continued)

| Name and symbol                                       | Z         | Number of<br>nucleons | Natural<br>abundance (%) | Average<br>mass (amu) | I   |
|-------------------------------------------------------|-----------|-----------------------|--------------------------|-----------------------|-----|
| Silver (Ag) [IB]                                      | <b>47</b> | 105*                  | 41.3 d                   |                       | 1/2 |
| [Kr] 4d <sup>10</sup> 5s                              |           | 107                   | (51.83)                  | 107.9                 | 1/2 |
|                                                       |           | 109                   | (48.17)                  |                       | 1/2 |
| Cadmium (Cd) [IIB]                                    | <b>48</b> | 106                   | (1.25)                   | 112.4                 | 0   |
| [Kr] 4d <sup>10</sup> 5s <sup>2</sup>                 |           | 108                   | (0.89)                   |                       | 0   |
|                                                       |           | 110                   | (12.49)                  |                       | 0   |
|                                                       |           | 111                   | (12.80)                  |                       | 1/2 |
|                                                       |           | 112                   | (24.13)                  |                       | 0   |
|                                                       |           | 113                   | (12.22)                  |                       | 1/2 |
|                                                       |           | 114                   | (28.73)                  |                       | 0   |
|                                                       |           | 116                   | (7.49)                   |                       | 0   |
| Indium (In) [IIIB]                                    | <b>49</b> | 111*                  | 2.805 d                  |                       | 9/2 |
| [Kr] 4d <sup>10</sup> 5s <sup>2</sup> 5p              |           | 113                   | (4.3)                    | 114.8                 | 9/2 |
|                                                       |           | 115*                  | (95.7)                   |                       | 9/2 |
|                                                       |           |                       | 4.4 × 10 <sup>14</sup> y |                       |     |
| Tin (Sn) [IVB]                                        | <b>50</b> | 112                   | (1.0)                    | 118.7                 | 0   |
| [Kr] 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>2</sup> |           | 114                   | (0.7)                    |                       | 0   |
|                                                       |           | 115                   | (0.4)                    |                       | 1/2 |
|                                                       |           | 116                   | (14.7)                   |                       | 0   |
|                                                       |           | 117                   | (7.7)                    |                       | 1/2 |
|                                                       |           | 118                   | (24.3)                   |                       | 0   |
|                                                       |           | 119                   | (8.6)                    |                       | 1/2 |
|                                                       |           | 120                   | (32.4)                   |                       | 0   |
|                                                       |           | 122                   | (4.6)                    |                       | 0   |
|                                                       |           | 124                   | (5.6)                    |                       | 0   |
| Antimony (Sb) [VB]                                    | <b>51</b> | 121                   | (57.3)                   | 121.8                 | 5/2 |
| [Kr] 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>3</sup> |           | 122*                  | 2.72 d                   |                       | 2   |
|                                                       |           | 123                   | (42.7)                   |                       | 7/2 |
|                                                       |           | 124*                  | 60.30 d                  |                       | 3   |
| Tellurium (Te) [VIB]                                  | <b>52</b> | 119*                  | 16 h                     |                       | 1/2 |
| [Kr] 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>4</sup> |           | 120                   | (0.09)                   | 127.6                 | 0   |
|                                                       |           | 122                   | (2.55)                   |                       | 0   |
|                                                       |           | 123                   | (0.89)                   |                       | 1/2 |
|                                                       |           | 124                   | (4.74)                   |                       | 0   |
|                                                       |           | 125                   | (7.07)                   |                       | 1/2 |
|                                                       |           | 126                   | (18.84)                  |                       | 0   |
|                                                       |           | 128                   | (31.74)                  |                       | 0   |
|                                                       |           | 130                   | (34.08)                  |                       | 0   |
| Iodine (I) [VIIB]                                     | <b>53</b> | 127                   | (100)                    | 126.9                 | 5/2 |
| [Kr] 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>5</sup> |           | 129*                  | 1.7 × 10 <sup>7</sup> y  |                       | 7/2 |

(continued)

| Name and symbol         | Z         | Number of<br>nucleons | Natural<br>abundance (%) | Average<br>mass (amu) | I   |
|-------------------------|-----------|-----------------------|--------------------------|-----------------------|-----|
| Xenon (Xe)              | <b>54</b> | 124                   | (0.10)                   | 131.3                 | 0   |
| [Kr] $d^{10} 5s^2 5p^6$ |           | 126                   | (0.09)                   |                       | 0   |
|                         |           | 127*                  | 3.64 d                   |                       | 1/2 |
|                         |           | 128                   | (1.91)                   |                       | 0   |
|                         |           | 129                   | (26.40)                  |                       | 1/2 |
|                         |           | 130                   | (4.10)                   |                       | 0   |
|                         |           | 131                   | (21.20)                  |                       | 3/2 |
|                         |           | 132                   | (26.90)                  |                       | 0   |
|                         |           | 134                   | (10.40)                  |                       | 0   |
|                         |           | 136                   | (8.90)                   |                       | 0   |
| Caesium (Cs) [IA]       | <b>55</b> | 133                   | (100)                    | 132.9                 | 7/2 |
| [Xe] $6s$               |           | 134*                  | 2.065 y                  |                       | 4   |
|                         |           | 135*                  | $2.3 \times 10^6$ y      |                       | 7/2 |
|                         |           | 137*                  | 30.2 y                   |                       | 7/2 |
| Barium (Ba) [IIA]       | <b>56</b> | 130                   | (0.106)                  | 137.3                 | 0   |
| [Xe] $6s^2$             |           | 132                   | (0.101)                  |                       | 0   |
|                         |           | 133*                  | 10.53 y                  |                       | 1/2 |
|                         |           | 134                   | (2.417)                  |                       | 3/2 |
|                         |           | 135                   | (6.592)                  |                       | 0   |
|                         |           | 136                   | (7.854)                  |                       | 3/2 |
|                         |           | 137                   | (11.23)                  |                       | 0   |
|                         |           | 138                   | (71.70)                  |                       | 0   |
| Lanthanum (La)          | <b>57</b> | 137*                  | 60,000 y                 | 138.9                 | 7/2 |
| [Xe] $5d 6s^2$          |           | 138                   | (0.09)                   |                       | 5   |
|                         |           | 139                   | (99.91)                  |                       | 7/2 |
| Cerium (Ce)             | <b>58</b> | 136                   | (0.19)                   | 140.1                 | 0   |
| [Xe] $4f 5d 6s^2$       |           | 138                   | (0.25)                   |                       | 0   |
|                         |           | 139*                  | 137.6 d                  |                       | 3/2 |
|                         |           | 140                   | (88.48)                  |                       | 0   |
|                         |           | 142                   | (11.08)                  |                       | 0   |
| Praseodymium (Pr)       | <b>59</b> | 141                   | (100)                    | 140.9                 | 5/2 |
| [Xe] $4f^3 6s^2$        |           |                       |                          |                       |     |
| Neodymium (Nd)          | <b>60</b> | 142                   | (27.13)                  | 144.2                 | 0   |
| [Xe] $4f^4 6s^2$        |           | 143                   | (12.18)                  |                       | 7/2 |
|                         |           | 144                   | (23.80)                  |                       | 0   |
|                         |           | 145                   | (8.30)                   |                       | 7/2 |
|                         |           | 146                   | (17.19)                  |                       | 0   |
|                         |           | 148                   | (5.76)                   |                       | 0   |
|                         |           | 150                   | (5.64)                   |                       | 0   |

