Solid State Physics

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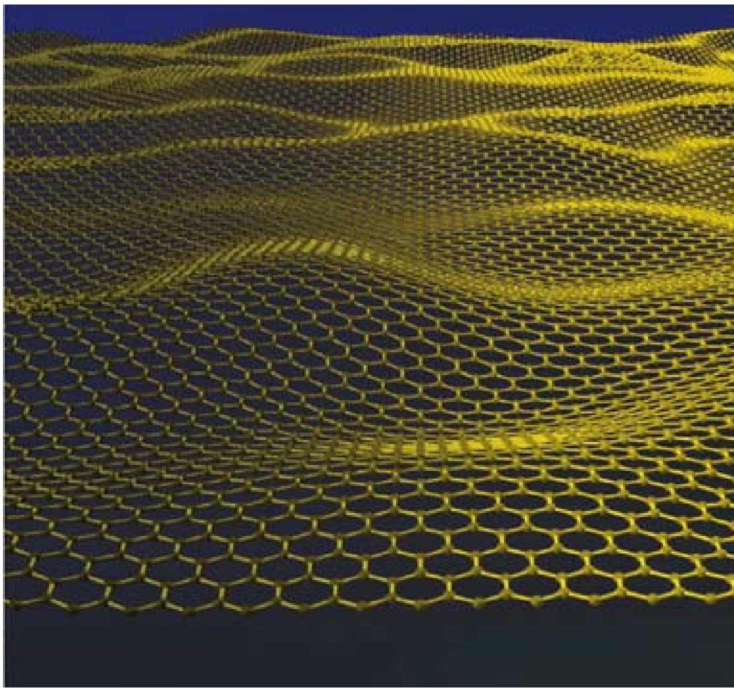
Prepared by Sam Kinyera OBWOYA



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NOTICE

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Foreword

This module has four major sections

The first one is the **Introductory** section that consists of five parts viz:

Title:- The title of the module is clearly described

Pre-requisit Knowledge: In this section you are provided with information regarding the specific pre-requisite knowledge and skills you require starting the module. Carefully look into the requirements as this will help you to decide whether you require some revision work or not.

Time Required: It gives you the total time (in hours) you require to complete the module. All self tests, activities and evaluations are to be finished in this specified time.

Materials Required: Here you will find the list of materials you require to complete the module. Some of the materials are parts of the course package you will receive in a CD-Rom or access through the internet. Materials recommended to conduct some experiments may be obtained from your host institution (Partner institution of the AVU) or you may acquire borrow by some other means.

Module Rationale: In this section you will get the answer to questions like “Why should I study this module as pre-service teacher trainee? What is its relevance to my career?”

The second is the CONTENT section that consists of three parts:

Overview: The content of the module is briefly presented. In this section you will fined a video file (QuickTime, movie) where the author of this module is interviewed about this module. The paragraph overview of the module is followed by an outline of the content including the approximate time required to complete each section. A graphic organization of the whole content is presented next to the outline. All these three will assist you to picture how content is organized in the module.

General Objective(S): Clear informative, concise and understandable objectives are provided to give you what knowledge skills and attitudes you are expected to attain after studying the module.

Specific Learning Objectives (Instructional Objectives): Each of the specific objectives, stated in this section, is at the heart of a teaching learning activity. Units, elements and themes of the module are meant to achieve the specific objectives and any kind of assessment is based on the objectives intended to be achieved. You are urged to pay maximum attention to the specific objectives as they are vital to organize your effort in the study of the module.

The third section is the bulk of the module. It is the section where you will spend more time and is referred to as the **Teaching Learning Activities**. The gist of the nine components is listed below:

Pre-assessment: A set of questions, that will quantitatively evaluate your level of preparedness to the specific objectives of this module, are presented in this section. The pre-assessment questions help you to identify what you know and what you need to know, so that your level of concern will be raised and you can judge your level of mastery. Answer key is provided for the set of questions and some pedagogical comments are provided at the end.

Teaching And Learning Activities: This is the heart of the module. You need to follow the learning guidance in this section. Various types of activities are provided. Go through each activity. At times you my not necessarily follow the order in which the activities are presented. It is very important to note:

- formative and summative evaluations are carried out thoroughly
- all compulsory readings and resources are done
- as many as possible useful links are visited
- feedback is given to the author and communication is done

Compiled List of All Key Concepts (Glossary): This section contains short, concise definitions of terms used in the module. It helps you with terms which you might not be familiar with in the module.

Compiled List of Compulsory Readings: A minimum of three compulsory reading materials are provided. It is mandatory to read the documents.

Compiled List of (Optional) Multimedia Resources: Total list of copyright free multimedia resources referenced in, and required for completion of, the learning activities is presented.

Compiled List of Useful Links: a list of at least 10 relevant web sites. that help you understand the topics covered in the module are presented. For each link, complete reference (Title of the site, URL), a screen capture of each link as well as a 50 word description are provided.

Synthesis of The Module: Summary of the module is presented.

Summative Evaluation:

Enjoy your work on this module.

I. Solid State Physics

By Sam Kinyera Obwoya Kyambogo University, Uganda.

II. Prerequisite Course Or Knowledge

The basic prerequisites for this module is the school physics that one has learnt. In particular, a knowledge of the following courses is essential for one to follow and understand the module effectively. One of the prerequisite courses is electricity and magnetism. The concept of force and Coulomb's law is essential as one learns atomic structure. A prior knowledge of heat and thermodynamics is also required in order to learn this module. In particular you need to revise heat capacity at constant volume and constant pressure. Further to this you need to revise topics on entropy, enthalpy and thermodynamic functions. As a general requirement, you need the knowledge of calculus in mathematics.

III. Time

This module can be completed in 120 hours.

IV. Materials

The materials required for the module include access to a computer, but more importantly one needs a steady access to internet. The internet will provide many of the essential references and multimedia resources. These multimedia are important as in some cases they serve as virtual lecturers and sources of equipment that can be used to perform virtual experiments. However, some CD-ROMS will also be available to supplement the use of internet. Other materials include compulsory readings and compulsory resources that may be available at nearby bookshops or schools.

V. Module Rationale

This module is intended to provide a basic foundation of physics to students. This will enable the students to learn the subject matter in order to explain and account for the physical, thermal, electrical and optical properties of solids. The module is structured such that the learner has to go through the activities as prescribed for maximum attainment. The overall module will provide the student with basic ideas of what solids are in terms of their behaviour and therefore will be able to teach most of the school physics effectively.

VI. Content

6.1 Overview

This course is intended for students enrolling for BSc with Education and BEd degrees. Solid state physics forms the backborn of physics. The module has four units: Introduction to solid state physics; Crystal defects and mechanical properties ; Thermal and electrical properties; and Band theory & Optical properties.In the first unit/activity i.e. introduction to solid state physics. The student is expected to explain the atomic structure, describe the various atomic bonds such as ionic bonds and covalent bonds. The learning will also require students to distinguish between crystalline and amorphous solids; polycrystalline and amorphous solids and to explain the production and use of X-ray diffraction. In the second unit i.e. crystal defects and mechanical properties, the learning includes, differentiating between the different types of crystal defects: the point defects (vacancy, interstitials, and substitutional) and dislocations (screw and edge). Here, the student learns that point defects are very localised and are of atomic size, while dislocation is a disorder which extend beyond the volume of one or two atoms. The effects of the defects on mechanical, and electrical properties of these defects are also part of the learning that will take place. In unit three the learning outcomes include definitions of heat capacity, and explanations of variation of heat capacity with temperature based on the classical, Einstein and Debye models. The students will be required to use the free electron theory to explain high thermal and electrical conductivities of metals and also be able to derive and apply the Wiedermann-Frantz law. Finally, in activity four, the expected learning should enable the students to use the band theory to explain the differences between conductors, semiconductors and insulators; explain the differences between intrinsic and extrinsic semiconductors in relation to the role of doping. At the end of it all, the students use the concepts of the interaction of electromagnetic waves (light) with materials to explain optical absorption, reflectivity and transmissivity.

6.2 Outline

The outline of this course consists of four activities: introduction to solid state physics; crystal defects and mechanical properties; thermal and electrical properties; and band theory & optical properties. The components of each activity are listed as follows.

Introduction to Solid State Physics **(40 hours)**

- Review of atomic structure Crystalline,
- Polycrystalline and Amorphous solids.
- X-Ray diffraction, Bragg’s law and applications.

Crystal Defects and Mechanical Properties (20 hours)

- *Vacancies, Interstitials,Dislocations,*
- *Mechanical properties*

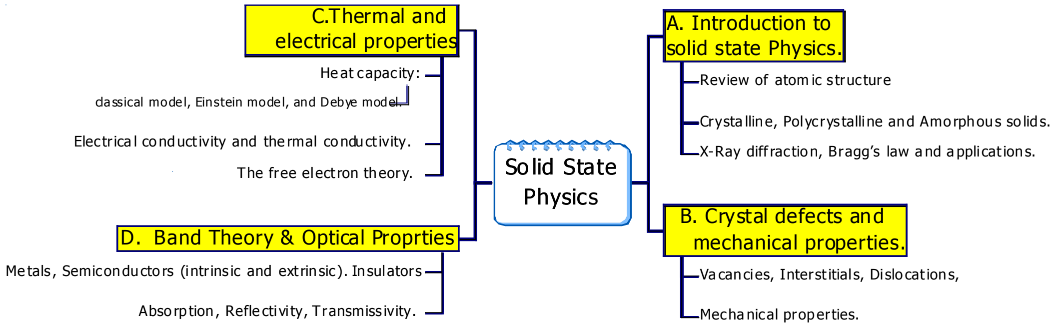
Thermal and electrical properties: (40 hours)

- *Heat capacity: classical model,*
- *Einstein model, and Debye model*
- *Electrical conductivity and thermal conductivity.*
- *The free electron theory*

Band Theory & Optical Properties: (20 hours)

- *Metals,*
- *Semiconductors (intrinsic and extrinsic).*
- *Insulators;*
- *Optical Properties*

6.3 Graphic Organizer



VII. General Objective(S)

After completing this module you will be able to

- understand the mechanical, thermal, electrical and optical behaviour of solids from a fundamental point of view.

VIII. Specific Learning Objectives (Instructional Objectives)

Content	**Learning objectives**
	After Completing this section you would be able to:
1. **Introduction to solid state Physics: (40 hours)** • Review of atomic structure • Crystalline, Polycrystalline and Amorphous solids. • X-Ray diffraction, Bragg's law and applications.	• Explain the atomic structure; • Describe the various atomic bonds; • Distinguish between crystalline, polycrystalline and amorphous solids, and explain how X-ray diffraction is used in this regard
2. **Crystal defects and mechanical properties: (20 hours)** • Vacancies, Interstitials,Dislocations, • Mechanical properties.	• Explain the concept of crystal defects • Relate crystal defects to some observed mechanical properties and other properties.
3. **Thermal and electrical properties: (40 hours).** • Heat capacity: classical model, • Einstein model, and Debye model • Electrical conductivity and thermal • conductivity. The free electron theory.	• Define heat capacity, and explain variation of heat capacity with temperature based on the classical, Einstein and Debye models; • Use free electron theory to explain high thermal and electrical conductivities of metals; • Derive and apply the Weidermann – Frantz law.

4. Band Theory & Optical Properties: (20 hours) • Metals, • Semiconductors (intrinsic and extrinsic) • Insulators; • Absorption, Reflectivity, &Transmissivity.	• Describe the band theory • Explain the difference between conductors, semiconductors and insulators; • Explain the difference between intrinsic and extrinsic semiconductors – the role of doping. & • Explain, based on the interaction of electromagnetic waves (light) and materials: - Absorption, Reflectivity and Transmissivity

IX. Pre-assessment

Are you ready for this module?

Title of Pre-assessment : **Solid state physics**

Rationale *:* The pre-assessment provided here is intended to determine how much a student knows about solid state physics. Thus, it serves to motivate students to be more involved in, and attentive to, instruction and learning experiences as the pre-assessment helps more clearly identify what they know and what they need to know The questions provided are also intended to alert the students of what he/she is expected to achieve in case one finds that he/she cannot provide any response to the question. This will appropriately raise the learners' level of concern by signaling what they need to learn.

Questions

Self Evaluation

1. Sites which are usually occupied by an atom but which are unoccupied are called

   (A) vacancies (B) interstitials (C) substitutional (D) dislocation

2. A dislocation caused by the termination of a plane of atoms in the middle of crystal is known as

   (A) screw (B) edge (C) burger (D) void

3. In a reciprocal lattice space, the vector **a*** is given by

   (A) $a^* = 2\pi \dfrac{b\times c}{a\times(b\times c)}$ (B) $a^* = 2\pi \dfrac{a\times b}{a\times(b\times c)}$

   (C) $a^* = 2\pi \dfrac{b\times c}{a.(b\times c)}$ (D) $a^* = 2\pi \dfrac{a\times c}{b.(a\times c)}$

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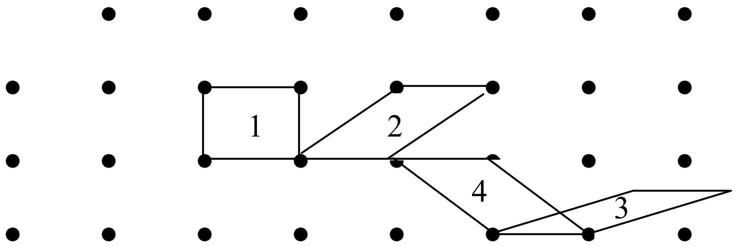

The diadram above represent a portion of 2D lattice. Which one of the outlines does NOT represent a primitive unit cell?

(A) 1 (B) 2 (C) 3 (D) 4

5. For the fcc lattice with one atom basis what is the coordination number?

(A) 4 (B) 6 (C) 8 (D) 12

6. A beam of X-ray of wavelength 0.25 nm is incident on a crystal of interplanal-separation 0.30 nm. Calculate the glancing angle for first order diffraction.

(A) 24.6^0 (B) 36.0^0 (C) 56.4^0 (D) 54.8^0

7. The lattice parameter of a cubic lattice is 2.4 nm. Find the lattice spacing for plane (122).

(A) 0.8 (B) 0.48 (C) 7.2 (D) 1.25

8. Which of the following statements is correct?

(A) The metallic bond has a non-directional characteristics:

(B) The metallic bond consists of a sea of free electrons surrounding the positive ions

(C) One of the characteristics that contributes to the properties of a metallic solid is having shiny surface

(D) A metallic bond is formed by electron sharing which occurs between two or more atoms

9. Which of the following is NOT the effects of dislocation

(A) The presence of dislocations results in lattice strain (distortion).
(B) The direction and magnitude of such distortion is expressed in terms of aBuger vector, b.
(C) For an edge type, b is perpendicular to the dislocation line, whereas in the cases of the screw type it is parallel.
(D) In metallic materials, b is aligned with close-packed crytallographic directions and its magnitude is equivalent to two interatomic spacing.

10. A force of 160 N acts perpendicularly to a cross section area of 0.002 m^2. Calculate Young's modulus of the material if the strain produced is 0.004.

(A) 1.28×10^{-7} (B) 5.0×10^{-6} (C) 2×10^{7} (D) 8.0×10

11. Which of these is *not* involved in the diffraction of x-rays through a crystal?

(A) Electron transitionS
(B) Crystallographic planes
(C) Nuclear interactions
(D) Constructive interference

12. A crystal has a primitive lattice with spacing between (100) planes is 0.420 nm. What will the value of the Bragg's angle be for the 100 reflection of X-rays of wavelength 0.154 nm.

(A) 5.3^0 (B) 10.6^0 (C) 21.2^0 (D) 42.6^0

13. Which of the following statement is NOT true?

(A) The Fermi level is the top of the collection of electron energy levels at absolute zero temperature.
(B) Since electrons are fermions and by the *Pauli exclusion principle* they cannot exist in identical energy states. So at absolute zero they pack into the lowest available energy states and build up a "Fermi sea" of electrons energy states.
(C) The Fermi level is the surface of that sea at absolute zero where electrons have enough energy to rise above the surface. Thus, the Fermi-Level is located in the band gap.
(D) In a conductor, the Fermi level lies *within* the conduction band, such that the band is only half filled with electrons. In this case, only a small amount of energy is needed for the electrons to find other unoccupied states to move into, and hence for current to flow.

14. In diatomic gases the presence of internal degrees of freedom are apparent that is, in addition to the three translational degrees of freedom, there are rotational and vibrational degrees of freedom.
    (i) there are a total of three rotational degrees of freedom, one corresponding to rotation about each of the axes of three dimensional space.
    (ii) only two degrees of rotational freedom for linear molecules are considered in practice because the moment of inertia about the internuclear axis is vanishingly small with respect to the other moments of inertia in the molecule.
    (iii) quantum mechanically, the interval between successive rotational energy, eigenstate, is directly proportional to the moment of inertia about that axis.

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15. Which of the following ststements is NOT true?
    (A) Electrical conductivity is more or less strongly dependent on temperature.
    (B) In metals, electrical conductivity decreases with increasing temperature.
    (C In semiconductors, electrical conductivity increases with increasing temperature.
    (D) Over a wide temperature range, the electrical conductivity can be approximated as being directly proportinal to temperature.

16. Which of the following expressions is correct?

(A) $C_V = \left(\frac{\partial S}{\partial T}\right)_V$ (B) $C_V = T\left(\frac{\delta Q}{\partial T}\right)_V$

(C) $C_P = \left(\frac{\partial H}{\partial T}\right)_P$ (D) $C_P = \left(\frac{\partial S}{\partial T}\right)_P$

where

C_V and C_P are heat capacities at constant volume and constant pressure respectively.

δQ is the infinitesimal amount of heat added,
dT is the subsequent rise in temperature.

∂ U is the change in internal energy

∂ H is change in enthalpy.

17. Which of the following is NOT true of charactertistics of materials

    (A) In crystalline solids, atoms interact with their neighbours, and the energy levels of the electrons in isolated atoms turn into bands

    (B) Electrons in a solid fill up the energy bands up to a certain level, called the Fermi energy.