(continued)

| Name and symbol                                                  | Z         | Number of<br>nucleons | Natural<br>abundance (%) | Average<br>mass (amu) | I   |
|------------------------------------------------------------------|-----------|-----------------------|--------------------------|-----------------------|-----|
| Promethium* (Pm)                                                 | <b>61</b> | 145*                  | 17.7 y                   |                       | 5/2 |
| [Xe] 4 <i>f</i> <sup>5</sup> 6 <i>s</i> <sup>2</sup>             |           | 146*                  | 5.53                     |                       | 3   |
|                                                                  |           | 147*                  | 2.62 y                   |                       | 7/2 |
| Samarium (Sm)                                                    | <b>62</b> | 144                   | (3.1)                    | 150.4                 | 0   |
| [Xe] 4 <i>f</i> <sup>6</sup> 6 <i>s</i> <sup>2</sup>             |           | 146*                  | 1.03 × 10 <sup>8</sup> y |                       | 0   |
|                                                                  |           | 147                   | (15.0)                   |                       | 7/2 |
|                                                                  |           | 148                   | (11.2)                   |                       | 0   |
|                                                                  |           | 149                   | (13.8)                   |                       | 7/2 |
|                                                                  |           | 150                   | (7.4)                    |                       | 0   |
|                                                                  |           | 151*                  | 90 y                     |                       | 5/2 |
|                                                                  |           | 152                   | (26.8)                   |                       | 0   |
|                                                                  |           | 154                   | (22.8)                   |                       | 0   |
| Europium (Eu)                                                    | <b>63</b> | 151                   | (47.8)                   | 152.0                 | 5/2 |
| [Xe] 4 <i>f</i> <sup>7</sup> 6 <i>s</i> <sup>2</sup>             |           | 152*                  | 13.5 y                   |                       | 3   |
|                                                                  |           | 153                   | (52.2)                   |                       | 5/2 |
|                                                                  |           | 154*                  | 8.59 y                   |                       | 3   |
|                                                                  |           | 155*                  | 4.76 y                   |                       | 5/2 |
| Gadolinium (Gd)                                                  | <b>64</b> | 152                   | (0.20)                   | 157.3                 | 0   |
| [Xe] 4 <i>f</i> <sup>7</sup> 5 <i>d</i> 6 <i>s</i> <sup>2</sup>  |           | 154                   | (2.18)                   |                       | 0   |
|                                                                  |           | 155                   | (14.80)                  |                       | 3/2 |
|                                                                  |           | 156                   | (20.47)                  |                       | 0   |
|                                                                  |           | 157                   | (15.65)                  |                       | 3/2 |
|                                                                  |           | 158                   | (24.84)                  |                       | 0   |
|                                                                  |           | 160                   | (21.86)                  |                       | 0   |
| Terbium (Tb)                                                     | <b>65</b> | 157*                  | 110 y                    |                       | 3/2 |
| [Xe] 4 <i>f</i> <sup>8</sup> 5 <i>d</i> 6 <i>s</i> <sup>2</sup>  |           | 158*                  | 180 y                    |                       | 3   |
|                                                                  |           | 159                   | (100)                    | 158.9                 | 3/2 |
| Dysprosium (Dy)                                                  | <b>66</b> | 156                   | (0.06)                   | 162.5                 | 0   |
| [Xe] 4 <i>f</i> <sup>9</sup> 5 <i>d</i> 6 <i>s</i> <sup>2</sup>  |           | 158                   | (0.10)                   |                       | 0   |
|                                                                  |           | 160                   | (2.34)                   |                       | 0   |
|                                                                  |           | 161                   | (18.90)                  |                       | 5/2 |
|                                                                  |           | 162                   | (25.50)                  |                       | 0   |
|                                                                  |           | 163                   | (24.90)                  |                       | 5/2 |
|                                                                  |           | 164                   | (28.20)                  |                       | 0   |
| Holmium (Ho)                                                     | <b>67</b> | 165                   | (100)                    | 164.93                | 7/2 |
| [Xe] 4 <i>f</i> <sup>10</sup> 5 <i>d</i> 6 <i>s</i> <sup>2</sup> |           |                       |                          |                       |     |
| Erbium (Er)                                                      | <b>68</b> | 162                   | (0.14)                   | 167.3                 | 0   |
| [Xe] 4 <i>f</i> <sup>11</sup> 5 <i>d</i> 6 <i>s</i> <sup>2</sup> |           | 164                   | (1.61)                   |                       | 0   |
|                                                                  |           | 166                   | (33.60)                  |                       | 0   |
|                                                                  |           | 167                   | (22.95)                  |                       | 7/2 |
|                                                                  |           | 168                   | (26.80)                  |                       | 0   |
|                                                                  |           | 170                   | (14.90)                  |                       | 0   |