    (C) Bands which are completely full of electrons can conduct electricity, because there is no state of nearby energy to which the electrons can jump.

    (D) In some cases, however, the band theory breaks down and materials that are predicted to be conductors by band theory turn out to be insulators. Mott insulators and charge transfer insulator are two such classes of insulators.

18. Which of the following statements is NOT true?

    (A) Thermal conductivity of a material depends on its structure.

    (B) Thermal conductivity of a material depends on temperature.

    (C) Pure crystalline substances exhibit highly variable thermal conductivities along different crystal axes, due to differences in phonon coupling along a given crystal dimension.

    (D) Air and other gases are generally good insulators, even in the presence of convection.

Answer Key

1. A
2. B
3. C
4. D
5. D
6. A
7. A
8. B
9. D
10. C
11. C
12. B
13. C
14. D
15. D
16. C
17. C
18. D

Pedagogical Comment For The Learner

You do not need to despair in case you perform poorly in the pre-assessment. What the outcome of the pre-assessment tells you is that you need to work and concentrate more while studying and learning the module. As you notice, most of the questions contain topics which are normally not done at school.

At the beginning of the module, you will learn about the atomic structures which is expected to provide a foundation for the study of this module. This ultimately takes you through to learning about lines of symmetry, Miller indices which are used for identification of planes. Bragg's law and finally construction of the Ewald's sphere which helps in determining planes responsible for diffraction of x-rays. A student is adviced to go through each section of the activity in a cronological order. Where prior knowledge is required, a student is adviced to go first through such topics like electricity and magnetism before proceeding further.

A number of references are referred to throughout the activity. A student needs to have access to these references. Most of them are on line. Where a student does not have permanent access to internet, the student is adviced to download such references and keep hard copies. A number of multimedia resources are also included. These are very useful as they may act as virtual lecturers or sources of virtual laboratory. Students are encouraged to use these multimedia resources all the time.

X. Teaching And Learning Activities

Activity 1: Introduction to Solid State Physics

You will require 40 hours to complete this activity. Ensure that you go through the activities systematically. In some cases you will need to go through pre-requisite courses before embarking on this module.

Specific Teaching and Learning Objectives:

The objectives for all these to take place require that the student should be able to:

- Explain the atomic structure
- Describe the various atomic bonds
- Distinguish between crystalline and amorphous solids; crystalline, polycrystalline and amorphous solids and explain the occurrence and use of X-ray diffraction

Summary of the learning activity

The learning outputs include knowing that an atom is made up of a combination of three types of particles: electrons, protons, and neutrons and that Avogadro's constant is the quantity which contains 6.02 x 10^{23} particles per mole**.** The learning and discussion also include similarities and differences of four types of bonds. This activity also include learning about crystal structures of polycrystalline and amorphous solids of which identification of planes using Miller indices forms a major part. Further learning include how packing density is calculated, derivation of Bragg's law and subsequent use of the construction of Ewald's sphere to determine planes responsible for x-ray diffraction.

List of Required Readings

Reading 1: Crystal Structure.

Complete reference :
From Wikipedia.
URL : http://en.wikipedia.org/wiki/Crystal_structure
Accessed on the 20th April 2007

Abstract : This reading material briefly describes the unit cell, classification of crystals by symmetry, Physical properties of crystals and links are given to various sites within wikipedia and other sites.

Rationale: This reading material provides elaborated discussion on the contents of the first activity of the module.

Reading 2: Crystal Structure.

Complete reference *:*
From University of Exeter
URL *:* http://newton.ex.ac.uk/teaching/resources/rjh/phy2009/
Accessed on the 20th April 2007

Abstract : In this article, crystal structure is described with well illustrated diagrams. The exercises in the article help the reader to consolidate the topics learnt.

Rationale: This article gives another way of looking at crystal structures. Further the sample tests and exercises given at the end provide good opportunity to use the theories and principles exercised from different perspectives.

List of Relevant Multimedia Resources

Resource #1
Title: The crystal structure of Cu-Zn brass
URL*:* http://video.google.com/videoplay?docid=5897475989157955721&q=crystal+structure&hl=en
Description*:* Appropriate illustrations and explanations are provided,
Date Consulted: 20/05/2007

Resource #2

Title: Great Ball of Glass
URL: http://video.google.com/videoplay?docid=2134572208219565504&q=polycrystalline+solid&hl=en
Description: This provides good learning resource.
Date Consulted: 20/05/2007

Resource #3

Title: Two Dimensional Lattice: Real and Reciprocal
URL: http://solidstate.physics.sunysb.edu/teach/intlearn/lattice/lattice.html
Description: The sites provide very good learning materials
Date consulted: 16/11/2007

Ressource #4

Title: Exploring materials engineering
URL: http://www.engr.sjsu.edu/WofMatE/Structure.htm
Description: This provides animation and learning materials on atomic structure: BCC, FCC.
Date consulted: 19/11/2007.

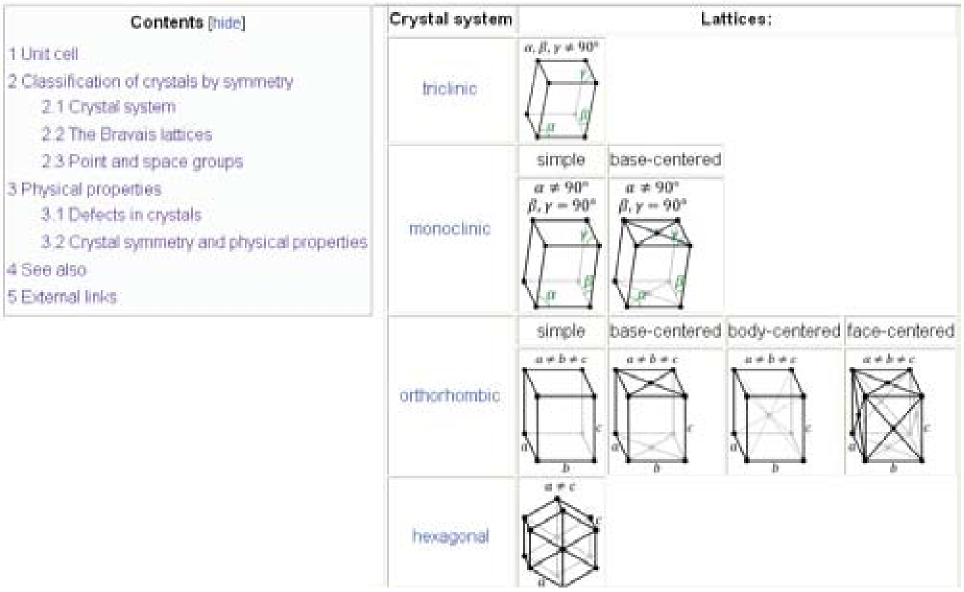
List of Relevant Useful Links

Useful Link #1: Wikipedia

Title: Crystal Structure

URL: http://en.wikipedia.org/wiki/Crystal_structure,

Screen Capture:



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4 See also
5 External links

Crystal system	Lattices:			
triclinic	$\alpha, \beta, \gamma \neq 90°$			
monoclinic	simple	base-centered		
	$\alpha \neq 90°$ $\beta, \gamma = 90°$	$\alpha \neq 90°$ $\beta, \gamma = 90°$		
orthorhombic	simple	base-centered	body-centered	face-centered
	$a \neq b \neq c$	$a \neq b \neq c$	$a \neq b \neq c$	$a \neq b \neq c$
hexagonal	$a \neq c$			

Description: The crystal structure of a material is often discussed in terms of its unit cell. The unit cell is a spatial arrangement of atoms which is tiled in three-dimensional space to describe the crystal. The unit cell is given by its lattice parameters, the length of the cell edges and the angles between them, while the positions of the atoms inside the unit cell are described by the set of atomic positions (x,y,z) measured from a lattice point. The wikipedia page has a good description of this as shown in the screen capture .

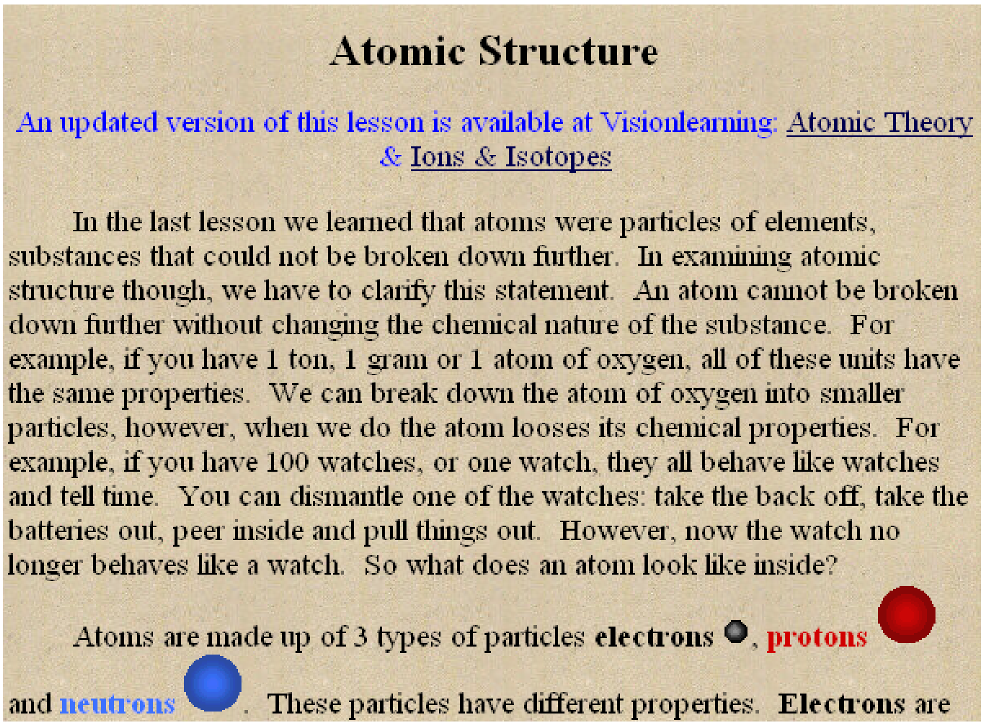
Rationale: - 29/11/2006:

Useful Link #2

Title: Atomic Structure

URL: http://web.jjay.cuny.edu/~acarpi/NSC/3-atoms.htm

Screen Capture:



Atomic Structure

An updated version of this lesson is available at Visionlearning: Atomic Theory & Ions & Isotopes

In the last lesson we learned that atoms were particles of elements, substances that could not be broken down further. In examining atomic structure though, we have to clarify this statement. An atom cannot be broken down further without changing the chemical nature of the substance. For example, if you have 1 ton, 1 gram or 1 atom of oxygen, all of these units have the same properties. We can break down the atom of oxygen into smaller particles, however, when we do the atom looses its chemical properties. For example, if you have 100 watches, or one watch, they all behave like watches and tell time. You can dismantle one of the watches: take the back off, take the batteries out, peer inside and pull things out. However, now the watch no longer behaves like a watch. So what does an atom look like inside?

Atoms are made up of 3 types of particles **electrons** ●, **protons** ● and **neutrons** ●. These particles have different properties. **Electrons** are

Description: This site is a journey through the wonders of natural science. Using animation and interaction to enhance the experience, the site allows the user to explore concepts in basic science including the scientific method, the nature of matter, atomic structure, chemical bonding, DNA, astronomy, cell structure and much more. This site was organized for NSC107: An Introduction to Science in Society at John Jay College of the City University of New York, however the lessons were designed for general use and all visitors are welcome. Use the menu bar at left to navigate through the course content. Please email comments and suggestions to help improve the site.

Rationale: the site provides useful learning materials for the course

Detailed Description of the Activity (Main Theoretical Elements)

In this section, a mixture of the theory, instructions of what the learner should do while learning the module are prescribed. The learner is advised to complete fully each section of the module before moving to the next section or activity. For each section, the learner is advised to consult the references recommended. This is important because the instructions and activities described are in brief forms.

Activity 1.1 Atomic structure

In this activity you will explain the atomic structure. In order to do this you will need prior knowledge of school physics.

While at school, you have learnt that atoms are particles of elements,or substances that can not be broken down further. But, in examining atomic structure though, we have to clarify this statement. An atom cannot be broken down further without changing the chemical nature of the substance. For example, if you have 1 kilogram, 1 gram or 1 atom of nitrogen, all of these units have the same properties. We can break down the atom of nitrogen into smaller particles; however, when we do, the atom loses its chemical properties. Here we learn that: that each atom is made up of a combination of three types of particles: electrons, protons, and neutrons.

(i) Use the references including multimedia resources and

- Prepare short notes detailing the different properties of these three particles.
- Describe how the existence of molecules/atoms can be demonstrated by Brownian motion experiment. *Use the references provided to do this.*

Activity 1.1.1 Avogadro's Constant, the mole

(a) Make a short note on atomic and molecular masses and describe how they are measured.

(b) Emphasize that on the carbon scale, the atomic mass of carbon-12 is taken as exactly 12, making that of hydrogen 1.008 and that of oxygen 16.

You should be able to draw a conclusion that:

- In general 1g of hydrogen contains the same number of atoms as 12g of carbon. i.e. the atomic mass of any element expressed in grams, contains the same number of atoms as 12g of atoms. This number by definition is thus a constant. It is called the Avogadro's constant. Its value is 6.02×10^{23}.
- A quantity which contains 6.02×10^{23} particles is the **mole.** We can have a mole of atoms, a mole of molecules, a mole of ions, a mole of electrons- all contain 6.02×10^{23} particles. Thus Avogadro's constant $N_A = 6.02 \times 10^{23}$ particles per mole.

Activity 1.1.2

Let us use an oxygen atom as an example to illustrate some of the properties. An oxygen atom has 8 electrons, 8 protons and 8 neutrons. This implies that an oxygen has a total of 8 negative charges carried by the 8 electrons; 8 positive charges carried by the 8 protons. Neutrons carry no electrical charge**.**

Activity 1.1.3

Repeat the same exercise with other atoms until you feel confident enough.

Activity 1.2 Atomic bonds

Use the references provided and any other that you have access to carry out the following activities.

(i) Explain how atoms are held together by the attractive forces

(ii) Write short notes including some illustrations of the different types of bonds: *Ionic bonds, Covalent bond, Metallic bond, and Van der Waals bond*. An illustration of a covalent bond is given as follows.

In covalent bonding, electron sharing occurs between two or more atoms. For example, each carbon atom (C), Fig. 1.1 has four outer electrons, and all can be shared with four other carbon atoms to make four bonds, each consisting of two interlocking electron clouds.

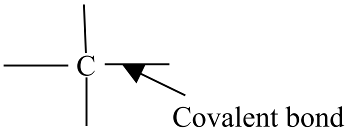


Figure 1.1 Carbon atom with its four bonds

You have to note that covalent bonds are also strong and many compounds have similar mechanical properties to ionic compounds. Unlike, ionic bonds, they do not conduct electricity when molten.

(iii) Show that the electrostatic force between two opposite point charges is given by Eq. 1.1

$$F = \frac{q^2}{4\pi\varepsilon_0 r^2} \tag{1.1}$$

(Hint: Use Coulomb's law).

(iv) Show also that the work done as the ions are brought to a separation r from infinity is

given by Eq. 1.2

$$U = \int_{r}^{\infty} F\,dr = \frac{q^2}{4\pi\varepsilon_0 r} \qquad (1.2)$$

(v) In your notes compare each of the type of bond with one another.

Activity 1.3 Crystalline, Polycrystalline and Amorphous solids

Activity 1.3.1 Crystalline solids

(a) Use the references and note down definitions of crystalline, polycrystalline and amorphous solids

(b) List examples of each type as part of your notes

Activity 1.3.2 Crystal

Background

In crystallography a **crystal structure** is a unique arrangement of atoms in a crystal. A crystal structure is composed of a *unit cell*, a set of atoms arranged in a particular way; which is periodically repeated in three dimensions on a lattice. The spacing between unit cells in various directions is called its *lattice parameters.* The symmetry properties of the crystal are embodied in its space group. A crystal's structure and symmetry play a role in determining many of its properties, such as cleavage, electronic band structure, and optical properties.

(a) In order to understand some of these concepts we must know for example the meaning of the *lattice*

(b) A lattice Is a simplified geometry of a crystal in which the atoms are swept away leaving only a skeleton of mathematical points whereby each point replaces anything from one to several hundred of original atoms. Each group of these atoms is called the *basis*

(c) In two dimensions, there are only five lattices: square, rectangular, centred rectangular, oblique and hexagonal. These are generally known as **Bravias lattice**.

(d) Consider an example given in Fig. 1.2 of how a lattice is constructed from a crystal structure

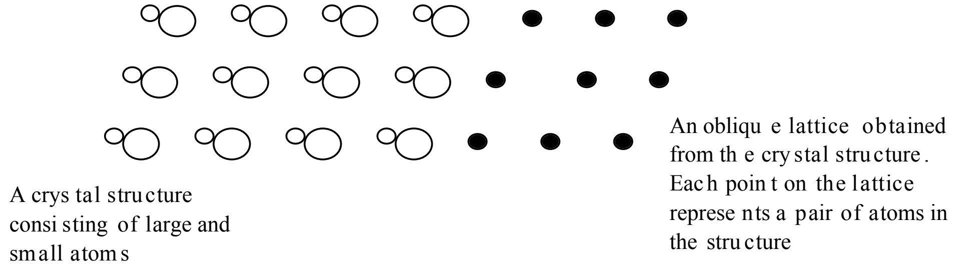


Figure 1.2 : A lattice constructed from a crytal structure

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Note that the lattice points drawn must conform to

- An infinite pattern of points
- All points having the same surrounding in the same orientation.

(e) The fundamental difference between single crystal , polycrystalline and amorphous solids is the length scale over which the atoms are related to one another by translational symmetry (‘periodicity’ or ‘long-range order’). Single crystals have infinite periodicity, polycrystals have local periodicity, and amorphous solids (and liquids) have no long-range order.

- An *ideal single crystal* has an atomic structure that repeats periodically across its whole volume. Even at infinite length scales, each atom is related to every other equivalent atom in the structure by translational symmetry.
- A *polycrystalline solid* or *polycrystal* is comprised of many individual *grains* or *crystallites*. Each grain can be thought of as a single crystal, within which the atomic structure has long-range order. In an *isotropic* polycrystalline solid, there is *no relationship* between neighbouring grains. Therefore, on a large enough length scale, there is no periodicity across a polycrystalline sample.

Amorphous materials, like window glass, have short-range order at all, so they have no translational symmetry.

Example

To identify and identify the number of atoms at each point that can be constructed from the crystal structure given in Fig. 1.3.

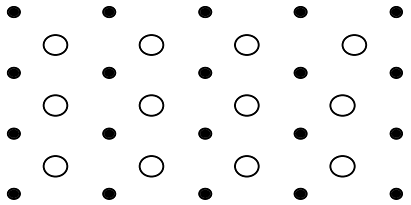

Figure 1.3: Crystal Structure

- *The lattice of this crystal structure is rectangular lattice, having two atoms per lattice point*

Activity 1.3.3 *Unit cell, and primitive cell*

(a) (i) Use the references (Steadman R, 1982, Crystallography, Van Nostrand Reinhold (UK) Co. Ltd, Norfolk), or any other one and define a unit cell and a primitive cell. Note the difference between the two.

(ii) A unit cell is defined in terms of six elements or parameters: **a, b, c** the lengths of the cell edges (taken as axes); $\alpha, \beta, \text{and} \gamma$, the angles between axial direction as shown in Fig. 1.4.

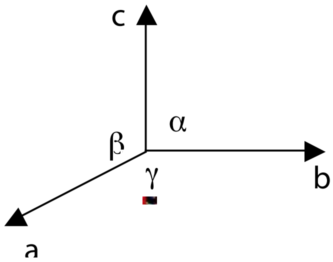

Figure 1.4: The six elements of a unit cell

(b) The patterns given in Fig.1.5 are examples of unit cells constructed from a given lattice.

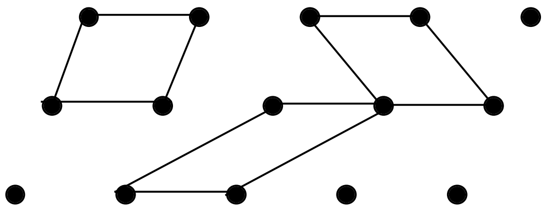

Figure 1.5: Examples of unit cells constructed from a given lattice

(c) Follow the instructions below and construct a Wigner-Seitz cell which is an example of a primitive cell. See Fig. 1.6.

1. Draw lines to connect a given lattice point to all nearby lattice points.
2. Draw new lines or planes at the midpoint and normal to these lines. The smallest volume enclosed in this way is the Wigner-Seitz primitive cell.

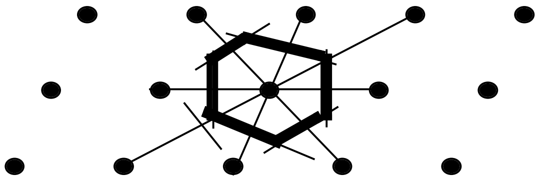

Figure 1.6: Construction of the Wigner-Seitz primitive cell

(d) Read more about this from http://newton.ex.ac.uk/teaching/resources/rjh/phy2009/

Activity 1.3.4 Crystal Systems; Three-dimensional lattices

(a) The three-dimensional lattice is understood by first recognizing the seven systems of axes which give the seven unit cells called crystal systems. These are the axes given above under unit cell. The magnitude of the vectors a, b, and c are *a, b,* and *c* respectively. These are the parameters of a unit cell.

(b) Use the references (http://en.wikipedia.org/wiki/Crystal_structure,) and describe the seven crystal systems (lattices): *cubic, tetragonal, orthorhombic (rhombohedral), monoclinic, triclinic, trigonal and hexagonal* in terms of the lattice parameters, *a, b, c* and ; α, β, γ , the angles between axial directions.

Activity 1.3.5 Classification of crystals by symmetry

The defining property of a crystal is its inherent symmetry, by which we mean that under certain *operations* the crystal remains unchanged when viewed from a given direction. For example, rotating the crystal 180 degrees about a certain axis may result in an atomic configuration which is identical to the original configuration. The crystal is then said to have a two-fold rotational symmetry about this axis. In addition to rotational symmetries like this, a crystal may have symmetries in the form of *mirror planes* and *translational symmetries*, and also the so-called *compound symmetries* which are a combination of translation and rotation/mirror symmetries. A full classification of a crystal is achieved when all of these inherent symmetries of the crystal are identified.

(a) Read about this and solve as many problems as possible. Use the references provided. Determine the number of rotational symmetry for rectangular,circular, equilateral, and hexagonal lattices.

(b) When a square lattice shown in Fig. 1.7 is rotated about an axis through it centre, it will appear exactly the same four times after being rotated through 360^0. Thus, a square lattice has a four-fold rotational symmetry. In each fold, the lattice is rotated through 90^0 or $\pi / 2$

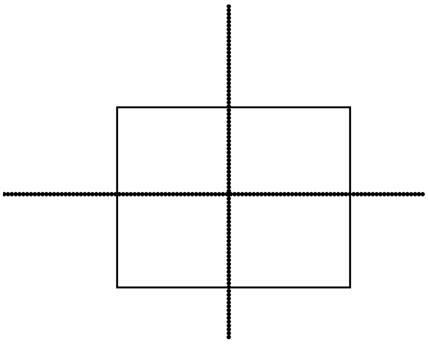

Figure 1.7: A square lattice

(i) Note that possible rotational symmetry are**:** one-, two- three-, four-, and six-fold rotation axes that carry the lattices onto itself corresponding to $2\pi/1,\ 2\pi/2, 2\pi/3, 2\pi/4, 2\pi/6$ .Relate these values to lattices given in activity 1.3.5 (a) above.

READ MORE ABOUT THIS!! (Blakemore J.S. 1974, Solid State Physics 2^{nd} ed., Cambridge University Press, Cambridge).

(c) Read and make notes about **Bravais lattices** (Use Introduction to solid state physics by C Kittel, Introduction to Solid State Physics, 5th Ed., New York: Wiley, 1976, including the websites; http://pages.physics.cornell.edu/sss/bravais/bravais.html : (Simulation of bravais lattice

Examples of cubic system

There are three lattices in the cubic system: the simple cubic (sc); the body-centred cubic (bcc); lattice, and the face centred cubic (fcc) lattice. These are shown in Fig. 1.8

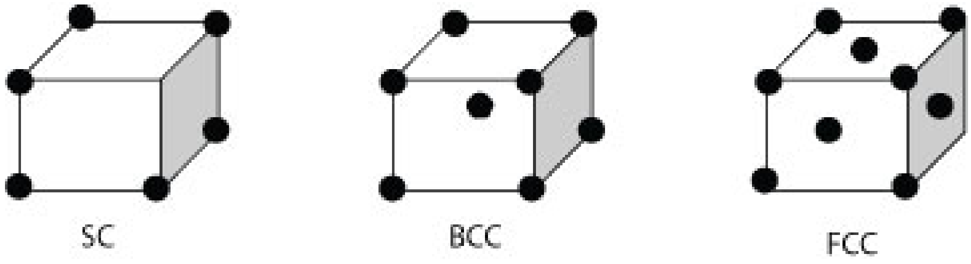

Figure 1.8 : The three lattices in the cubic system

(ii) Check in other references for comparison (You can get this from any of the references)

Activity 1.3.6 Lines of symmetry

A general expression for allowed rotation in a periodic lattice is obtained as follows.

Consider a lattice of lattice parameter as shown in Fig. 1.9.

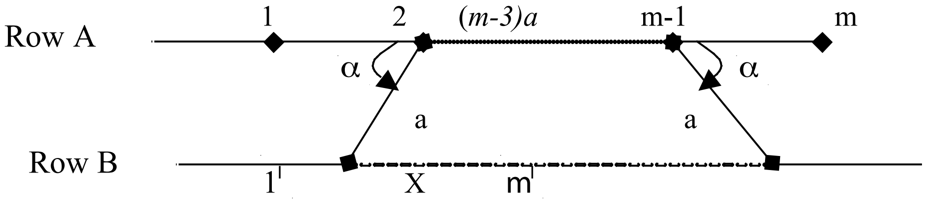

Figure 1.9 : Rotation in allowed periodic lattice.

Along row A atoms *1* and *m* are separated by a distance (m-1)a. Let rotation α be allowed by this lattice. Rotation about atom 2 moves 1 to position originally occupied by some atom 1^{1}. Similarly, clockwise rotation of *m* about *m-1* moves m to m^{1}. Both 1^{1} and m^{1} are on row B. Their separation X is a multiple of *a* if α is allowed rotation.

Let X = pa *p* is unknown.

The difference between integers *m* and *p* can be described in terms of α as

$$X = pa = (m-3)a + 2a\cos\alpha$$

$$\Leftrightarrow \cos\alpha = \frac{3+p-m}{2} \qquad (1.3)$$

The solutions show that attempts to fill an area with regular polygons of any rotational symmetry lead to either overlapping or wasted spaces.

Solution to equation 1.3

If *m* and *p* are integers, there are only 5 solutions to the equation as shown in Table 1.1

Table 1.1: Solutions to equation 1.3.

p-m	Cosα	α	Order of rotation
-1	1	0	One-fold
-2	½	$\pi/3$	6-fold
-3	0	$\pi/2$	4-fold
-4	-1/2	$2\pi/3$	3-fold
-5	-1	π	2-fold

(iii)

Check that the information in the table are correct.

Activity 1.3.7 Index system for crystal planes (Miller indices)

In this activity you will learn how to define positions, directions and planes in crystals; how closed pack structures are formed and the two distinct types.

(a) Positions and directions

- (i). The position of any lattice is given by **r** = u**a** + v**b** + w**c,** where u, v, and w are integers
- (ii) The position of any general point is **r** = u**a** + v**b** + w**c,** but in this case u, v, and

  w need not be integers
- (iii) Directions are also defined in terms of **r,** from the origin. Direction is denoted as [uvw].

(b) To illustrate the two concepts: the position at the centre of a bcc has fractional coordinates (½,½,½) while the direction of this point from the origin is [½½½]

(c) Miller Indices

Miller indices are useful for defining sets of planes in crystals.It is useful to specify the orientation of a plane by indices determined by the following rules.

(i) Find the intercepts on the axes in terms of the lattice parameters, **a, b, and c.** In the case of a cubic lattice, **a = b =c .** Let these intercepts be 3**a,** 2**b,** 3**c ,** Fig. 1.10

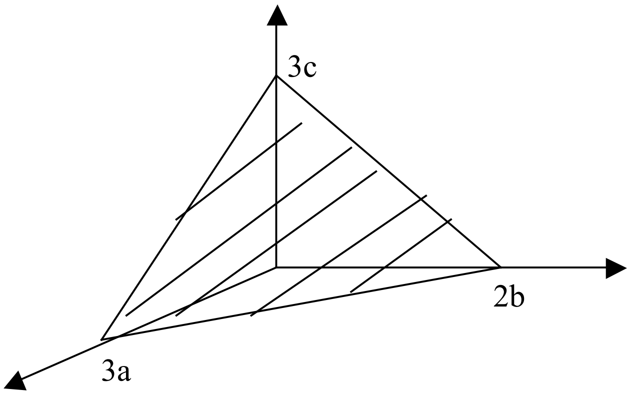

Figure 1.10: Plane used to derive miller indices

(ii) Take the reciprocals of these numbers.

(iii) Reduce the reciprocals to three integers having the same ratios, usually the smallest three integers *h, k, l.* This done by multiplying the reciprocals with their LCM.

(iv) Enclose the three integers in a parentheses as (*hkl*). There should be no commas between the indices. (*hkl*) is called the index of the plane or Miller indices for the plane.

Illustration of the above procedures:

1. Intercept values on the x-, y-, and z-axis are 3**a**, 2**b** and 3**c** respectively.

2. The reciprocals of the intercepts are $\frac{1}{3a},\frac{1}{2b},\frac{1}{3c}=\frac{1}{3},\frac{1}{2},\frac{1}{3}$ since **a, b,** and **c** are unit vectors along the respective axis.

3. Reducing the reciprocals i.e. multiplying throughout by LCM. In this case the LCM is 6. The reciprocals reduce to 2,3,2 respectively.

4. The miller indices for the plane is thus (232).

If a plane cuts an axis on the negative side of the origin, the corresponding index is negative and is indicated by a minus sign written as a bar e.g. $(h\bar{k}l)$. The index $\bar{k}$ is read as bar *k*.

- Note that in the case of a cubic lattice all the faces look identical. For this matter these planes are equivalent by symmetry. Planes equivalent by symmetry are denoted by curly brackets around the indices.

READ MORE ABOUT THIS AND MAKE NOTES
(Steadman R, 1982, Crystallography, Van Nostrand Reinhold (UK) Co. Ltd, Norfolk)

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Example

For a cubic lattice, a plane with miller indices $(1\bar{2}\bar{3})$ is given as follows.

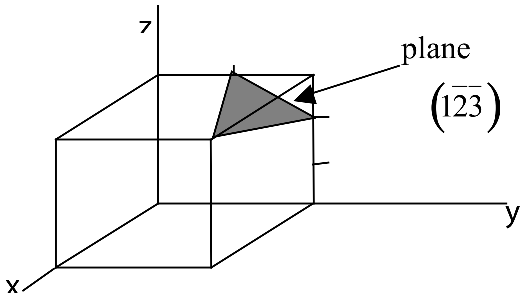


Figure 1.11: Sketching a plane in a cubic lattice

- Note that the choice of the origin is important when sketching a plane. In the example in Fig. 1.11, the origin is at the topmost right corner. Note also the way the edges are subdivided according to the corresponding indices before sketching the plane.

(d) Simple closed-packed structure

In any closed-packed plane array of spheres, each sphere (representing an atom) has six touching neighbours for a monatomic solid considered to be incompressible. Such planes in hexagonal symmetry can be stacked together to make a compact solid in two simple ways. In both arrangements, each atom has 12 nearest neighbours, - six in its plane, three in the plane above and three in the plane below. See Fig. 1.12

Stacking Sequence

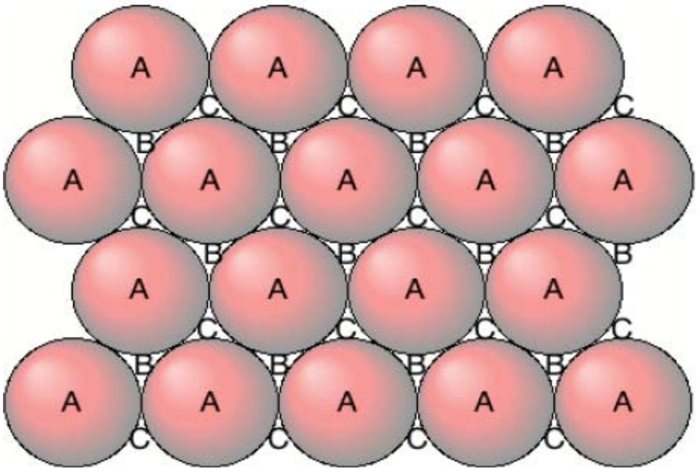


Figure 1.12: Stacking sequence in a simple closed-packed structure

Spheres are arranged in a single closest-packed layer A by placing each sphere in contact with six others. This layer may serve as either the basal plane of an hcp structure or the (111) plane of the fcc structure. A second and identical layer of spheres can be placed on top of this, above and parallel to the plane of the drawing with centres over the points marked B. There are two choices for a third layer. It can go in over A or over C. If it goes in over A the sequence is *ABABAB*....and the structure is hexagonal close-packed. If the third layer goes in over C the sequence is *ABCABCABC*...and the structure is face-centred cubic.

❋ **To appreciate what has been described about stacking sequence, get yourself marbles or sphereical models and try arranging them as described.**

Activity 1.3.8 Packing fraction (density)

In this activity you be able to calculate the packing fraction/density of different crystals.

(a) Read the theory and example provided about packing fraction (packing density). Use other references to supplement what is provided below.
(b) The packing fraction is defined as the maximum proportion of the available volume that can be filled with hard spheres.
(c) Write down a mathematical expression for the statement in (b).
(d) An example in how to calculate packing fraction. Consider a simple cubic lattice (sc) shown in Fig. 1.13.

To determine the packing fraction, one has to find first the number of lattice points in a given cell.

(i) The lattice point in this case refers to a complete number of atoms that a unit cell contains.

(ii) In a sc, the atoms are in contact with one another only along the edges of the cell as shown in Fig. 1.13.

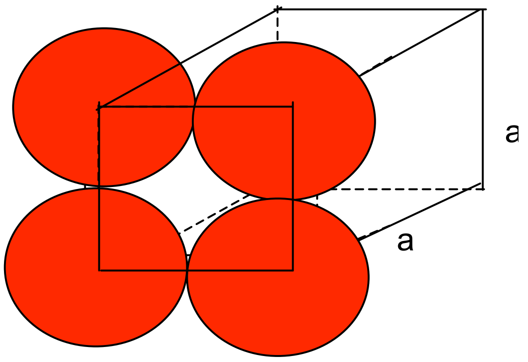


Figure 1.13: A simple cubic lattice showing relative positions of atoms on one face.

(iii) All the atoms are at the corners of the cubic lattice.

(iv) Each atom at the corner is shared by 8 cells. Thus, each atom contributes $\frac{1}{8}$th of it to a unit cell. Since there are 8 atoms at the corners;

The lattice points in sc $= \frac{1}{8} \text{ x } 8 = 1$.