(continued)



| Name and symbol                                                               | Z         | Number of<br>nucleons | Natural<br>abundance (%) | Average<br>mass (amu) | I   |
|-------------------------------------------------------------------------------|-----------|-----------------------|--------------------------|-----------------------|-----|
| Thulium (Tm)                                                                  | <b>69</b> | 169                   | (100)                    | 168.93                | 1/2 |
| [Xe] 4 <i>f</i> <sup>12</sup> 5 <i>d</i> 6 <i>s</i> <sup>2</sup>              |           | 171*                  | 1.92 y                   |                       | 1/2 |
| Ytterbium (Yb)                                                                | <b>70</b> | 168                   | (0.13)                   | 173.0                 | 0   |
| [Xe] 4 <i>f</i> <sup>13</sup> 5 <i>d</i> 6 <i>s</i> <sup>2</sup>              |           | 170                   | (3.05)                   |                       | 0   |
|                                                                               |           | 171                   | (14.30)                  |                       | 1/2 |
|                                                                               |           | 172                   | (21.90)                  |                       | 0   |
|                                                                               |           | 173                   | (16.12)                  |                       | 5/2 |
|                                                                               |           | 174                   | (30.80)                  |                       | 0   |
|                                                                               |           | 176                   | (12.70)                  |                       | 0   |
| Lutecium (Lu)                                                                 | <b>71</b> | 173*                  | 1.37 y                   | 175.0                 | 7/2 |
| [Xe] 4 <i>f</i> <sup>14</sup> 5 <i>d</i> 6 <i>s</i> <sup>2</sup>              |           | 174*                  | 3.3 y                    |                       | 1   |
|                                                                               |           | 175                   | (97.41)                  |                       | 7/2 |
|                                                                               |           | 176                   | (2.59)                   |                       | 7   |
| Hafnium (Hf)                                                                  | <b>72</b> | 174                   | (0.16)                   | 178.5                 | 0   |
| [Xe] 4 <i>f</i> <sup>14</sup> 5 <i>d</i> <sup>2</sup> 6 <i>s</i> <sup>2</sup> |           | 176                   | (5.20)                   |                       | 0   |
|                                                                               |           | 177                   | (18.60)                  |                       | 7/2 |
|                                                                               |           | 178                   | (27.10)                  |                       | 0   |
|                                                                               |           | 179                   | (13.74)                  |                       | 9/2 |
|                                                                               |           | 180                   | (35.20)                  |                       | 0   |
| Tantalum (Ta)                                                                 | <b>73</b> | 180                   | (0.012)                  | 180.9                 | 0   |
| [Xe] 4 <i>f</i> <sup>14</sup> 5 <i>d</i> <sup>3</sup> 6 <i>s</i> <sup>2</sup> |           | 181                   | (99.988)                 |                       | 7/2 |
| Tungsten (W)                                                                  | <b>74</b> | 180                   | (0.13)                   | 183.9                 | 0   |
| [Xe] 4 <i>f</i> <sup>14</sup> 5 <i>d</i> <sup>4</sup> 6 <i>s</i> <sup>2</sup> |           | 182                   | (26.30)                  |                       | 0   |
|                                                                               |           | 183                   | (14.30)                  |                       | 1/2 |
|                                                                               |           | 184                   | (30.67)                  |                       | 0   |
|                                                                               |           | 186                   | (28.60)                  |                       | 0   |
| Rhenium (Re)                                                                  | <b>75</b> | 185                   | (37.4)                   | 186.2                 | 5/2 |
| [Xe] 4 <i>f</i> <sup>14</sup> 5 <i>d</i> <sup>5</sup> 6 <i>s</i> <sup>2</sup> |           | 187                   | (62.6)                   |                       | 5/2 |
| Osmium (Os)                                                                   | <b>76</b> | 184                   | (0.02)                   | 190.2                 | 0   |
| [Xe] 4 <i>f</i> <sup>14</sup> 5 <i>d</i> <sup>6</sup> 6 <i>s</i> <sup>2</sup> |           | 186                   | (1.58)                   |                       | 0   |
|                                                                               |           | 187                   | (1.6)                    |                       | 1/2 |
|                                                                               |           | 188                   | (13.3)                   |                       | 0   |
|                                                                               |           | 189                   | (16.1)                   |                       | 3/2 |
|                                                                               |           | 190                   | (26.4)                   |                       | 0   |
|                                                                               | <b>77</b> | 192                   | (41.0)                   | 192.2                 | 0   |
| Iridium (Ir)                                                                  |           | 191                   | (37.3)                   |                       | 3/2 |
| [Xe] 4 <i>f</i> <sup>14</sup> 5 <i>d</i> <sup>7</sup> 6 <i>s</i> <sup>2</sup> |           | 193                   | (62.7)                   |                       | 3/2 |
| Platinum (Pt)                                                                 | <b>78</b> | 190                   | (0.01)                   | 195.1                 | 0   |
| [Xe] 4 <i>f</i> <sup>14</sup> 5 <i>d</i> <sup>9</sup> 6 <i>s</i>              |           | 192                   | (0.79)                   |                       | 0   |
|                                                                               |           | 193*                  | 60 y                     |                       | 1/2 |
|                                                                               |           | 194                   | (32.90)                  |                       | 0   |

(continued)

| Name and symbol                                                                                                             | Z         | Number of<br>nucleons | Natural<br>abundance (%) | Average<br>mass (amu) | I   |
|-----------------------------------------------------------------------------------------------------------------------------|-----------|-----------------------|--------------------------|-----------------------|-----|
| Gold (Au) [IB]<br>[Xe] 4 <i>f</i> <sup>14</sup> 5 <i>d</i> <sup>10</sup> 6 <i>s</i>                                         | <b>79</b> | 195                   | (33.80)                  | 197.0                 | 1/2 |
|                                                                                                                             |           | 196                   | (25.30)                  |                       | 0   |
|                                                                                                                             |           | 198                   | (7.20)                   |                       | 0   |
|                                                                                                                             |           | 193*                  | 17.62 h                  |                       | 3/2 |
|                                                                                                                             |           | 195*                  | 186.12 d                 |                       | 3/2 |
| Mercury (Hg) [IIB]<br>[Xe] 4 <i>f</i> <sup>14</sup> 5 <i>d</i> <sup>10</sup> 6 <i>s</i> <sup>2</sup>                        | <b>80</b> | 197                   | (100)                    | 200.6                 | 3/2 |
|                                                                                                                             |           | 193*                  | 3.80 h                   |                       | 3/2 |
|                                                                                                                             |           | 195*                  | 9.5 h                    |                       | 1/2 |
|                                                                                                                             |           | 196                   | (0.15)                   |                       | 0   |
|                                                                                                                             |           | 198                   | (10.10)                  |                       | 0   |
|                                                                                                                             |           | 199                   | (17.00)                  |                       | 1/2 |
|                                                                                                                             |           | 200                   | (23.10)                  |                       | 0   |
|                                                                                                                             |           | 201                   | (13.20)                  |                       | 3/2 |
|                                                                                                                             |           | 202                   | (29.65)                  |                       | 0   |
|                                                                                                                             |           | 204                   | (6.80)                   |                       | 0   |
| Thallium (Tl) [IIIB]<br>[Xe] 4 <i>f</i> <sup>14</sup> 5 <i>d</i> <sup>10</sup> 6 <i>s</i> <sup>2</sup> 6 <i>p</i>           | <b>81</b> | 201                   | (29.524)                 | 204.4                 | 1/2 |
|                                                                                                                             |           | 204*                  | 3.78 y                   |                       | 2   |
|                                                                                                                             |           | 205                   | (70.476)                 |                       | 1/2 |
| Lead (Pb) [IVB]<br>[Xe] 4 <i>f</i> <sup>14</sup> 5 <i>d</i> <sup>10</sup> 6 <i>s</i> <sup>2</sup> 6 <i>p</i> <sup>2</sup>   | <b>82</b> | 204                   | (1.4)                    | 207.2                 | 0   |
|                                                                                                                             |           | 206                   | (24.1)                   |                       | 0   |
|                                                                                                                             |           | 207                   | (22.1)                   |                       | 1/2 |
|                                                                                                                             |           | 208                   | (52.4)                   |                       | 0   |
| Bismuth (Bi) [VB]<br>[Xe] 4 <i>f</i> <sup>14</sup> 5 <i>d</i> <sup>10</sup> 6 <i>s</i> <sup>2</sup> 6 <i>p</i> <sup>3</sup> | <b>83</b> | 207*                  | 35 y                     | 208.98                | 9/2 |
|                                                                                                                             |           | 209                   | (100)                    |                       | 9/2 |
| Polonium* (Po)<br>[Xe] 4 <i>f</i> <sup>14</sup> 5 <i>d</i> <sup>10</sup> 6 <i>s</i> <sup>2</sup> 6 <i>p</i> <sup>4</sup>    | <b>84</b> | 207*                  | 2.898 y                  |                       | 1/2 |
|                                                                                                                             |           | 209*                  | 102 y                    |                       | 0   |
|                                                                                                                             |           | 210*                  | 138.38 d                 |                       | 0   |
| Astatine* (At)<br>[Xe] 4 <i>f</i> <sup>14</sup> 5 <i>d</i> <sup>10</sup> 6 <i>s</i> <sup>2</sup> 6 <i>p</i> <sup>5</sup>    | <b>85</b> | 210*                  | 8.1 h                    |                       | 5   |
|                                                                                                                             |           | 211*                  | 7.2 h                    |                       | 9/2 |
| Radon* (Rn)<br>[Xe] 4 <i>f</i> <sup>14</sup> 5 <i>d</i> <sup>10</sup> 6 <i>s</i> <sup>2</sup> 6 <i>p</i> <sup>6</sup>       | <b>86</b> | 211*                  | 14.6 h                   |                       | 1/2 |
|                                                                                                                             |           | 222*                  | 3.824 d                  |                       | 0   |
| Thorium* (Th)<br>[Rn] 6 <i>d</i> <sup>2</sup> 7 <i>s</i> <sup>2</sup>                                                       | <b>90</b> | 229*                  | 7,900 y                  | 232.04                | 5/2 |
|                                                                                                                             |           | 232*                  | (100)                    |                       | 0   |
|                                                                                                                             |           |                       | 1.4 × 10 <sup>10</sup> y |                       |     |
| Protactinium* (Pa)<br>[Rn] 5 <i>f</i> <sup>2</sup> 6 <i>d</i> 7 <i>s</i> <sup>2</sup>                                       | <b>91</b> | 231*                  | 32,000 y                 |                       | 3/2 |
| Uranium (U)<br>[Rn] 5 <i>f</i> <sup>3</sup> 6 <i>d</i> 7 <i>s</i> <sup>2</sup>                                              | <b>92</b> | 233*                  | 2.45 × 10 <sup>5</sup> y | 238.03                | 5/2 |
|                                                                                                                             |           | 234                   | (0.0055)                 |                       | 0   |
|                                                                                                                             |           | 235*                  | (0.7200)                 |                       | 7/2 |
|                                                                                                                             |           |                       | 7.04 × 10 <sup>8</sup> y |                       |     |
|                                                                                                                             |           | 238                   | (99.2745)                |                       | 0   |

## Appendix E

---

### Some Tensor Properties

This appendix is based on the one in the paper by Baldereschi and Lipari [1] and it outlines the fundamental tensor properties of  $P_{ij}$  and  $J_{ij}$  introduced in Sect. 5.3, with reference to Luttinger's Hamiltonian for holes in the  $J = 3/2$  VB. In an orthogonal reference frame, a tensor  $T_{ij}^{(k)}$  of rank  $k$  can be reduced to a sum of irreducible spherical tensors  $T_q^{(k)}$  of ranks  $0, 1, \dots, k$  with  $2k + 1$  values of  $q$ , sometimes called the dimension of the tensor (see, for instance, Edmonds [3]). Two spherical tensors  $T_{q_1}^{(k_1)}$  and  $U_{q_2}^{(k_2)}$  of ranks  $k_1$  and  $k_2$  can be coupled together to give a set of spherical tensors whose ranks  $k$  are limited by the condition  $|k_1 - k_2| \leq k \leq k_1 + k_2$ , and defined by:

$$\left[ T^{(k_1)} \times U^{(k_2)} \right]_q^{(k)} = (-1)^{k_1 - k_2 + q} (2k + 1)^{1/2} \times \sum_{q_1, q_2} \begin{pmatrix} k_1 & k_2 & k \\ q_1 & q_2 & -q \end{pmatrix} T_{q_1}^{(k_1)} U_{q_2}^{(k_2)} \quad (\text{E.1})$$