This means that a unit cell in sc system has one atom to itself.
Thus, volume, *V*, occupied by this atom is,

$$V = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi\left(\frac{a}{2}\right)^3, \qquad r = \frac{a}{2} \quad \text{(radius of atom in terms of lattice parameter)}$$

$$\text{Packing fraction } = \frac{\text{volume occupied by lattice points}}{\text{Volume occupied by unit cell}}$$

$$= \left(\frac{\left(\frac{4}{3}\right)\pi\,(a/2)^3}{a^3} \right) = \frac{\pi}{6} = 52\%$$

This means that 48% of the volume of a sc is empty, while 52% is filled with atoms.

Activity 1.3.10 Diffraction and reflection of X-rays

(a) In this activity we look at elastic scattering of waves in periodic structures. This includes the simple derivation of Bragg's conditions. See reference for animation of crystal diffraction. http://www2.wwnorton.com/college/chemistry/gilbert/tutorials/ch10.htm

(b) When a beam of parallel X-rays of wavelength, λ is incident on planes of crytals as shown in Fig. 1.14, the reflection of x-rays by planes in a crystal can be shown to take place only when

$$2d_{(hkl)}\sin\theta = n\lambda\,, \quad n = 1,2,3.... \qquad (1.4)$$

Equation (1.4) is known as Bragg's law. *d* is the spacing between planes in the crystal. In general Bragg's reflection can only occur for wavelength $\lambda \leq 2d$. This explains why visible light is not used. Visble light have much longer wavelengths.

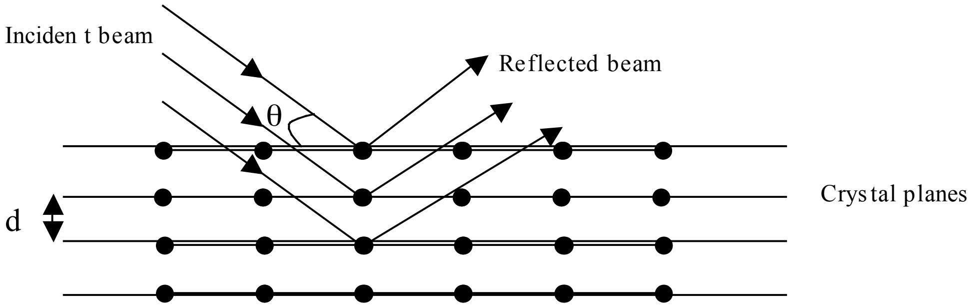


Figure 1.14: Reflection of X-rays from crystal planes.

A set of layers of a crystal only reflects at a certain angle and the angle θ i.e. the angle between the beam and the planes increases as the spacing decreases. θ is the glancing angle.

(c) In advanced books it can be shown that the planal separation, *d*, lattice parameter, *a*, and the Miller indices *(hkl)* have a relation given by Eq. 1.4.

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \qquad (1.4)$$

If a cubic unit cell has lattice parameter *a* = 1.20 nm, then

$$d_{221} = 0.4\text{nm}, \quad d_{224} = 0.2\text{nm}.$$

(d) Show that the above values of, d, in 1.3.10(c) are correct.

Proof of Bragg law

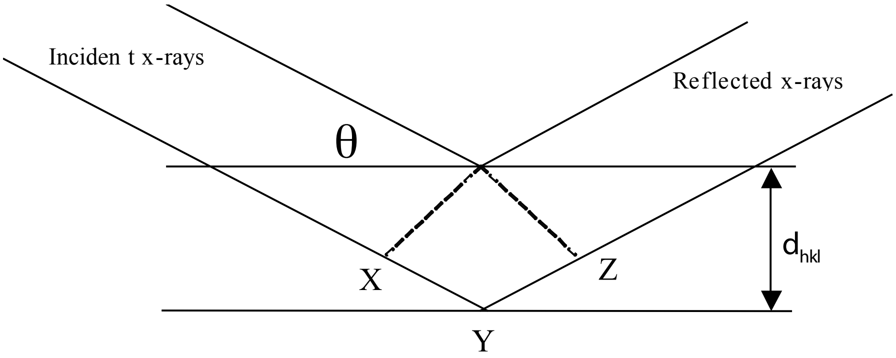


Figure 1.15: X-rays reflected from crystal planes

In Fig. 1.15, the overall path difference = 2x, where x = XY = YZ But $\sin\theta = \frac{x}{d} \Rightarrow x = d\sin\theta$ Path difference therefore $= 2d_{(hkl)}\sin\theta$. Constructive interference occurs when the path difference equals to an integral multiple of λ.

i.e when $2d_{(hkl)}\sin\theta = n\lambda$. *n = 1,2 3.......*

Example

Show that interplanal separation, *d*, lattice parameter, *a* and miller indices *h, k,* l is given by

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

.

Solution

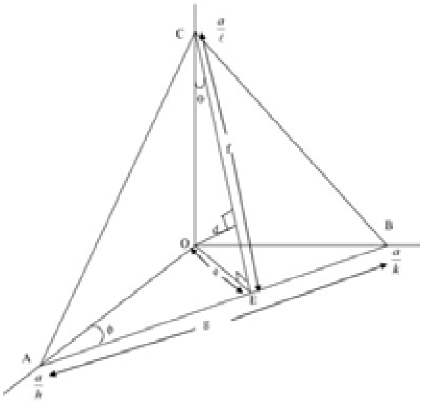


Figure 1.16: Plane used for derivation of expression of interplanal separation

Let us use Fig. 1.16 in order to derive the expression for interplanal separation, *d*.

From triangle OAB
(1)

$$g^2 = \left(\frac{a}{h}\right)^2 + \left(\frac{a}{k}\right)^2$$

Also we have
(2)

$$\sin\phi = \frac{a/k}{g} = \frac{e}{a/h} \Leftrightarrow e^2 g^2 = \left(\frac{a}{k}\right)^2 . \left(\frac{a}{h}\right)^2$$

From triangle OCE
(3)

$$\left(\frac{a}{l}\right)^2 + e^2 = f^2$$

Also
(4)

$$\sin\theta = \frac{e}{f} = \frac{d}{a/l} \Leftrightarrow f^2 = \frac{e^2}{d^2.(a/l)^2}$$

From equations (2), (3) and (4), it can be shown that

$$d^2 = \frac{a^2}{\sqrt{h^2 + k^2 + l^2}}$$

Activity 1.3.11 X-ray Powder Camera

In this activity you will read and find how X-ray powder camera is used in the study of crystal structure. In particular, for the identification of planes in crystal and hence providing an appropriate means of determining the glancing angle. (Steadman. R, 1982 is particular very good for this).

(a). Use the references provided to make notes on the use of X-ray powder camera.

(b) In your note-making consider simple cubic crystal (sc), face-centred cubic (fcc) and body-centred cubic (bcc) crystals.

Activity 1.3.12 Reciprocal lattice space and Ewald sphere

In this activity we will determine the planes in a crystal which are responsible for diffraction of X-rays.

(a) You need to note that it is difficult to imagine how a beam of x-rays entering a crystal might behave, with so many planes set at all angles to the beam and all with different d-spacing. Which of them if any, will satisfy the Bragg's law and reflect the beam? The use of the reciprocal lattice to understand diffraction was demonstrated in 1913 by P. P. Ewald. The points of a reciprocal lattice represent the planes of the *direct* (i.e. real) lattice that it is formed from. The direct lattice determines (through defined relationships) the reciprocal lattice vectors, the lattice points spacings and the associated reciprocal directions.

Consider the two-dimensional direct lattice shown in Fig. 1.17. It is defined by the real vectors **a** and **b**, and the angle γ . The spacings of the (100) and (010) planes (i.e. d_{100} and d_{010}) are shown. A three-dimensional direct lattice would introduce a lattice vector **c** perpendicular to the plane of the diagram.

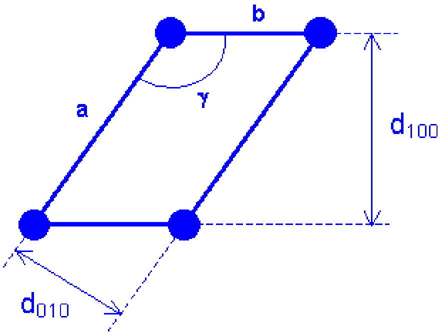


Figure 1.17: Two-dimensional direct lattice

The reciprocal lattice of this will have reciprocal vectors **a*** and **b***, separated by the angle γ^*. **a*** will be perpendicular to the (100) planes, and equal in magnitude to the inverse of d_{100}. Similarly, **b*** will be perpendicular to the (010) planes and equal in magnitude to the inverse of d_{010}. Hence γ and γ^* will sum to 180°.

- Carefully study how an example of construction of reciprocal space from a real space is done below.

Let $\mathbf{a}^*$, $\mathbf{b}^*$, and $\mathbf{c}^*$ be reciprocal lattice vectors.

$\mathbf{a}^*$ is perpendicular to the (100) planes.

$\mathbf{b}^*$, is perpendicular to the (010) planes.

$\mathbf{c}^*$, is perpendicular to the (001) planes.

The length of a^* is $\dfrac{1}{d_{100}}$, b^* is $\dfrac{1}{d_{010}}$, and c^* is $\dfrac{1}{d_{001}}$.

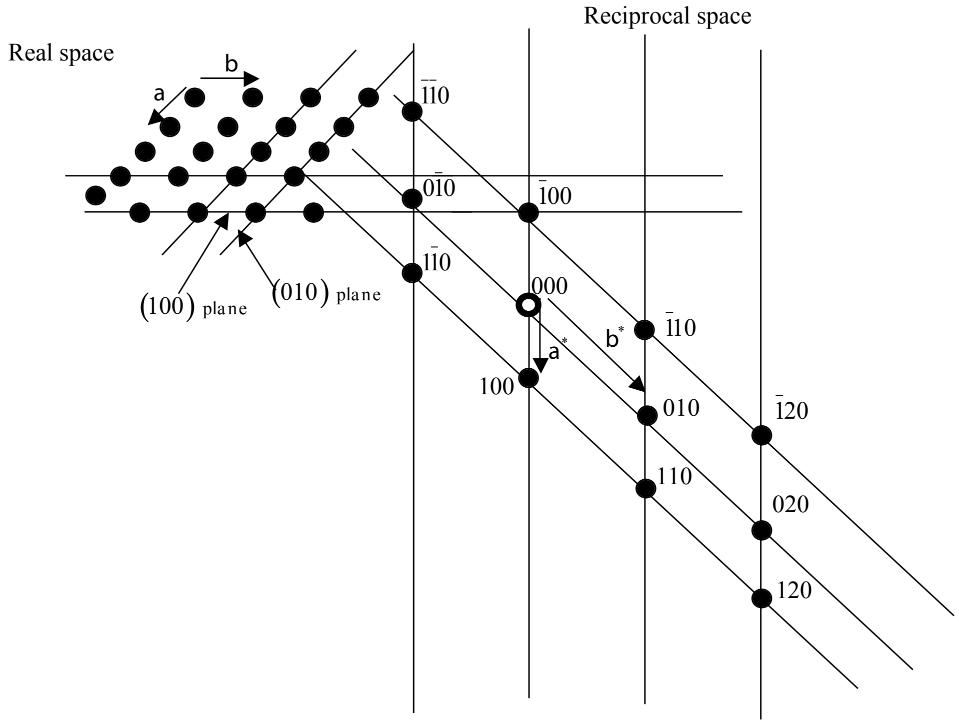


Figure 1.18: Construction of reciprocal space from a real space

Note that vectors **a*** and **b*** are drawn perpendicularly to planes (100) and (010) respectively.

Important points to note about construction of Ewald sphere

(i) In constructing reciprocal lattice, one starts by setting the origin 000 and then the axes. This origin is fixed and is central to the whole lattice and it is the point to which the indices of all other points are related. The real lattice, on the other hand has no such fixed origin and all points are identical.

(ii) The reciprocal lattice differs in this fundamental way from the real lattice in that it is not repetitive (apart from having equally spaced points). Its origin remains the origin, and the 001 and 002 points for example have their own identity and cannot be interchanged, unlike in real lattices. These points represent planes unlike in the case of a real space, where the points represent atoms.

The reciprocal lattice and the Bragg's law

The reciprocal lattice gives a simple and elegant way of picturing the reflection of x-rays by crystal planes. This is achieved by constructing the Ewald sphere.

Essential steps to follow while constructing of the Ewald sphere

Use the lattice parameters given to determine the length of the vectors in the reciprocal apace i.e. The length of a^* is $\frac{1}{d_{100}}$, b^* is $\frac{1}{d_{010}}$, and c^* is $\frac{1}{d_{001}}$

Let a = 0.3 nm; b = 0.5 nm; λ *=0.25 nm*

If n = 1 then

$$\sin\theta = \frac{0.25}{0.5} \Leftrightarrow \theta = 14.5^0 .$$

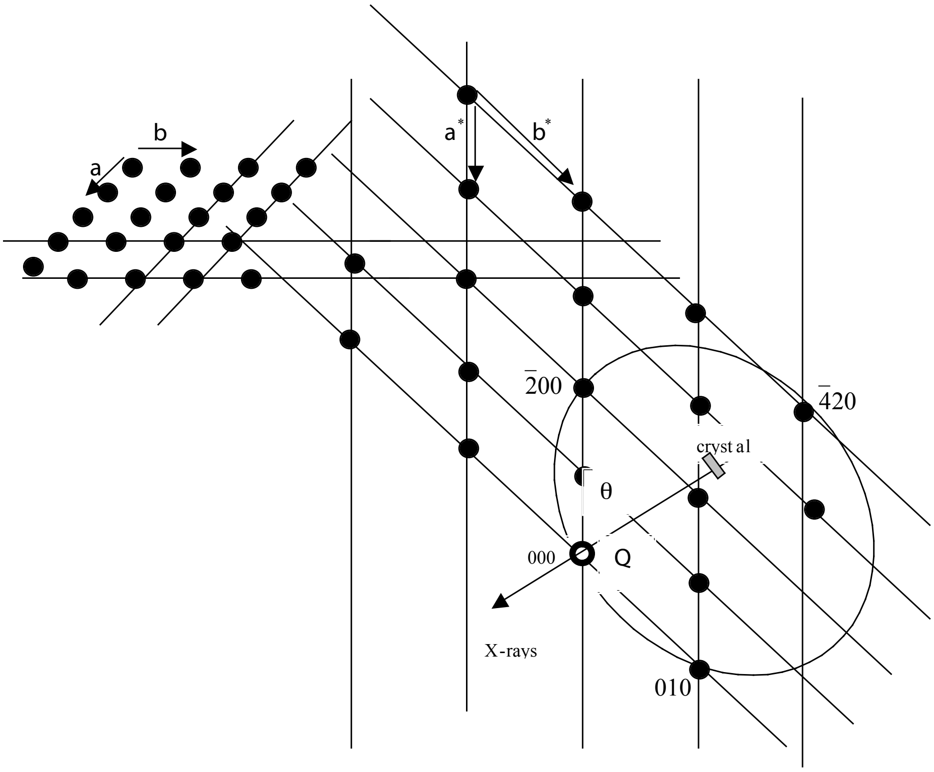


Figure 1.19: Construction of Ewald Sphere

1. Construct the reciprocal space from the real space as shown in Fig. 1.19.
2. Choose one of the points on the reciprocal lattice for 000.
3. Label all the other points which in this case represent the planes.
4. Use Bragg's equation and calculate the glancing angle using the variables provided. Suppose the instruction is that, the reflection is taking place from the (010), the interplanal separation, *d* equals to the value of the lattice parameter *b.* If the reflection is from the (100) planes, then the value of *d* equals the value of the lattice parameter *a.*

5. Using one of the axes, measure angle θ from it . Draw a line marking off this angle such that, this line passes through the origin 000. This line represents the direction of the x-rays.
6. Calculate the reciprocal of λ , the wavelength of the x-rays being used for diffraction. The reciprocal of λ ,equals the radius, *r;* of the Ewald sphere,

i. i.e $r = \frac{1}{\lambda}$

7. Starting from 000, measure off *r* along the line marking off the glancing angle. The end of *r* in this case represents the centre of the Ewald sphere where the crystal is assumed to be placed. Call this point P.
8. Draw a sphere of radius *r* about P. This sphere forms the Ewald sphere. Of course in 2-dimensions, it is a circle.
9. On construction of the sphere, identify points which lie on the sphere. The points that lie on the sphere e.g. point Q represent the planes which are responsible for reflection of x-rays, while the points e.g. S which only touch the sphere, only partially reflect the x-rays. If *n* is one then these planes are responsible for first order diffraction.

Higher orders diffractions

There are two ways of doing this. The first one could be by following the above procedures, but while determining θ using Bragg's equation, n should be taken as 2, for second order diffraction, and taken as 3, for third order diffraction etc.

Secondly, planes responsible for higher order diffractions are obtained as follows:

1. Use the Ewald sphere used for determining planes responsible for first order diffraction.
2. With the help of a tracing paper, trace the outline of the sphere on the paper.
3. Fix the outline using a pin or pen about 000.
4. Rotate the outline about 000 clockwise until new sets of points again lie on the sphere. These points will correspond to planes responsible for second order diffraction.
5. To obtain planes responsible for 3rd, 4th etc continue rotating the outline clockwise, while locating any other new planes that will lie on the sphere.

General Approach to Reciprocal lattice.

Scattering Wave Amplitude

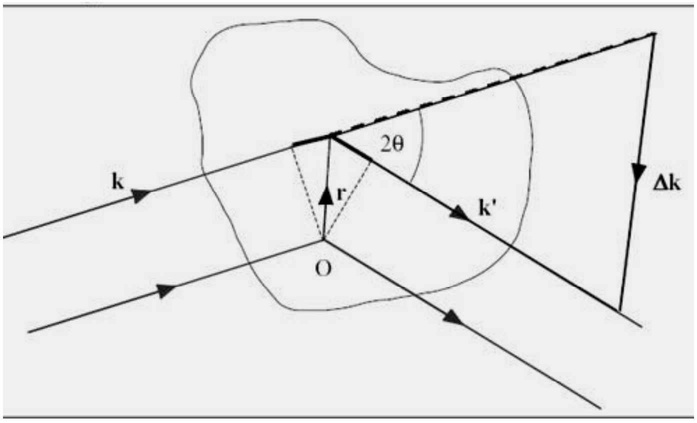


Figure 1.20: Scattering wave amplitude.