The  $\begin{pmatrix} k_1 & k_2 & k \\ q_1 & q_2 & -q \end{pmatrix}$  quantities are the Wigner 3- $j$  coefficients or symbols (see, for instance, [3]) and their values for the lowest values of the parameters have been tabulated by [2]. The zero-rank compound tensor operator  $\left[ T^{(k)} \times U^{(k)} \right]_0^{(0)}$  of two tensors of rank  $k$ , or scalar tensor operator, is related to the scalar product of tensors  $T$  and  $U$ :

$$\left( T^{(k)} \cdot U^{(k)} \right) = \sum_q (-1)^q T_q^{(k)} U_{-q}^{(k)} = (-1)^k (2k + 1)^{1/2} \left[ T^{(k)} \times U^{(k)} \right]_0^{(0)} \quad (\text{E.2})$$

With the second-rank tensors  $P^{(2)}$  and  $J^{(2)}$  defined in (5.14), it can be shown that:

$$\begin{aligned} (p_x^2 J_x^2 + p_y^2 J_y^2 + p_z^2 J_z^2) &= \frac{1}{3} p^2 J^2 + \frac{2}{45} \left( P^{(2)} \cdot J^{(2)} \right) + \frac{1}{18} \left\{ \left[ P^{(2)} \times J^{(2)} \right]_{-4}^{(4)} \right. \\ &\quad \left. + \frac{\sqrt{70}}{5} \left[ P^{(2)} \times J^{(2)} \right]_0^{(4)} + \left[ P^{(2)} \times J^{(2)} \right]_4^{(4)} \right\} \end{aligned}$$

and

$$\begin{aligned} \{p_x p_y\} \{J_x J_y\} + \{p_y p_z\} \{J_y J_z\} + \{p_z p_x\} \{J_z J_x\} = \\ \frac{1}{30} \left( P^{(2)} \cdot J^{(2)} \right) - \frac{1}{36} \left\{ \left[ P^{(2)} \times J^{(2)} \right]_{-4}^{(4)} + \frac{\sqrt{70}}{5} \left[ P^{(2)} \times J^{(2)} \right]_0^{(4)} \right. \\ \left. + \left[ P^{(2)} \times J^{(2)} \right]_4^{(4)} \right\} \end{aligned}$$

These expressions remain valid if operator  $\mathbf{J}$  is replaced by operator  $\mathbf{I}$  of Hamiltonian (5.16) of Chap. 5.

## References

1. A. Baldereschi, N. Lipari, Spherical model of shallow acceptor states in semiconductors. Phys. Rev. B **8**, 2697 (1973)
2. M. Rotenberg, R. Bivins, N. Metropolis, J.K. Wooten, The 3- $j$  and 6- $j$  symbols, Technology Press, Cambridge, Mass. (1959)
3. A.R. Edmonds, *Angular momentum in quantum mechanics* (Princeton University Press, 1<sup>st</sup> edition (1960) (there are several reprints))

---

# Index

- 1/ $f$  noise, 110
- 3D rotation group, 151, 440
- 450°C thermal donors, 220
- 6H-SiC, 195, 311, 447
  
- $A^+$  acceptor ions, 13, 254, 269, 327
- AlSb, 267
- absorbance, 47
- absorption
  - coefficient, 46, 55, 70, 71, 79, 85
  - cross-section, 86, 160, 171, 295
  - intrinsic, 62, 85
  - saturated, 87
- acceptor
  - complexes, 281, 304, 305
  - deformation potentials, 378, 379
  - double, 7, 311, 334
  - $g$ -factors, 398, 401, 405, 409, 411
  - isocoric, 154, 157
  - pseudo-, 7, 16, 281
  - quenched-in, 30, 304, 306
  - spin-orbit splitting, 154, 289
  - triple, 281, 311
  - $X$  centre, 297
- acoustic mode or phonon, 51
- acoustic phonon spectroscopy, 89, 270, 327
- activation energy, 35, 38, 230
- admittance spectroscopy, 311
- Ag, *see* silver
- aligning stress, 372
- amphoteric behaviour, 32, 247
  
- angular momentum, 64
  - effective, 393
  - matrix, 398
  - pseudo, 148, 150, 284
- anharmonic coupling, 55
- anisotropy, 129, 265
- anti-crossing, 348, 362, 378, 380
- antisite, 11, 30, 32
- atomic spectroscopy notation, 127, 129
- Au, *see* gold
- autoionizing states, 268
- axial rotation group, 129
- axial vector, 348, 388, 440
  
- background radiation noise, 106
- backward-wave tube, 90, 187
- band gap, 1, 449
  - direct, 61, 68
  - indirect, 59, 62, 63, 265
  - isotopic dependence, *see* isotopic shift
  - magnetic field dependence, 71
  - pressure dependence, 73, 268
  - temperature dependence, 72
- binding energy, *see* ionization energy
- Bloch functions, 128, 158
- blue diamond, *see* diamond, blue
- Bohr magneton, 16, 389, 398, 432
- bolometer, 101
  - free-electron, 102
- breakdown field, 411
- Bridgman method, 24
- Brillouin zone, 51, 65, 139, 196, 435, 437, 444