The diagram in Fig. 1.20 shows a wave scattered from origin O and from point **r.**

(a) Use some of the references (**:** http://en.wikipedia.org/wiki/Crystal_structure), provided and show that condition for all lattice vectors **R,** constructive interference in a reciprocal lattice is

$$\Delta\, \mathbf{k}.\mathbf{R} = \mathbf{G}.\mathbf{R} = 2n\pi\,. \qquad (1.5)$$

k is the wavevector given by $\mathbf{k} = (2\pi)/\lambda$.

R = u**a** + v**b** + w**c** is the lattice vector. *u, v*, and *w* are integers.

(b) Determine the properties of the wave exp(i**G.r)** satisfying the condition

$$\mathbf{G}.\mathbf{R} = 2n\pi\,.$$

(c) Laue Conditions for diffraction

An alternative way to state the condition that

$$\Delta\, \mathbf{k}.\, \mathbf{R} = \mathbf{G}.\mathbf{R} = 2n\pi$$

is that **R** = u**a** + v**b** + w**c** is to say

$$\mathbf{G}.\mathbf{a} = 2\pi h.$$

$$\mathbf{G}.\mathbf{b} = 2\pi k.$$

$$\mathbf{G}.\mathbf{c} = 2\pi l\,.$$

h, k, and l are integers.

This condition is satisfied if we define $\mathbf{G}_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\,\mathbf{c}^*$ with

$$\mathbf{a}^*.\mathbf{a} = 2\pi\ ,\quad \mathbf{a}^*.\mathbf{b} = 0,\quad \mathbf{a}^*.\mathbf{c} = 0.$$

$$\mathbf{b}^*.\mathbf{b} = 2\pi\ ,\quad \mathbf{b}^*.\mathbf{a} = 0,\quad \mathbf{b}^*.\mathbf{c} = 0.$$

$$\mathbf{c}^*.\mathbf{c} = 2\pi\ ,\quad \mathbf{c}^*.\mathbf{b} = 0,\quad \mathbf{c}^*.\mathbf{a} = 0.$$

The statements above means that **a*** is perpendicular to the primitive vectors **b** and **c** of the direct (real) lattice.

(e) Use Laue conditions for diffraction and show that:

(i) $\mathbf{a}^* = 2\pi \dfrac{b \times c}{a.(b \times c)}$

(ii) $\mathbf{b}^* = 2\pi \dfrac{c \times a}{a.(b \times c)}$ and (iii) $\mathbf{c}^* = 2\pi \dfrac{a \times b}{a.(b \times c)}$.

Self Evaluation 1

1. Discuss the characteristics of an ionic compound at room temperature
2. Identify the lattice given in Fig. 1.21 and state the number of atoms per lattice point.

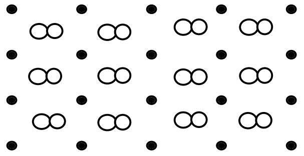


Figure 1.21: Crystal structure

3. Determine the number of rotational symmetry for :
   (i) rectangular lattice.
   (ii) an equilateral crystal.
4. Why do all lattices possess have translational symmetry?
5. Explain why the order of rotation corresponding to 5-fold or 7-fold do not exist.
6. Shade in a (100) plane, a (001) plane and a (111) plane
7. Show that packing fraction in
   (i) a body-centred cubic crystal is 68%.
   (ii) a face-centred cubic crystal is 74%.
8. Explain how X-ray diffraction takes place

Activity 2 : Crystal Defects and Mechanical Properties

You will need about 20 hours to complete this activity.

Summary of the Learning Activity

The learning outcomes, requires differentiating between the different types of crystal defects: the point defects (vacancy, interstitials, and substitutional) and dislocations (screw and edge). You will learn that point defects are very localised and are of atomic size, while dislocation is a disorder which extend beyond the volume of one or two atoms. In the activity you will learn about the effects of the defects on mechanical, and electrical properties. The key objectives for this activity requires the students to:

- Explain the concept of crystal defects.
- Relate crystal defects to some observed mechanical properties and other properties.

List of Required Readings

Reading 1 : Crystal Structure

Complete reference :
From University of Exeter
URL : http://newton.ex.ac.uk/teaching/resources/rjh/phy2009/
Accessed on the 20th April 2007

Abstract : In this article, crystal structure is described with well illustrated diagrams. The exercises in the article help the reader to consolidate the topics learnt.

Rationale: This article gives another way of looking at crystal structures. Further the sample tests and exercises given at the end provide good opportunity to use the theories and principles exercised from different perspectives.

Reading 2 : Atomic Scale Structure of Materials

Complete reference :
From DoITPoMS Teaching and Learning Packages
URL :
Accessed on the 24th April 2007

Abstract : Various crystal types are described and worked example are given in topics of crystal and defects in crystal.

Rationale: This material is part of the DoITPoMS Teaching and Learning Packages. The packages are intended to be used interactively at a computer! This print-friendly extract is provided for convenience, but does not display all the content of the TLP. For example, any video clips and answers to questions are missing. If you have internet access take time to visit and interact with the exercises It supplements the second activity of the module.

List of Relevant MM Resources

Resource # 1

Title: Defects in crystals

URL: http://www.tf.uni-kiel.de/matwis/amat/def_en/index.html

Description: Provides experimental techniques of studying point defects, dislocations and other defects.

Date Consulted: 19/11/2007

Resource # 2

Title: Crystal structure

URL: http://www.eserc.stonybrook.edu/ProjectJava/Bragg/index.html

Description: Provides animation on how waves reveal the atomic structure of crystals.

Date consulted: 19/11/2007.

List of Relevant Useful Links

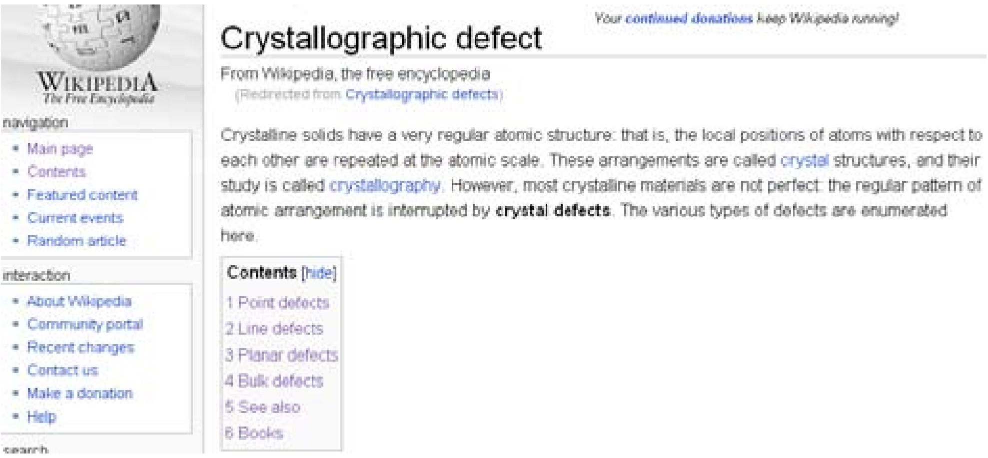
Useful Link #4

From Wikipedia, the free encyclopedia

Title: crystal defects

URL: http://en.wikipedia.org/wiki/crystallographic_defects#Point_defects

Screen Capture:



Crystallographic defect

From Wikipedia, the free encyclopedia
(Redirected from Crystallographic defects)

Crystalline solids have a very regular atomic structure: that is, the local positions of atoms with respect to each other are repeated at the atomic scale. These arrangements are called crystal structures, and their study is called crystallography. However, most crystalline materials are not perfect: the regular pattern of atomic arrangement is interrupted by **crystal defects**. The various types of defects are enumerated here.

Contents [hide]
1 Point defects
2 Line defects
3 Planar defects
4 Bulk defects
5 See also
6 Books

Description: A good description of defects (point defects, line defects, planar defect and bulk defects explained at this site.

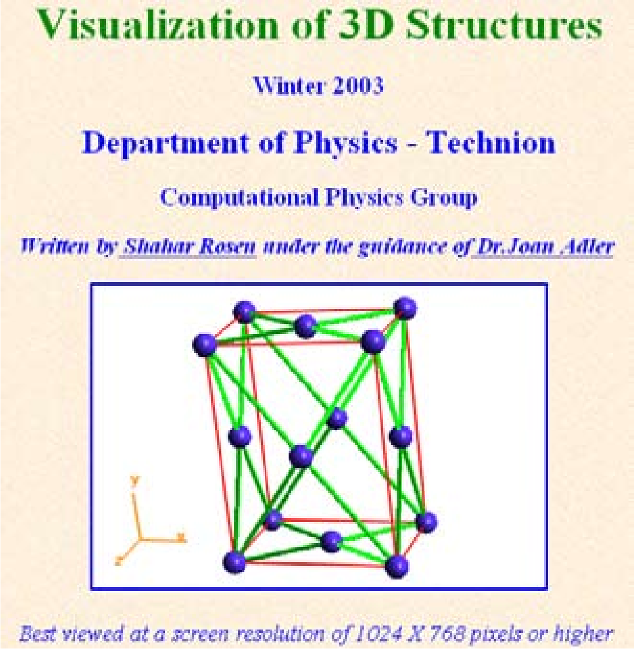
Visited on:- April 24 2007:

Useful Link #5

Title: Crystal structures

URL: http://phycomp.technion.ac.il/~sshaharr/

Screen Capture:



Visualization of 3D Structures

Winter 2003

Department of Physics - Technion

Computational Physics Group

Written by Shahar Rosen under the guidance of Dr.Joan Adler

Best viewed at a screen resolution of 1024 X 768 pixels or higher

Description: This website has a good collection of links to visualizations of three dimensional structure.

Visited on:- April 24 2007:

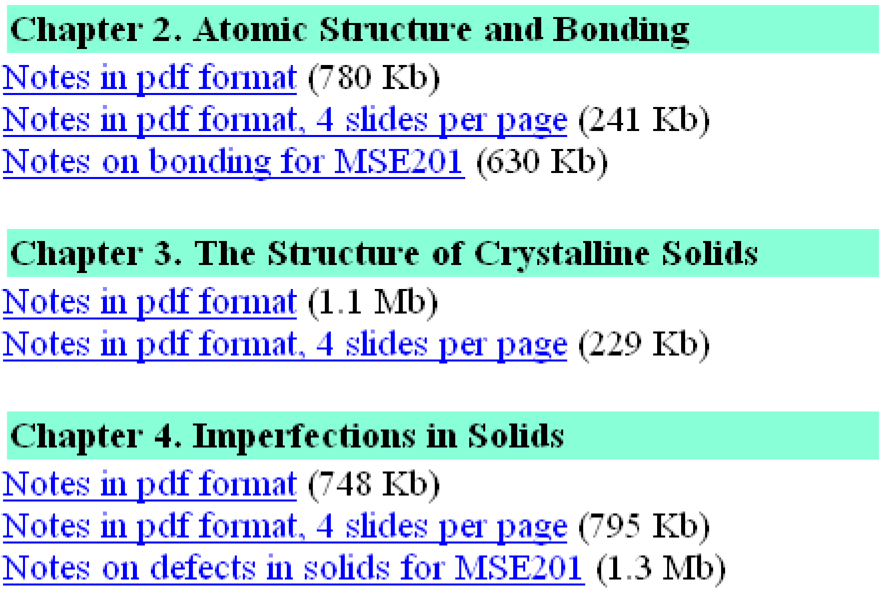
Useful Link #6

From University of Virginia, Department of Materials Science.

Title: Structure, and imperfections in solids

URL: http://people.virginia.edu/~lz2n/mse209/

Screen Capture:



Chapter 2. Atomic Structure and Bonding

Notes in pdf format (780 Kb)
Notes in pdf format, 4 slides per page (241 Kb)
Notes on bonding for MSE201 (630 Kb)

Chapter 3. The Structure of Crystalline Solids

Notes in pdf format (1.1 Mb)
Notes in pdf format, 4 slides per page (229 Kb)

Chapter 4. Imperfections in Solids

Notes in pdf format (748 Kb)
Notes in pdf format, 4 slides per page (795 Kb)
Notes on defects in solids for MSE201 (1.3 Mb)

Description: This link leads to University of Virginia, Department of Materials Science and Engineering . The course (Introduction to the Science and Engineering of Materials) chapters indicated in the screen capture are well organized documentation and relevant to this activity.:

Rationale: It provides good reading materials.

Detailed description of the activity:

Activity 2.1 Crystal defects

In this activity you will learn about and explain the effects of defects on properties of materials. Two types of defects namely: point defects and dislocations will be focussed on. Read through and learn about the differences between the defects.

Point defects

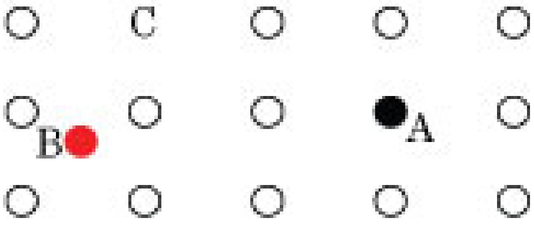
There are two main types of geometrical defects in a crystal. There are those which are *very localised and are of atomic dimensions*. These are called **point defects.** An example of this is an impurity atom which can be either a *substitutional* or an *interstitial* impurity.

(a) When some atoms are not exactly in their right place, the lattice is said to contain *imperfections or defects.*

(b) Many properties of solids e.g. the electrical resistance and mechanical strength are governed by the presence of certain types of defects in the lattice.

2.1.1 Substitutional impurity

This is when the impurity replaces an atom on the host lattice e.g. A, and interstitial is when the impurity is between the host atoms on a non-lattice site e.g. B. In both cases there will be some lattice distortion around it.



Fgure 2.1: Examples of point defects

A third form of point defect is when an atom is missing from its site in the lattice e.g. at C. This type forms the simplest defect. This vacant lattice is called a *vacancy* or *schottky defect.* These are shown in Fig. 2.1.

a) Use the references provided and explain the effects of impurities such as A or B on the physical property of the crystal.

http://www.people.virginia.edu/~lz2n/mse209/Chapter4.pdf. 20/05/2007

http://www.msm.cam.ac.uk/doitpoms/tlplib/dislocations/raftseq2.php. 20/05/2007.

2.2.2 *Effects of the presence of a vacancy at a positive-ion site*

- The presence of a vacancy at a positive-ion site may be presented as shown in Fig. 2.2.
- Study the diagram in Fig. 2.2 and provide answers to the questions posed below.

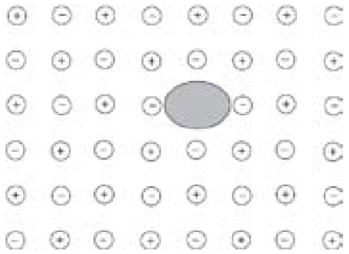


Figure 2.2: Effects of a vacancy at a positive-ion site

(i) What happens to the electrical neutrality in the vicinity of the vacancy?

(ii) What happens to the electrostatic energy of the crystal and what will be its effect?

(iii) Otherthan, the electrical property, explain the effect of the vacancy.

Activity 2.1.3 Dislocations

Unlike point defects, these are types of disorder which extend beyond the volume of one or two atoms. It is a line defect which can extend right through a crystal or it can form closed loops.

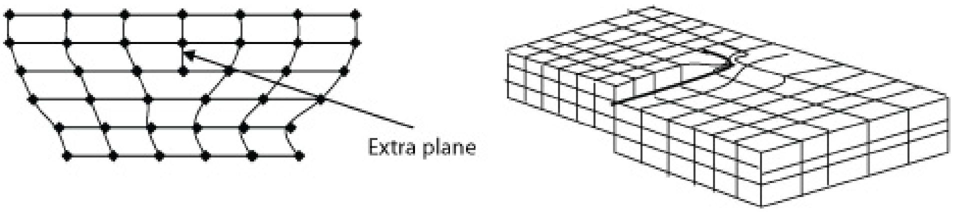
(a) There are two basic types of dislocations, *edge* dislocation and *screw* dislocation. («MIXED» dislocations combining aspects of both types are also common).

(i) Edge dislocations

These are caused by the termination of a plane of atoms in the middle of a crystal. In such a case, the adjacent planes are not straight, but instead bend around the edge of the terminating plane so that the crystal structure is perfectly ordered on either side. See Fig. 2.3. The analogy with a stack of paper is apt: if a half a piece of paper is inserted in a stack of paper, the defect in the stack is only noticeable at the edge of the half sheet. See Fig. 2.3.

(ii) The screw dislocation

This is more difficult to visualise, but basically comprises a structure in which a helical path is traced around the linear defect (dislocation line) by the atomic planes of atoms in the crystal lattice. See Fig. 2.3.



Edge dislocation

screw dislocation

Figure 2.3

Note that in a screw dislocation, the plane of the dislocation extends part way into the crystal from the front. Atoms on one side are shifted downwards by one unit cell relative to atoms on the other side.

Other forms of defects

(a). Under this section you need to:

- (i) Read about *planar defects* and *bulk defects*. http://en.wikipedia.org/wiki/crystallographic_defects#Point_defects
- (ii) Make short notes on them.
- (iii) How do they compare with *point defects*, and dislocations?

(b) Use the references and make notes on:

- (i) Mechanical strength of materials. Discuss it in relation to the defects so far identified.
- (ii) Grain boundaries within crystal (You should discuss about twin boundaries). You should also note that grain boundaries in polycrystals can be considered as two-dimensional defects in the perfect crystal lattice.

Activity 2.1.4 Crystal growth

In this activity, the outlines below gives you the effects of dislocation on solids. Read through and try relating each one to real life stuations. You will learn that:

- (i) The presence of dislocations results in lattice strain (distortion).
- (ii) The direction and magnitude of such distortion is expressed in terms of a Buger vector, **b**.
- (iii) For an edge type, **b** is perpendicular to the dislocation line, whereas in the cases of the screw type it is parallel.
- (iv) In metallic materials, **b** is aligned with close-packed crytallographic directions and its magnitude is equivalent to one interatomic spacing.
- (v) Dislocations can move if the atoms from one of the surrounding planes break their bonds and rebond with the atoms at the terminating edge.It is the presence of dislocations and their ability to readily move (and interact) under the influence of stresses induced by external loads that leads to the characteristic malleability of metallic materials.

Activity 2.1.5 Plastic deformation

In this activity you are given some of the planes along which slip in materials occur.

(i) Microscopic investigations show that when a metal is plastically deformed, the deformation occurs by a slip of plane of closest packing along the direction of the line of closest packing in that plane.
(ii) For face centred cubic crystals, slip normally occur along the four equivalent {111} planes.

- Identify the planes along which slip occur in a body centred crystal. Sketch the crystal to show the planes.

Activity 2.2 Mechanical properties

(a) Read and make notes on response of materials to applied force. In particular take note of two important regimes of mechanical behaviour, namely:

(i) Elastic (non-permanent) deformation which is governed by the stretching of atomic bonds.
(ii) Plastic (permanent) deformation which is governed by the motion of dislocations.

(b) The discussion should include

(i) definitions of stress (including tensile and shear). In addition consider also the common states of stress (simple tension, simple compression, biaxial tension, hydrostatic pressure and pure shear).
(ii) Definitions of strain which should include tensile strain; lateral strain and shear strain.

Activity 2.2.1 Poison's Ratio

- Make brief notes on definition of Poison's ratio, and its relation given by Eq.2.1.

$$v = -\frac{\varepsilon_x}{\varepsilon_z} \qquad (2.1)$$

ε_z is the strain due to elongation and ε_x is the strain due to contraction perpendicular to

extension caused by tensile stress

Activity 2.2.2 Elastic properties

In this activity you will carry out experiments to verfy Hookes law. You will also use the

results of the experiment to show how Young's modulus of a material is obtained.

(a) Tensile strain and stress:

Use the results of the experiment and write short notes on:

(i) how Hookes law for small strains is established.

(ii) how to show that for small strains, stress, σ Young's modulus, *E,* and strain, ε , have a relation given by:

$$\sigma = E.\varepsilon$$

Whereby:

(i) Tensile strain $\varepsilon = \frac{l - l_0}{l_0} = \frac{\Delta l}{l_0}$, Where l_0 is the unstretched length and l is the stretched length.

(ii) Tensile stress $\sigma = \frac{F_\perp}{A}$, where $F_\perp$ is the magnitude of the force and A is the cross sectional area.

(iii) Young's modulus = $\frac{\text{stress}}{\text{strain}} = \frac{F_\perp / A}{\Delta l / l_0} = \frac{F_\perp}{A} . \frac{\Delta l}{l_0}$

The units of Young's modulus are the same as those of stress, since strain is a pure number. Thus, the unit of Young's modulus is the Pascal (Pa)

1 pascal = 1 Pa = 1 Nm^{-2}.

(iv) Your notes should include labelled sketch graphs of stress-strain relation.

Adequate explanations of the different parts of the graph should be provided in the notes.

(b) *Compressive stress and strain*

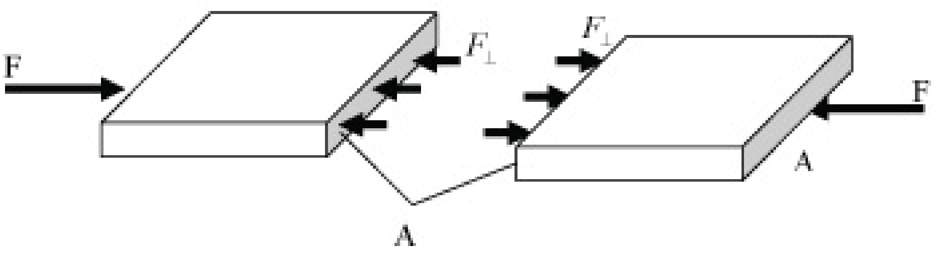


Figure 2.4: Compressive forces

When forces, *F* act at the ends of a bar as shown in Fig. 2.4, then the bar is in compression.

(i) The compression strain of a bar in compression is defined in the same way as tensile strain, but Δl has the opposite direction.

(ii) Hooke's law is valid for compression as well as tension if the compressive stress is not too great.

(iii) For many materials, Young's modulus has the same value for both tensile and compressive stresses, composite materials such as concrete are an exception.

(c) *Shear Stress and strain*

Shear stress is defined as the force tangent to a material surface divided by the area A on which the force acts: See Fig. 2.5

$$\text{Shear stress} = \frac{F_P}{A}$$

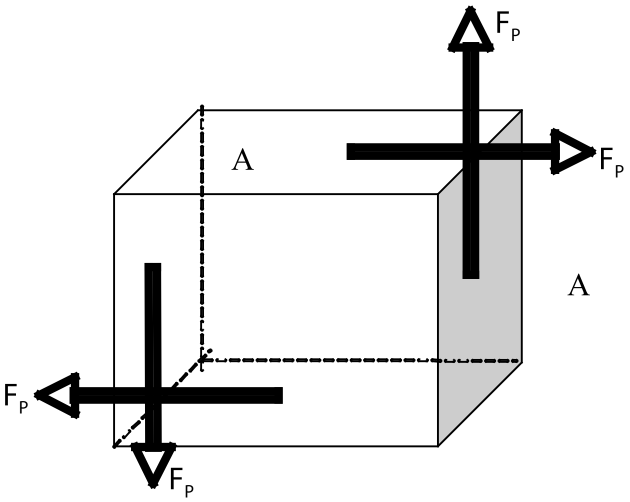


Figure 2.5: A body under shear stress. The area A is the edge area on which each force F_P acts.

(d) *Shear deformation*

The diagram of a deformed body is given in Fig.2.6, where abcd represents an unstressed block material such a book, or a wall. The area $a^/b^/c^/d^/$ shows the same block under shear stress.

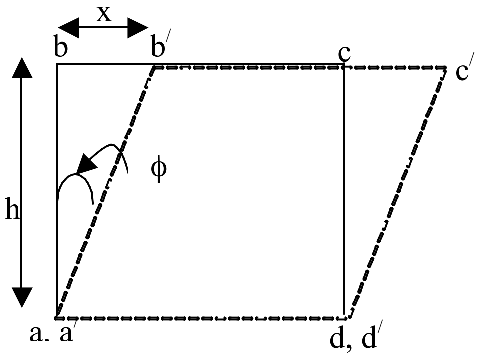


Figure 2.6: A body deformed under shear stress

(i) Shear strain = $\frac{x}{h} = \tan\phi$. But in real situations, *x* is much smaller than *h.* This means that $\tan\phi \approx \phi$ (in radians)

(ii) If forces are small such that Hooke's law is obeyed, the shear strain would be proportional to the shear stress. The corresponding elastic modulus is caled the *shear modulus, S.* Thus

$$S = \frac{\text{shear stress}}{\text{shear strain}} = \frac{F_P / A}{x/h} = \frac{F_P}{A}.\frac{h}{x} = \frac{F_P/A}{\phi} \qquad (2.2)$$

❖ Use the argument above to derive equation 2.2 and its unit.

(e) *Yield stress by the simultaneous slip of atoms*

Example:

This example gives an illustration of the calculation of yield stress. You need to know that to move a particular plane, a shear stress must be applied. In Fig. 2.7, shear strains are measured by the shear angle of displacement, α , so that if *d,* is the interplanal spacing and, *x,* the linear displacement then

$$\alpha = \frac{x}{d}$$

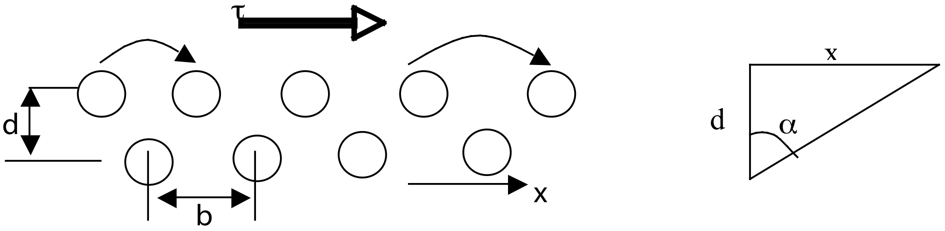


Figure 2.7: A small elastic displacement

For a small elastic displacement the shear stress τ is given by Eq. 2.3.

$$\tau = G\alpha = \frac{Gx}{d} \qquad (2.3)$$

Where G is the shear (or rigidity) modulus.

For larger displacement, τ must be a function which has the periodicity of the inter-atomic spacing *b* of the atoms within the slip plane. This is given by equation 2.4. That is,

$$\tau = \text{constant} \times \sin\left(\frac{2\pi x}{b}\right) \qquad (2.4)$$

From Eq. (2.3) and (2.4) if displacement ,*x,* is small we have:

$$\text{constant} \times \frac{2\pi x}{b} = \frac{Gx}{d}$$

Therefore $\text{constant} = \frac{Gb}{2\pi d} \approx \frac{G}{2\pi}$

Since *b* is approximately equal to *d,*

$$\tau \approx \frac{G}{2\pi}\sin\left(\frac{2\pi x}{b}\right) \qquad (2.5)$$

Thus, τ has a maximum value of $\frac{G}{2\pi}$ and it should correspond to the yield stress of the material, but in reality, it does not. The yield stresses of all metals are always very much smaller than $\frac{G}{2\pi}$ by two or four orders of magnitude.

Self evaluation 2

1. (a) Using relevant examples, clearly distinguish between *point defects* and *dislocations*

   (b) Explain the possible effects of planar defects.

2 (a) Define the lattice.

   (b) Describe how a primitive cell may be chosen by a Wigner- Seitz procedure.

   (c) Derive an expression for an allowed rotation, α, in a periodic lattice and show how the possible solutions to the equation are obtained.

Activity 3: Thermal and Electrical Properties

You will need 40 hours in order to complete this module.

Title of Learning Activity : **Thermal and Electrical properties**

Summary of the Learning Activity

This activity has two major parts: thermal and electrical properties of solids. Under thermal properties, the following topics are form parts of the learning activities: heat capacity, specific heat capacity, theoretical model of heat capacity and thermal conductivity. As for electrical properties the activity involve learning about electical conductivity, free electron theory of metals and Wiedemann-Franz law.

Specific objectives

The specific objectives require the students to

- Define heat capacity, and explain variation of heat capacity with temperature based on the classical, Einstein and Debye models
- Use free electron theory to explain high thermal and electrical conductivities of metals
- Derive and apply the Wiedermann-Frantz law

List of Required Readings

Reading 4: Heat Capacity

Complete reference :
From Wikipedia, the free encyclopedia.
URL : http://en.wikipedia.org/wiki/Heat_capacity
Accessed on the 20th April 2007

Abstract : Heat capacity is defined and quantitatively described for compressible bodies. Specific heat capacity is defined and theoretical models are described. Heat capacity at various temperatures is described..

Rationale: This material supplements the thermal properties section of the third activity in the module. Links are provided for further reading.

Reading 5: Electrical Conductivity

Complete reference :
From Wikipedia, the free encyclopedia.
URL : http://en.wikipedia.org/wiki/Electrical_Conductivity
Accessed on the 24th April 2007

Abstract : Classification of materials by conductivity, Some typical electrical conductivities temperature dependence of conductivity are discussed. Links to other sides is also provided.

Rationale: This material supplements the electrical properties section of the third activity in the module. Links are provided for further reading..

List of Relevant Multimedia Resources

Resource #1

Title: Thermodynamic equilibrium

URL: http://www.hazelwood.k12.mo.us/~grichert/sciweb/applets.html

Description: Provides suitable virtuaal experiments for students. In addition it has simulation of diffusion process when gases of different temperatures are mixed.

Date consulted 16/11/2007.

Resource #2

Title: Structure and bonding

URL:http://learningzone.coruseducation.com/schoolscience/KS5specialiststeels steelch 1pg2.html

Description: This site gives animation showing electrons moving randomly and movement of electrons through a wire. It contains also simulation showing delocalised electrons, both for thermal and electrical conductivity.

Date consulted: 16/11/2007.

Resource #3

Title: Heat transfer mechanism

URL: http://www.engr.colostate.edu/~allan/heat_trans/page4/page4f.html.

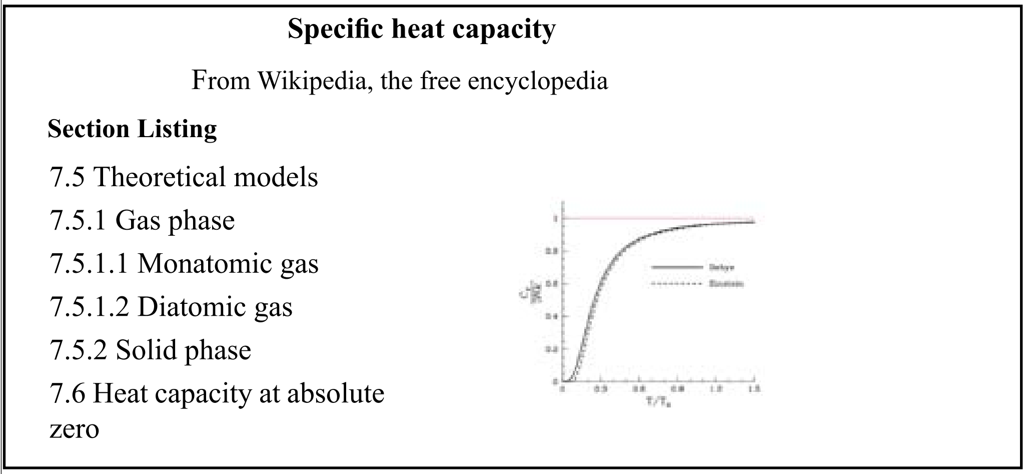
Description: This site has discussion on the three mechanisms of heat transfer: Conduction, convection and radiation. It also provides numerical calculations to be done on line

Date consulted: 19/11/2007.

List of Relevant Useful Links

Useful Link #4: Wikipedia

Title: Heat capacity.
URL: http://en.wikipedia.org/wiki/Heat_capacity
Sceen Capture



Specific heat capacity

From Wikipedia, the free encyclopedia

Section Listing

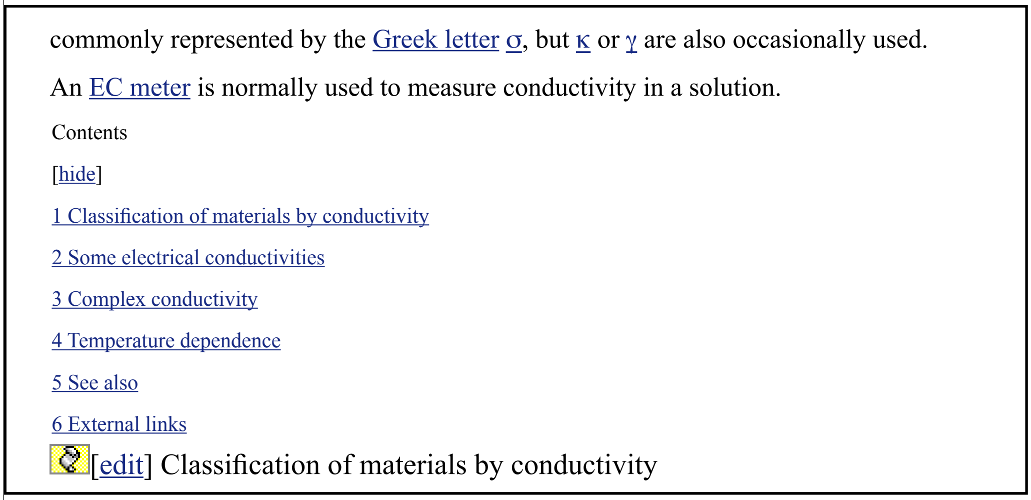
7.5 Theoretical models
7.5.1 Gas phase
7.5.1.1 Monatomic gas
7.5.1.2 Diatomic gas
7.5.2 Solid phase
7.6 Heat capacity at absolute zero

Description: This site provides basic reading materials on heat capacity including theoretical models (gas phase, monatomic gas, and diatomic gas) and solid phase.

Date consulted: 16/11/2007.

Useful Link #5 Wikipedia

Title: Electrical conductivity
URL: http://en.wikipedia.org/wiki/Electrical_conductivity,3/12/2006
Screen Capture:



commonly represented by the Greek letter σ, but κ or γ are also occasionally used.

An EC meter is normally used to measure conductivity in a solution.

Contents

[hide]

1 Classification of materials by conductivity

2 Some electrical conductivities

3 Complex conductivity

4 Temperature dependence

5 See also

6 External links

[edit] Classification of materials by conductivity

Date consulted: 16/11/2007

http://en.wikipedia.org/wiki/Thermal_conductivity, 3/12/2006

http://hyperphysics.phy-astr.gsu.edu/hbase/thermo/thercond.html

Detailed description of the activity

Activity 3.1 Heat capacity

In this activity you will:

1) define and learn about heat capacity and specific heat capacity.
2) derive and apply relevant equations in numerical problems.
3) use the references provided for more relevant information as you make notes and do assignments/quizes.

(a) Key learning points about heat capacity are that, *heat capacity* is:

(i) usually denoted by a capital *C,* often with subscripts.
(ii) a measurable physical quanity that characterizes the ability of a body to store heat as it changes in temperature.
(iii) defined as the rate of change of temperature as heat is added to a body at the given conditions and state of the body.
(iv) expressed in units of joules per kelvin in the International System of Units,
(v) termed an «extensive quantity».
(vi) specific heat capacity when divided by the body's mass yields

(b) Definition

Heat capacity is mathematically defined as the ratio of a small amount of heat δQ added to the body, to the corresponding small increase in its temperature dT:

$$c = \left(\frac{\delta Q}{dT}\right)_{cond} = T\left(\frac{dS}{dT}\right)_{cond} . \qquad (3.1)$$

Where S is entropy and the subscript defines the condition under which heat capacity is being defined.