- broadening
  - anomalous, *see* resonant
  - concentration, 422
  - dislocation, 383
  - inhomogeneous, 87, 113, 382, 423
  - instrumental, 86
  - phonon, 419
  - resonant, 174, 289, 380, 418
  - Stark, 192, 213
  - thermal, 421
- Burstein–Moss shift, 77
- calibration factor, 31, 86, 185, 193, 247, 295, 304, 309, 311
- calorimetric absorption spectroscopy, 103
- camel's back structure, 66, 263, 267, 413
- cathodoluminescence, *see* electroluminescence
- CdSe, 262
- CdTe, 145, 146, 257, 337, 338
- central-cell correction, 145, 154, 241, 257, 262, 295
- central-cell potential, 253
- centre of gravity of split components, 386
- chalcogens, 198, 218
  - complexes, 198, 204, 214, 217
  - isotope effects, 210, 212
  - pairs, 33, 199–201, 204, 363
- channelled spectrum, 47, 98
- chemical vapour deposition (CVD), 24
- class (in group theory), 438
- Clausius Mossotti relation, 48
- closed cycle cryostat, 112
- clusters, 184
- compensation, 8, 197, 208, 232, 295
  - ratio, 8, 12, 27, 271, 411, 417
- compliance coefficient, 352
- conduction band
  - deformation potentials, 140, 350, 352
  - parameters, 63, 66, 67, 69
  - see also* effective masses, 67
- configuration coordinate diagram, 40
- confinement, 74
- constant-energy ellipsoid, 59, 351
  - oblate, 132
  - prolate, 132, 374
  - see also* effective mass ratio, 59
- continuous-flow cryostat, 113
- copper, 25, 314
- correlated distribution, 416
- Coulomb
  - interaction, 129, 169
  - potential, 148, 150
  - screened potential, 138, 161
- critical point, 52
- crystal field, 68, 243
- cyclotron resonance (CR), 65
- Czochralski method, 23
  - liquid encapsulated, 23
- $D^-$  donor ion, 13, 269
- deep-level transient spectroscopy (DLTS), 25, 217, 241, 248, 316, 372
- degeneracy
  - electronic, 140, 347
  - multi-valley or  $CB$ , 140, 350
  - orientational, 16, 140, 347, 349, 363, 365, 370, 384
- density of states (DoS), 6, 77
- detectivity, 110
- diamond
  - I, 21
  - IIa, 21
  - IIb, 21
  - anvil cell, 116
  - blue, 21
  - P-doped, 196
  - p-type, B-doped, 307
  - synthetic, 115, 196, 307
- dichroism, 88
- dielectric constant, 45, 260, 338
  - relative, 48
  - static, 49, 125, 129, 329
- dielectric function, 79, 142, 149, 257
  - wave-vector-dependence, 142, 154
- dielectric screening, 143, 331
- dielectric strength, 411
- differential contraction, 377
- diffusion coefficient, 25, 36, 37
- diffusion mechanisms, 38
- diluted magnetic semiconductor, 335

- dilution refrigerator, 112
- dipole moment, 51, 145
  - magnetic, 16
  - operator, 380
  - second-order, 55
- dispersive monochromator, 91
- donor
  - deformation potentials, 350, 360
  - double, 7, 138, 198
  - electron spin, 17, 182, 197, 202, 209, 234, 247
  - g*-factors, 213, 234, 371, 394
  - pairs, 169, 199, 204, 348, 363
  - pseudo-, 7, 16, 170, 249
  - quasi-hydrogenic, 145, 147, 163, 257, 260
  - single, 7, 238
  - spin-orbit interaction, 267, 363
  - spin-orbit splitting, 180, 267
- donor-acceptor pair (DAP) spectra, 13, 196, 263, 266, 270
- donor exciton, 184
- dopant reactivation, 11
- double group representation, 60, 68, 144, 214, 441
- dye laser, 89
- dynamic tunnelling, 189
  
- effective Bohr radius, 130, 146, 260, 419
- effective magnetic field parameter, 146, 261, 389
- effective mass
  - anisotropy, 129, 261, 265
  - approximation, 5, 126
  - longitudinal, 59, 129
  - non-isotropic, 145
  - ratio, 129, 131, 135, 197, 374
  - reduced, 69
  - spherical, 145
  - tensor, 58
  - theory, 126
  - transverse, 59, 129, 267, 390, 393
- effective Rydberg, 75
  - acceptors, 151, 331, 412
  - donors, 130, 133, 135, 145, 194, 257
- EL2, 11, 328
  - metastability, 328
- elastic compliance tensor, 351, 374
- elastic moduli, 351
- electric dipoles, selection rules, *see* selection rules
- electric field, 411
  - homogeneous, 411
  - internal, 415
  - ionization, 412
- electric moment, 55
  - second order, 55
- electric vector, 160, 188
- electrical mobility, 3, 7, 31, 80, 197, 257, 295
- electroluminescence, 14
- electron-phonon interaction, 170, 181, 310, 419, 421
- electron-phonon scattering, 187
- electron spin resonance (ESR), 16, 31
  - acceptors, 311, 319
  - chalcogens, 199, 212, 217
  - pseudo- and isoelectronic donors, 252
  - shallow thermal donors, 238
  - single donors, 142, 171, 174, 182, 189, 197
  - thermal donors, 226, 233, 234
  - TMs, Au, Ag, Pt, 244, 246
- ellipsoid, *see* constant-energy ellipsoid
- encapsulant, 23
- ENDOR, 17, 217, 227
- energy levels
  - acceptors in germanium, 156, 157
  - acceptors in silicon, 155, 157
  - donors in germanium, 137, 138
  - donors in silicon, 136, 138
- envelope wave function, 131, 141, 146
- EXAFS, 39
- excitation spectroscopy, 87
- exciton
  - bound, 14, 183, 250
  - free, 14, 74
  - isoelectronic bound (IBE), 16, 249, 324
- excitonic molecule, 15
- extinction coefficient, 46
- extrinsic photodetector, *see* photodetector, extrinsic
  
- Fano resonance, 13, 170, 196, 200, 208, 248, 289, 315, 317, 321, 363
- Faraday configuration, 119, 390, 394
- Fermi-Dirac statistics, 6