Important things to learn from equation (3.1)

(i) For thermodynamic systems with more than one physical dimension, the above definition does not give a single, unique quantity unless a particular infinitesimal path through the system's phase space has been defined (this means that one needs to know at all times where all parts of the system are, how much mass they have, and how fast they are moving).

(ii) For all real systems, the path through which these changes take place must be explicitly defined, since the value of heat capacity depends on the path taken from one temperature to another.

Activity 3.1.1 ***Heat capacity at constant volume,*** C_V ***, and heat capacity at constant pressure,*** C_P ***:***

In this activity you will:

(a) distinguish between *heat capacity at constant volume*, C_V , and *heat capacity at constant pressure*, C_P :

(b) write down the first law of thermodynamics and use it together with the definitions of, C_V and C_P to show that

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \qquad (3.2)$$

$$C_P = \left(\frac{\partial Q}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right) P \qquad (3.3)$$

where

∂Q is the infinitesimal amount of heat added,

∂T is the subsequent rise in temperature.

∂U is the change in internal energy

∂H is change in enthalpy.

Remember that

(i) The increment of internal energy is the heat added and the work done:
$dU = TdS - PdV.$ (3.4)

(ii) Enthalpy is defined by $H = U + PV$. Thus the increment of enthalpy is given by $dH = dU + (PdV + VdP)$. (3.5)

❖ Many books on heat and thermodynamics treat this topic quite well, therefore you should refer to them.

Activity 3.1.2 Specific heat capacity

(a) Under this activity, we define the term specific heat capacity in a mathematical form. Thus, specific heat capacity, c, of a material is

$$c = \frac{\partial C}{\partial m} , \qquad (3.6)$$

which in the absence of phase transitions is equivalent to

$$c = \frac{C}{m} = \frac{C}{\rho V} . \qquad (3.7)$$

where,

C is the heat capacity of a body ($\mathrm{J \cdot K^{-1}}$)

m is the mass of the body (kg).

V is the volume of the body (m^3).

$\rho = mV^{-1}$ is the density of the material (kgm^{-3}).

(b) For gases, and also for other materials under high pressures, there is need to distinguish between different boundary conditions for the processes under consideration (since values differ significantly between different conditions). Typical processes for which a heat capacity may be defined include *isobaric* (constant pressure, $dP = 0$) and *isochoric* (constant volume, $dV = 0$) processes, and one conventionally writes for gases:

$$c_P = \left(\frac{\partial C}{\partial m}\right)_P \qquad (3.8)$$

$$c_V = \left(\frac{\partial C}{\partial m}\right)_V \qquad (3.9)$$

(c) ***Dimensionless heat capacity***

The dimensionless heat capacity, C^*, of a material is given by

$$C^* = \frac{C}{nR} = \frac{C}{Nk}, \tag{3.10}$$

where,

C is the heat capacity of a body (JK^{-1}),

n is the number of moles in the body (mol),

R is the gas constant ($JK^{-1}\ mol^{-1}$),

nR=Nk is the amount of matter in the body (JK^{-1}),

N is the number of molecules in the body. (dimensionless),

k_B is Boltzmann's constant ($JK^{-1}molecule^{-1}$)

- Using the information provided above show that C^* has no dimension.

(d) Dulong-Petit law

(i) For matter in a crystalline solid phase, the Dulong-Petit law states that the dimensionless specific heat capacity assumes the value 3. Indeed, for solid metallic chemical elements at room temperature, heat capacities range from about 2.8 to 3.4 (beryllium being a notable exception at 2.0).

(ii) The Dulong-Petit «limit» results from the equipartition theorem, therefore it is only valid in the classical limit of a microstate continum, which is a high temperature limit.

Note also that:

(iii) The theoretical maximum heat capacity for larger and larger multi-atomic gases at higher temperatures, also approaches the Dulong-Petit limit of 3R, so long as this is calculated per mole of atoms, not molecules. The reason is that gases with very large molecules, in theory have almost the same high-temperature heat capacity as solids, lacking only the (small) heat capacity contibution that comes from potential energy that cannot be stored between separate molecules in a gas.

(iv) For light and non-metallic elements, as well as most of the common molecular solids based on carbon compounds at standard ambient temperature, quantum effects may also play an important role, as they do in multi-atomic gases. These effects usually combine to give heat capacities lower than 3 R per mole of atoms in the solid, although heat capacities calculated per mole of molecules in molecular solids may be more than 3 R. For example, the heat capacity of water ice at the melting point is about 4.6 R per mole of molecules, but only 1.5 R per mole of atoms. The lower number results from the «freezing out» of possible vibration modes for light atoms at suitably low temperatures, just as in many gases. These effects are seen in solids more often than liquids: for example the heat capacity of liquid water is again close to the theoretical 3 R per mole of atoms of the Dulong-Petit theoretical maximum.

Activity 3.1.3 Theoretical model of heat capacity

This activity is presented in two parts, that is, under gases and solids as will soon be discussed.

Before moving on, read and make short notes on kinetic theory of gases.

Gases:

1. Monoatomic

According to the equipartition theorem from classical statistical mechanics, for a system made up of independent and quadratic degrees of freedom any input of energy into a closed system composed of N molecules is evenly divided among the degrees of freedom available to each molecule. In the classical limit of statistical mechanics, for each independent and quadratic degree of freedom,

$$E_i = \frac{k_B T}{2} . \qquad (3.11)$$

Where E_i is the mean energy (measured in joules) associated with degree of freedom *i*.

T is the temperature (measured in kelvins),

k_B is Boltzmann's constant, ($1.3807\times10^{-23}\ \mathrm{JK}^{-1}$).

❖ In general, the number of degrees of freedom, *f*, in a molecule with n_a atoms is $3\,n_a$:

$$f = 3\,n_a \qquad (3.12)$$

❖ ***use the references, and derive equation (3.11)***

Example 1

The following example is intended to illustrate how heat capacity for gases may be calculated. Let's consider a monatomic gas.

1) In the case of a monatomic gas such as helium under constant volume, if it assumed that no electronic or nuclear quantum excitations occur, each atom in the gas has only 3 degrees of freedom, all of a translational type.
2) No energy dependence is associated with the degrees of freedom which define the position of the atoms. While, in fact, the degrees of freedom corresponding to the momenta of the atoms are quadratic, and thus contribute to the heat capacity.
3) For *N* atoms, each of which has 3 components of momentum, means that there are *3N* total degrees of freedom. Thus:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2} N k_B = \frac{3}{2} nR \quad . \qquad (3.13)$$

$$C_{V,m} = \frac{C_V}{n} = \frac{3}{2} R = 1.5R \quad . \qquad (3.14)$$

Where,

C_V is the *heat capacity* at constant volume of the gas,

$C_{V,m}$ is the *molar heat capacity* at constant volume of the gas,
N is the total number of atoms present in the container,
n is the number of moles in a body,

R is the ideal gas constant, (8.3145 $\mathrm{J K^{-1} mol^{-1}}$). *R* is equal to the product of

Boltzmann's constant, k_B and Avogadro's number.

In general, the experimental heat capacities of the monatomic noble gases agrees with a simple application of statistical mechanics to a very high degree.

2. Diatomic gases

(a) Read about diatomic gases and confirm that:

(i) In a diatomic gas,the presence of internal degrees of freedom are apparent that is, in addition to the three translational degrees of freedom, there are rotational and vibrational degrees of freedom.

(ii) There are a total of three rotational degrees of freedom, one corresponding to rotation about each of the axes of three dimensional space.

(iii) In practice only two degrees of rotational freedom for linear molecules are considered because the moment of inertia about the internuclear axis is vanishingly small with respect to the other moments of inertia in the molecule. (Why?) (this is due to the extremely small radii of the atomic nuclei, compared to the distance between them in a molecule).

(iv) Quantum mechanically, the interval between successive rotational energy, eigenstate, is inversely proportional to the moment of inertia about that axis.

The number of vibrational degrees of freedom is

$$f_{vib} = f - f_{trans} - f_{rot} = 6 - 3 - 2 = 1$$

This is because there are three degrees of translational freedom, and two degrees of rotational freedom.

(b) Expected molar constant-volume heat capacity of diatomic gas.

(i) Each rotational and translational degree of freedom is expected to contribute $R/2$ in the total molar heat capacity of the gas.

(ii) Each vibrational mode contributes R to the total molar heat capacity because for each vibrational mode, there is a potential and kinetic energy component, where each of the contribution by the potential and kinetic components to the total molar heat capacity of the gas is $R/2$.

(iii) Thus, the expected molar constant-volume heat capacity of a diatomic molecule is

$$C_{V,m} = \frac{3R}{2} + R + R = \frac{7R}{2} = 3.5R. \quad (3.15)$$

Exercise 1

a) Check that the value of $C_{v,m}$ is correct
b) Check for values of some molal-volume heat capacities of various diatomic gases and record them in a table.
c) The values you will record will show that most of the lighter diatomic gases have heat capacities that are lower than those predicted by the Equipartition Theorem, unlike in the case of heavier molecules.
d) EXPLAIN WHY THIS IS SO?

(3) Before continuing to activity 3.1.4, you need to:

Read and make short notes on limitations of the classical specific theory at low temperatures.

Activity 3.1.4 Solid phase: Debye and Einstein model

(a) In this activity, you will learn briefly learn that:

(i) The Debye model is a method developed for estimating the phonon contribution to the specific heat (heat capacity) in a solid.
(ii) It treats the vibrations of the atomic lattice (heat) as phonons in a box, in contrast to Einstein model, which treats the solid as many individual, non-interacting quantum harmonic oscillators.
(iii) The Debye model correctly predicts the low temperature dependence of the heat capacity, which is proportional to T^3.
(iv) While Einstein model of the solid predicts the heat capacity accurately at high temperatures, it noticeably deviates from experimental values at low temperatures.
(v) Just like the Einstein model, it also recovers the Dulond-Petit law at high temperatures. But due to simplifying assumptions, its accuracy suffers at intermediate temperatures.

(b) The variation of dimensionless heat capacity, equation (3.9), with temperature is shown in Fig. 3.1 as predicted by the Debye model and by Einstein's model. **Einstein solid** is a model of a solid based on two assumptions:

(i) Each atom in the lattice is a 3D quantum harmonic oscillator.
(ii) Atoms do not interact with each another.

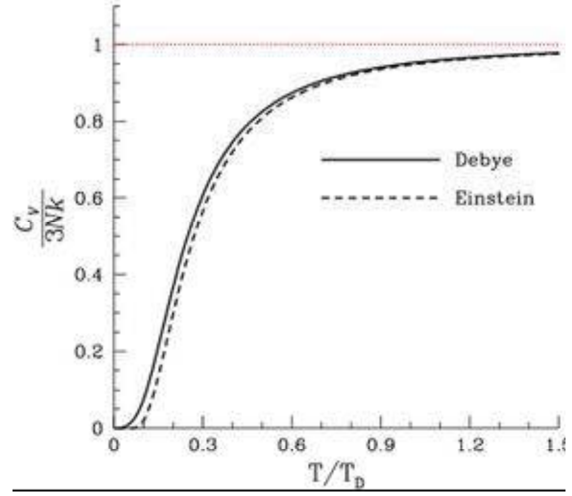


Figure 3.1: Variation of dimensionless heat capacity.

(c) Features of the graph:

- (i) The dimensionless heat capacity is zero at absolute zero, and rises to a value of three as the temperature becomes much larger than the Debye temperature. Thus, one of the strengths of the Debye model is that it predicts an approach of heat capacity toward zero as zero temperature is approached, and also predicts the proper mathematical form of this approach.
- (ii) For Einstein solid the value of $3Nk$ is recovered at high temperatures.
- (iii) The horizontal line corresponds to the classical limit of the Dulong-Petit law.

Read more about this.and Make comprehensive notes on the Debye and Einstein models.

Activity 3.1.5 Electrical conductivity

In this activity, a number of definitions and derivations of equations will be made. Along with all these, questions that will help you understand the topic better will be posed as you

continue learning. As you progress, you must make your notes at every stage of learning activity.

(a) Electrical conductivity

(i) Electrical conductivity is a measure of a material's ability to conduct an electric current. When an electrical potential difference is applied across a conductor, its movable charges flow, giving rise to an electric current. The conductivity σ is defined as the ratio of the current density (current per area), **J**, to the electric field strength, **E**, i.e.

$$\vec{J} = \sigma \vec{E} = \frac{\overline{E}}{\rho} \tag{3.16}$$

(ii) Conductivity is the reciprocal of electrical resistivity, ρ .

(iii) Materials can be classified according to their conductivity. A conductor such as a metal has high conductivity; an insulator or a vacuum has low conductivity; while that of a semiconductor is generally intermediate, although it varies widely under different conditions, such as exposure of the material to electric fields or specific frequencies of light, and, most importantly, with temperature.

(b) Charactertistics of materials

(i) In crystalline solids, atoms interact with their neighbours, and the energy levels of the electrons in isolated atoms turn into bands

(ii) Whether a material conducts or not is determined by its band structure.

(iii) Electrons in a solid fill up the energy bands up to a certain level, called the Fermi energy.

(iv) Bands which are completely full of electrons cannot conduct electricity, because there is no state of nearby energy to which the electrons can jump.

(v) Materials in which all bands are full (i.e. the Fermi energy is between two bands) are insulators.

(vi) In some cases, however, the band theory breaks down and materials that are predicted to be conductors by band theory turn out to be insulators. Mott insulators and charge transfer insulator are two such classes of insulators.

(c)

(i) Make a short explaining why metals are good conductors

(ii) Use Drude model and show that, conductivity, σ, relaxation time, τ , n , the density of conduction electrons, e is the electron charge, and m the mass, m, of the electron is given by

$$\sigma = \frac{ne^2\tau}{m} \qquad (3.17)$$

❖ *Show that the dimension in equation (3.17) are consistent.*

(iii) For purposes of comparison, write short notes about electrical conduction in *semiconductors, gases and plasma; and a vacuum.*

Activity 3.1.6 Thermal conductivity

In this activity, a number of definitions and derivations of equations will be made. Along with all these, questions that will help you understand the topic better will be posed as you continue learning. As you progress, you must make your notes at every stage of learning activity.

(a) Thermal conductivity, κ , is the intensive property of a material that indicates its ability to conduct heat.

(i) It is defined as the quantity of heat, Q, transmitted in time t through a thickness L, in a direction normal to a surface of area A, due to a temperature difference ΔT, under steady state conditions and when the heat transfer is dependent only on the temperature gradient.

(ii) Thermal conductivity = heat flow rate × distance / (area × temperature difference) i.e.

$$\kappa = \frac{Q}{t} \times \frac{L}{A \times \Delta T} \qquad (3.18)$$

❖ *Derive the DIMENSIONS and UNIT of thermal conductivity from equation (3.18)*

NOTE THAT:

(1) Conceptually, the thermal conductivity can be thought of as the container for the medium-dependent properties which relate the rate of heat loss per unit area to the rate of change of temperature i.e.

$$\frac{\Delta Q}{A\Delta T} = -\kappa \frac{\Delta T}{\Delta x} \qquad (3.19)$$

Power per unit area

(2) For an ideal gas the heat transfer rate is proportional to the average molecular velocity, the mean free path, and the molar heat capacity of the gas.

$$\kappa = \frac{n\langle c\rangle \lambda C_V}{3N_A} \quad (3.20)$$

where

κ is thermal conductivity,

$\langle c\rangle$ is mean particle speed,

n is particles per unit volume,

λ is mean free path,

C_V is molar heat capacity,

N_A is Avogadro's number.

- **Check that the dimensions in equation (3.19) are consistent**

(b) Thermal properties of materials

Write short notes on similaities AND differences between electrical and thermal conduction.

(i) However, thermal conductivity depends on many properties of a material, notably its structure and temperature.
(ii) For instance, pure crystalline substances exhibit highly variable thermal conductivities along different crystal axes, due to differences in phonon coupling along a given crystal dimension. (READ MORE ABOUT THIS)
(iii) Air and other gases are generally good insulators, in the absence of convection.

(c) Measurement

Write precise short notes on measurements of

(i) good conductors of heat by Searle's bar method
(ii) poor conductors of heat by Lees' disc method

Activity 3.1.6 Free electron theory of metals

(a) Background information

(i) This was first propounded by Drude and Lorentz in the early years of the 20th century.
(ii) It considers that some electrons act as if they were able to move freely within the solid and that the free electrons are in thermal equilibrium with their atoms.
(iii) That free electrons are held in the solid by a potential well or box, but are not affected by the local potential associated with individual atoms.
(iv) However, transition metals, such as iron, have partially filled electronic *d* states and are not treated by the free-electron model.

❖ **By assuming that the mean free path of electrons was limited by collisions this theory was made more quantitative by H.A Lorentz. In this way, he was able to derive Ohm's law for the electrical conductivity and obtain the ratio of thermal to electrical conductivity in excellent agreement with experiment.**

(b) Shortcoming of the theory.

(i) First, it predicted a large component of the specific heat of a metal, not present in insulators, which was not observed.
(ii) Second, comparison of the theory with experiment indicated that the mean free path of the electrons became extremely large at low temperatures; and the model offered no justification.

However, these shortcomings were overcome by use of quantum statistics, which removed the difficulty of the specific heat without losing the successful description of transport properties. The resulting theory remains the basis for the understanding of most transport properties of metals and semiconductors. At about the same time, W. V. Houston and F. Bloch solved the quantum-mechanical wave equation for electrons in a regular periodic structure, finding that they could indeed have arbitrarily large mean free paths if there were no defects in the periodicity, thereby putting the free-electron theory on a firm basis.