- Fermi level, 6, 80
- float zone (FZ) method, 23
- folded acoustical phonons, 55
- Fourier transform spectrometer (FTS), 94
- Franck–Condon shift, 40
- free-carrier absorption, 3, 79
- free-carrier concentration, 10
- free electron laser (FEL), 89, 90
- frequency-domain spectroscopy, 424
- full width at half maximum (FWHM), 85, 87, 171, 212, 251, 258, 283, 294
  - acceptors (double), 320, 323
  - acceptors (single), 269, 283, 290, 292, 294, 301, 308, 330
  - donors (double), 203, 204, 208, 210, 212
  - donors (single), 171, 182, 185, 191, 197, 257, 263, 264
- g*-factors
  - acceptors, 397, 400, 401, 410, 411
  - electron, 71
- GaN, 145, 148, 261, 262
- GaP, 16, 263–267, 331, 335
- generation-recombination noise, 109
- gold, 247, 320
- ground state energy, 126
- ground-state splitting, 312, 315, 320
- growth atmosphere, 22
- H<sup>−</sup> ion, 10, 13, 270
- Hall coefficient, 8
- Hall effect measurements, 31, 65, 175, 246, 268, 297, 305, 311
- harmonic crystal, 51
- harmonic potential, 50
- He<sup>0</sup>, He<sup>+</sup>, 138
- He-like, 198, 204, 213, 221, 337
- high-field limit (magnetic), 147, 261, 394
- high-stress limit, 188, 358, 374, 382
- hole burning, 87
- hole pseudo-spin, 250
- homogeneous width, 87, 192
- hydrogen, 5, 11
  - complexes, 25, 191, 217, 237, 240, 242, 318
  - contamination, 23, 25
  - defects, 21
  - passivation, 11, 216, 314
- hydrogen-like centres, 5
- hydrostatic
  - pressure, 118, 268, 349
  - shift, 350
  - stress, 348, 386
- hyperfine interaction, 17, 182, 183
- hyperfine splitting, 212
- impact ionization, 412
- implantation, 29
- impurity band, 7, 260
- impurity pairs, 33
- impurity photoconductivity, 88
- insulator, 7
- interferogram, 94
- interstitial site, 32
- inter-valley coupling, 142, 143
- inter-valley phonons, 196, 248, 358, 423
- inter-valley scattering, 170, 174
- inversion asymmetry, 64, 333
- ionization energy
  - optical, 176, 195, 196, 267, 286, 313
  - thermal, 197, 282, 315
- ionization threshold, 412
- iron, 243
- irreducible representations (*IR*), 59, 127, 139, 152, 439
- isocoric impurity, 126
- isoelectronic centres, 7, 15, 250
  - acceptors (IAs), 323
  - donors (IDs), 169, 249, 253
- isotope shift (IS)
  - band gap, 74
  - boron, 293
  - carbon, 310
  - hydrogen, 191, 217, 240, 242, 243, 314
  - oxygen, 264
  - selenium, 212, 219
  - silicon, 210, 263, 292
  - sulphur, 210, 214
  - zinc, 319
- isotopic disorder, 292
- isotopic distribution, 282, 419
- isotopic shift model, 202
- isotopic splitting, 163



- $j$ - $j$  coupling, 312
- Jahn-Teller (JT)
  - coupling, 245
  - effect, 39, 282
  - splitting, 308
- Johnson noise, 109
  
- Kramers doublet, 150, 282, 308, 388, 413
  
- labelling, 17, 283, 307
- lamellar grating interferometer, 97
- Landau levels, 71, 89, 148, 389, 395
- laser
  - calorimetry, 103
  - diode, 89
  - emission, 182
- lattice
  - deformation, 143
  - distortion, 32, 38, 41, 202
  - relaxation, 40
- Li complexes in germanium, 189–192
- lifetime, 87, 88, 170, 211, 249, 325, 358, 422–424
- lines positions
  - acceptors:
    - in II–VI compounds, 338
    - in III–V compounds, 330, 332, 333, 336
    - in germanium, 302, 306, 313, 316
    - in silicon, 287, 297, 299, 319, 322
  - donors:
    - in 3C-SiC, 195
    - in GaP and AlSb, 265, 268
    - in germanium, 190, 233, 234
    - in silicon, 177, 205, 213, 215, 223, 225, 237, 243, 246, 252
  - temperature dependence, 181
- localization energy, 14
- longitudinal effective mass, *see* effective mass, longitudinal
- Lorentz oscillator, 47
- Luttinger
  - Hamiltonian, 64
  - VB parameters, 64, 65, 67, 149
- Lyddane–Sachs–Teller relation, 52
- Lyman spectrum, 12
  
- magnesium, 198, 200, 208, 311, 312
- magnetic circular dichroism, 88
- magnetic dipole transition, 16
- magneto-Raman, 402, 409
- majority impurity, 8
- manganese, 335
- metal-insulator transition (MIT), 7, 184
- metastability, 38, 221, 227, 234, 253
- minority impurity, 8
- multi-exciton complexes, 15
  
- neutron transmutation doping (NTD), 25
- nitrogen split pair, 34, 238
- nitrogen, substitutional, 171
- no-phonon line, *see* zero-phonon line
- noise equivalent power (NEP), 100, 109
- non-variational method, 130, 133, 154, 157
- notation, 17, 152
- nuclear spin, *see also* donor, 17
  
- one-phonon band, 332
- one-valley approximation, 129, 138, 143
- optical mode, 51
- orbital momentum
  - electron, 243
  - hole, 249, 250
- orientational degeneracy, *see* degeneracy
- oscillator strength, 86, 126, 159, 160
  - acceptors, 163, 283, 291, 299, 301, 304
  - donors, 162, 173, 176, 178, 192
- oxygen (interstitial), 32
- oxygen-related thermal donors, 220
- oxygen thermal double donors (TDDs)
  - germanium, 231
  - metastability, 227, 234
  - silicon, 220
  - stability, 220
  
- $p_{1/2}$  spectrum, 154, 282, 298, 300, 307, 317
- $p_{3/2}$  spectrum, 154, 282, 283, 287, 307, 317
- parabolic band, 158
- parity, 126–128, 131, 139, 152, 259
- passivation, *see also* hydrogen
  - partial, 217, 314
- Pauli's principle, 312

- phase correction process, 96
- phonon gap, 53, 57
- phonon replica, 13, 15, 55, 248, 320, 332
- phonon spectroscopy, *see* acoustic phonon spectroscopy
- photoacoustic spectroscopy, 103
- photodetectors, 4
  - extrinsic, 104
  - intrinsic, 103
- photoinduced spectrum, 253, 325
- photoionization, 224
  - cross-section, 185, 193
  - spectrum, 12, 126, 162, 163, 196, 200, 248, 263, 295, 309, 310, 413
- photoluminescence excitation (PLE), 183, 250
- photo-thermal ionization spectroscopy (PTIS), 25, 88, 105, 188, 189, 192, 236, 258, 295, 300, 328, 333, 380, 381, 391, 397, 424
  - contactless, 106
- photon-induced hopping, 270
- piezospectroscopic tensor, 369, 385, 386
- platinum, 243, 320
- polar vector, 348
- polarization rules, 357
- potassium, 7
- proton tunnelling, 318, 319
- pump-probe experiment, 87, 423
  
- quadratic diamagnetic coefficients, 398
- quadrupole broadening, 416
- quadrupole interaction, 417
- quantum computing, 411, 422
- quasimonoisotopic (qmi) crystals
  - diamond, 74, 310
  - germanium, 74, 76
  - silicon, 74, 172, 175, 178, 182, 203, 210–214, 253, 282, 292, 420
  
- radiation damages, 242
- radiative recombination, 13
- Raman scattering, 12, 182, 264, 288, 308, 330, 335
- random
  - impurity distribution, 183, 416, 418
  - internal electric fields, 411, 415
  - isotopic distribution, 210, 282, 420
  - splitting, 382
  - stress, 384, 402
- reduced effective mass, *see* effective mass, reduced
- reference level, 77, 286
- reflectance, 47, 81
- refractive index, 46, 97, 132
- relative intensities, 188
- reorientation
  - atomic, 372
  - electronic, 372
- residual impurities, 10, 22, 295
- resistivity, 3, 10, 11, 21
- resolving power, 91
- resonant
  - spectrum, 163
- resonant broadening, *see* broadening, resonant
- resonant polarization, 48
- resonant states, 150, 154, 157–159
- responsivity, 100
  
- (S,Cu) centre in silicon, 253
- saturated absorption, *see* absorption
- saturation effect, 86, 104, 106
- secondary ion mass spectroscopy (SIMS), 31, 261, 311
- segregation coefficient, 35
- selected pair luminescence, 14, 331
- selection rules, 127, 195, 356, 358, 371, 398–400
  - electric dipole, 12
- self-compensation, 10
- semi-insulating, 11, 328
- semiconducting alloys, 68, 104
- semiconductors, 4
  - direct-band-gap, 61, 68, 257, 389
  - extrinsic, 2
  - indirect-band-gap, 63, 69
  - intrinsic, 3, 57
  - n-type, 3
  - p-type, 3
- semimetals, 1, 65
- shallow thermal donors (STDs), 30, 220, 236
  - H-related families, 240
- shear deformation potential, 350, 360
- silver, 247
- sodium, 7, 175

- solubility, 35
- spectral resolution, 86, 92, 93, 97
- spherical approximation, 150, 159
- spherical harmonics, 139
- spin, 212
  - electron, 183
  - electronic, 142
  - nuclear, 17, 141, 182, 213, 253
  - splitting, 397
- spin-orbit (s-o)
  - coupling, 59, 144, 148, 245, 247, 250, 393
  - interaction, 59, 248, 267, 363
  - splitting, *see* valence band
- spin-valley
  - coupling, 209
  - splitting, 214
- Stark effect, 412, 413, 415
  - first order, 413, 414
  - linear, 415, 416
  - quadratic, 412, 413, 415, 416
- Stark splitting, 414
  - inhomogeneous, 12, 348, 415, 418
- states *or* levels
  - even parity, 127, 131, 138, 145, 153–157, 182, 192, 208, 251, 266, 301
  - even parity resonant, 157, 158
  - odd parity, 127, 131, 136–138, 142–145, 154–158, 160, 178, 251, 255, 288, 298, 301
  - odd parity resonant, 154, 159
- stimulated emission, 12, 422
- strain, 144, 349
- strain tensor, 351
- stress isotropy, 374
- stress tensor, 351, 352, 386
- stress-induced reorientation, 192
- susceptibility, 48
  - nonlinear, 187
- synthetic diamond, *see* diamond, synthetic
- thallium, 286, 300, 301
- thermal annealing, 23, 27, 29, 220, 241
- thermal conductivity, 45, 187
- thermal donors, 30, 220
- thermal double donors, *see* oxygen thermal double donors
- thermal quenching, 30, 191
- thermal stability, 220, 236, 241, 306
- thermalization, 180, 187, 194
- thermalized transitions, 309, 314, 325
- three-phonon
  - process, 56
- three-phonon spectrum, 291, 308
- time constant, 100–103
- time domain spectroscopy, 88
- time-reversal symmetry, 388
- transient decay method, 423
- transition metals (TMs), 5, 25, 243, 305, 306, 320
- transition probability, 127, 160, 243
- transitions, 214
  - “hot”, 188
  - parity-allowed, 127, 128, 139, 159, 200
  - parity forbidden, 144, 145, 171
  - Raman-allowed, 128
  - spin-forbidden, 200
  - symmetry-allowed, 179, 199, 202, 248
  - two-electron, 128
  - two-hole, 128
- transmittance, 47
- transverse effective mass, *see* effective mass, transverse
- triplet state, 202, 270
- tunable lasers, 89
- tunnelling, 192, 318, 412
- two-electron PL, 15, 182, 257, 262
- two-hole PL, 15
- two-phonon
  - processes, 56
  - spectrum, 263, 267, 308, 315, 320, 334, 420
- two-photon absorption, 88, 259
- ultrashallow thermal donors (USTDs), 220, 241
- uncertainty, 98
- uniaxial crystals, 134
- valence band
  - bands parameters, 63, 64, 67, 69
  - coupling parameters, 149
  - g*-factors, 65
  - heavy hole, 60, 63, 67
  - light hole, 60, 63, 67

- parameters, 63, 67, 69
- spin-orbit splitting, 60, 63, 67, 299
- valley-orbit
  - coupling, 141, 142, 144
  - interaction, 186
  - splitting, 141–144, 175, 187, 194, 214, 263, 354, 412
- valley symmetry point group, 353
- variational calculations, 130–134, 150–156
- variational method, 130
- variational parameters, 130
- Vegard’s law, 38
- vibrational lines, 226, 236
- vibrational modes, 11, 335
- vibronic sidebands, 15
- virtual crystal approximation, 54
- Voigt configuration, 119, 390, 394
- wavenumber calibration, 96
- wire grid polarizers, 99
- X-ray diffraction, 39
- Zeeman
  - effect, 388, 397, 409
  - quadratic shift, 391, 395
  - splitting, 119, 133, 261, 393, 395
  - transition, 148
- zero-field splitting, 182, 183
- zero-phonon-line, 15, 183, 250, 263, 266, 320
- zero-radius central cell approximation, 154
- ZnO, 30, 337
- ZnSe, 145, 154, 257, 337