Activity 3.1.7 The Wiedemann-Franz Law

(a) In this activity the relation between electrical and thermal conductivities are discussed. A number of information are provided for you to follow how the relation is derived. It is observed that:

- (i) The ratio of the thermal conductivity to the electrical conductivity of a metal is proportional to the temperature.
- (ii) Qualitatively, this relationship is based upon the fact that the heat and electrical transport both involve the free electrons in the metal.
- (iii) The thermal conductivity increases with the average particle velocity since that increases the forward transport of energy.
- (iv) However, the electrical conductivity decreases with particle velocity increases because the collisions divert the electrons from forward transport of charge.
- (v) This means that the ratio of thermal to electrical conductivity depends upon the average velocity squared, which is proportional to the kinetic temperature. The molar heat capacity of a classical monoatomic gas is given by

$$c_V = \frac{3}{2}R = \frac{3}{2}N_A k \qquad (3.21)$$

(b) Derivation of Wiedemann-Franz Law

- (i) Wiedemann-Franz law is derived by treating the electrons like a classical gas and comparing the resultant thermal conductivity to the electrical conductivity. The expressions for thermal and electrical conductivity become:

$$\text{conductivities} \quad \kappa = \frac{n\langle c\rangle \lambda k}{2}; \qquad \sigma = \frac{ne^2\lambda}{m\langle c\rangle}. \qquad (3.22)$$

Thermal Electrical

- (ii) But mean particle speed from kinetic theory is given by Eq. (3.23)

$$\langle c\rangle = \sqrt{\frac{8kT}{\pi m}}. \ (3.23)$$

(iii) Thus, the ratio of thermal to electrical conductivity gives the Wiedemann-Franz Law as

$$\frac{\kappa}{\sigma} = \frac{4k^2T}{\pi e^2} = LT \quad . \tag{3.24}$$

L is Lorentz number.

❖ ***See C. Kittel, Introduction to Solid State Physics, 5th Ed., New York:Wiley, 1976, p. 178.***

Self Evaluation 3

1. (i) Why is heat capacity referred to as an entensive quantity?

   (ii) Why is specific heat capacity referred to as an extensive quantity?
2. Critcally compare the Debye and Einstein models.
3. Derive the unit of conductivity from equation (3.16).
4. Compare conductivity of different materials (conductors, and semiconductors) on temperature. Describe how they can be compared.
5. Explain the:

   (i) notion of heat transfer by conduction.

   (ii) reasons for wide variations in thermal conductivity
6. Use equation 3.23 and determine

   (i) the value of Lorentz number, L.

   (ii) the unit of L.

Learnig activity 4

Title of Learning Activity : BAND THEORY AND OPTICAL PROPERTIES.

You will need 20 hours to complete this activity.

Summary of the learning activity

This model consists of two parts: Band theory and Optical properties. The basic components of the activity include learning about: Electronic band structure in which conductors insulators and semiconductors are part**.** Further learning is on doping**,** t*he Fermi Level* , and Energy Bands in Solids. Under Optical Properties, the topic learnt include *absorption and extinction coefficient*, *reflectivity* and *transmissivity*.

The objectives of learning the modules require that the students should be able to:

(i) Describe the band theory,
(ii) Explain the differences between conductors, semiconductors and insulators,
(iii) Explain the differences between intrinsic and extrinsic semiconductors- the role of doping.

The objectives for learning the optical properties are to enable the student to

(i) Explain, based on the interaction of electromagnetic waves (light) and materials:- absorption, reflectivity and Transmissivity.

List of Required Readings

Reading 4: Heat Capacity.

Complete reference *:*
From Wikipedia, the free encyclopedia.
URL : http://en.wikipedia.org/wiki/Heat_capacity
Accessed on the 20th April 2007

Abstract : Heat capacity is defined and quantitatively described for compressible bodies. Specific heat capacity is defined and theoretical models are described. Heat capacity at various temperatures is described..

Rationale: This material supplements the thermal properties section of the third activity in the module. Links are provided for further reading.

Reading 5: Electrical Conductivity.

Complete reference *:*
From Wikipedia, the free encyclopedia.
URL : http://en.wikipedia.org/wiki/Electrical_Conductivity
Accessed on the 24th April 2007

Abstract : Classification of materials by conductivity, Some typical electrical conductivities temperature dependence of conductivity are discussed. Links to other sites is also provided.

Rationale: This material supplements the electrical properties section of the third activity in the module. Links are provided for further reading.

List of useful Multimedia Resources

Resource#1

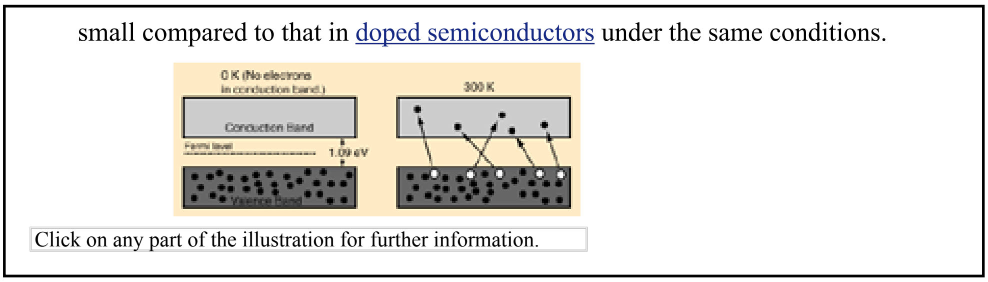
Title: Fermi Level and carrier concentration
URL: http://jas.eng.buffalo.edu/education/semicon/fermi/bandAndLevel/intro.html
Description: This provides good introductory notes and simulation of Fermi level and carrier concetration
Date Consulted: 16/11/2007

List of Relevant Useful Links

Title*:* Energy Bands

URL*:* http://hyperphysics.phy-astr.gsu.edu/hbase/hframe.html

Screen Capture:


small compared to that in doped semiconductors under the same conditions.

Click on any part of the illustration for further information.

Description: This provides adequate reading materials on theory of solids: Energy bands comments; insulator energy bands; semiconductor energy bands; conductor energy bands; silicon energy bands…

Date Consulted*: 16/11/2007*

Activity 4.1 Electronic band structure

In this activity we will define and describe and discuss some of the basic terms, in relation to metals; semiconductor; and insulators. As you progress on with your study you will be required to provide responses to some questions which are posed within the activity.

(1) The activity is introduced by first giving definitions of some key terms such as *band structure.*

(i) In solid state physics, the **electronic band structure** (or simply **band structure**) of a solid describes *ranges of energy* that an electron is «forbidden» or «allowed» to have.
(ii) The band structure determines a material's electronic properties, optical properties, and a variety of other properties.

(2) Basic facts about Formation of bands.

From your reading you will note that:

(i) The electrons of a single free-standing atom occupy *atomic orbitals*, which form a *discrete set of energy levels*.

❖ **(IN THIS STATEMENT, WHAT IS MEANT BY:** ***atomic orbital; and discrete set of energy levels?)***

(ii) In a molecule, where there are many atoms, their atomic orbitals split due to the Pauli exclusion principle.

❖ **(EXPLAIN WHAT PAULI EXCLUSION PRINCIPLE IS)**

(iii) Accordingly, a number of molecular orbitals proportional to the number of atoms are produced.
(iv) In solids, the number of orbitals is exceedingly large,

❖ **(*Why is this so?*).**

(v) Thus, the difference in energy between them becomes very small. However, *YOU NEED TO NOTE THAT*, some intervals of energy contain no orbitals, no matter how many atoms are aggregated.

(3) Let's consider now the three types of materials separately.

(a) Metals

- (i) Metals contain bands which are partly empty and partly filled regardless of temperature. Thus, they have very high conductivity.
- (ii) Because of very large number of atoms that interact in a solid material, the energy levels are so closely spaced that they form band thus, *electrons in metal are arranged in energy bands*.
- (iii) The highest energy filled band is called the *valence band*, the next higher band is the *conduction band*.
- (iv) Regions of energy for which no wavelike electron orbitals exist may separate these two. Such forbidden regions are called *energy gaps or band gaps,*
- (v) If the number of electrons is odd, then there is an unpaired electron in each unit cell, and therefore the valence band is not fully occupied, thus making the material a conductor.
- (vi) Their valence electrons are essentially free because in the band theory, there is an overlap of the valence band and the conduction band so that at least a fraction of the valence electrons can move through the material.

(b) Semiconductor

- (i) A semiconductor is a solid whose electrical conductivity can be controlled over a wide range, either permanently or dynamically.

❖ **Read and make notes on uses and applications of semiconductors**

- (ii) One of the main mechanisms for electrons to be excited to the conduction band is due to thermal energy, Because of this, the conductivity of semiconductors is strongly dependent on the temperature of the material.

(**EXPLAIN WHY THIS IS SO**).

- (iii) Semiconductors may be elemental materials such as silicon and germanium, or compound semiconductors such as gallium and indium phophide, or alloys such as silicongermanium or aluminium gallium arsenide.
- (iv) Semiconductors and insulators have valence band which is very nearly full under normal conditions.
- (v) The ease with which electrons in a semiconductor can be excited from the valence band to the conduction band depends on the band gap between the bands.
- (vi) In order to conduct electric current, electrons must move between states. Due to the Pauli exclusion principle full bands do not contribute to the electrical conductivity. But, as the temperature of a semiconductor rises above absolute zero, the states of the electrons are increasingly randomized, and some electrons can be found in the conduction band.

(vii) In semiconductors, movement of charge current is facilitated by both electrons and holes. (READ ABOUT HOLES AND MAKE A SHORT NOTE)

- ***Write short notes on intrinsic semiconductor and extrinsic semiconductor.***
- ***Compare the two types of semiconductor.***

(c) Insulator

(i) Insulators contain bands which are filled up completely. Thus, they have very low conductivity

(ii) Insulators have large forbidden gap between the energies of the valence electrons and the energy at which the electrons can move freely through the material (the conduction band). It is the size of this energy bandgap that serves as an arbitrary dividing line between semiconductors and insulators.

- *****Read more about insulators and make notes.***

(4) **Doping**

(i) The process of adding controlled impurities to the crystal lattice of a semiconductor in order to modify their conductivity is known as *doping*. The amount of impurity, or dopant, added to an *instrinsic* (pure) semiconductor varies its level of conductivity. Doped semiconductors are often referred to as *extrinsic.*

- ***Write a short note on how a dopant influences the conductivity of a semiconductor.***

(5) The Fermi Level

(i) The Fermi level is the top of the collection of electron energy levels at absolute zero temperature.

(ii) Since electrons are fermions and by the *Pauli exclusion principle* they cannot exit in identical energy states. So at absolute zero they pack into the lowest available energy states and build up a "Fermi sea" of electrons energy states.

(iii) The Fermi level is the surface of that sea at absolute zero where no electrons will have enough energy to rise above the surface. Thus, the Fermi level is located in the band gap.

(iv) The position of the Fermi level with the relation to the conduction band is a crucial factor in determining electrical properties.

(v) In a conductor, the Fermi level lies *within* the conduction band, such that the band is only half filled with electrons. In this case, only a small amount of energy is needed for the electrons to find other unoccupied states to move into, and hence for current to flow.

(vi) For intrinsic semiconductors like silicon and germanium, the Fermi level is essentially halfway between the valence and conduction bands. Although no conduction occurs at 0 K, at higher temperatures, a finite number of electrons can reach the conduction band and provide some current. In doped semiconductors, extra energy levels are added.

For simulation of some of these concepts see **http://www.collage.soe.ucsc.edu/JavaFiles/ElectronDopedSimulation.html. 12/11/2007.

(6) Energy Bands in Solids

Fig. 4.1 represents schematic diagrams of energy bands in solid insulator, semiconductor and conductor. Study the three diagrams carefully and note the relative positions of *conduction band, valence band and energy gap.*

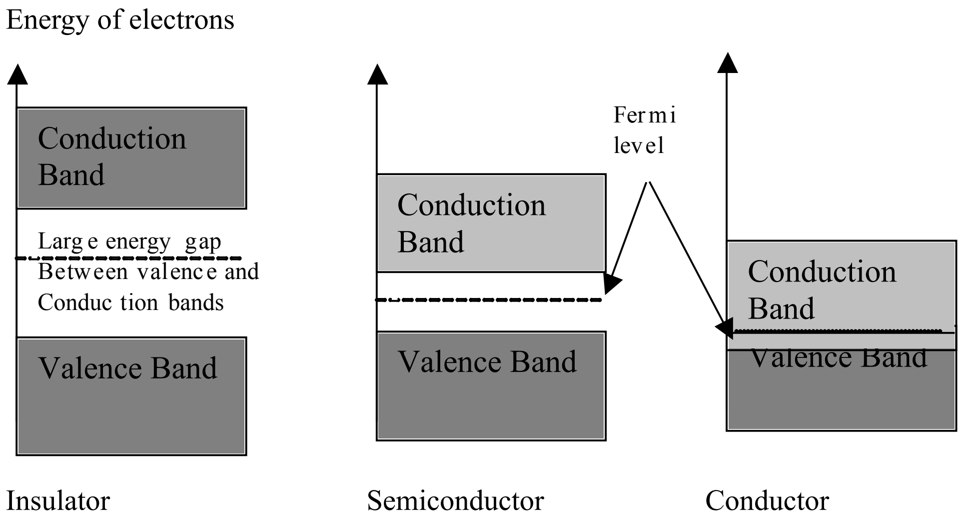


Figure 4.1: Schematic diagrams of energy bands

Activity 4.2 Optical Properties

In this section we shall consider optical properties of materials. The most important optical properties of a material are its internal and external transmittances, surface reflectance, and refractive indices. The following discussions include: *absorption*, *reflectivity* and *transmissivity*.

Let's us consider each one at a time.

1. Absorption.

In this section we will explain how photons are absorbed by materials.

- (i) You need to know that photons are electromagnetic waves with a particular frequency and that; *molecules* are a system with charge separation (negative electron field and positive nucleus).
- (ii) The optical properties of the solid are governed by the interaction between the solid and the electric field of the electromagnetic wave.

The important concept you have to learn here is that:

- (i) The state of the molecular charge separation can change in a quantized fashion by «absorbing» the energy of a photon.
- (ii) FOR THIS TO HAPPEN: The photon frequency must match the «frequency» associated with the molecule's energy transition in order for energy transfer to occur. This energy is given by equation (4.1) as:

$$E = h\nu = \frac{hc}{\lambda} . \qquad (4.1)$$

Where E is energy, h is Planck's constant; ν is frequency, c is speed of light in a vacuum and λ is the wavelength.

a) You need also to know that photon absorption occurs <u>as a quantum event</u>, an all or none phenomenon. (TRY TO UNDERSTAND WHAT THIS STATEMENT MEANS)

b) In biomedical optics, **absorption** of photons is a most important event i.e.

- (i) Absorption is the primary event that allows a laser or other light source to cause a potentially *therapeutic* (or damaging) effect on a tissue. Without absorption, there is no energy transfer to the tissue and the tissue is left unaffected by the light.
- (ii) Absorption of light provides a *diagnostic* role such as the spectroscopy of a tissue. Absorption can provide a clue as to the chemical composition of a tissue, and serve as a mechanism of optical contrast during imaging. Absorption is used for both spectroscopic and imaging applications.

(c) Definition and units of absorption coefficient.

Absorption coefficient, μ_a is a parameter that is used to describe the effectiveness of absorption. If a beam of light falls on a sphere as shown in Fig. 4.2.

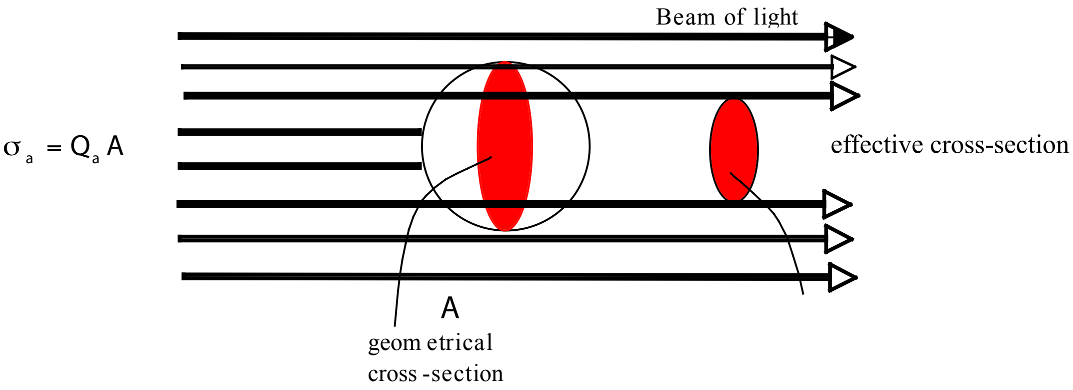


Figure 4.2: A beam of light falling on cross-sectional area A.

If the size of the absorption shadow is σ_a cm^2 and the geometrical size of the sphere is A cm^2 then **absorption efficiency** Q_a [dimensionless], is given by equation 4.2.

$$\sigma_a = Q_a A \qquad (4.2)$$

If ρ_a is a volume density, then the **absorption coefficient** μ_a is given by equation 4.3.

$$\mu_a = \rho_a \sigma_a \qquad (4.3)$$

The unit of absorption coefficient is cm^{-1}, and that of volume density is cm^{-3}.

If L (cm) is the a photon's path length of travel through the medium, then the probability of survival (transmission T) of the photon is given by equation (4.4)

$$T = \exp\left(-\mu_a L\right) \qquad (4.4)$$

The expression in equation (4.4) is true for any path that the photon passes through.

(d) Absorption and Extinction Coefficient

In this section, we derive expressions for *absorption* and *extinction* coefficients.

(i) The velocity of propagation of an electromagnetic wave through a solid is given by the frequency-dependent complex refractive index

$$N = n - ik, \qquad (4.5)$$

where the real part, n is related to the velocity, and k, the extinction coefficient is related to the decay, or damping of the oscillation amplitude of the incident electric field.

(ii) If a plane wave of frequency (f) propagates through a solid with velocity, v , in x-direction, then the electric field, E, is given by equation (4.6)

$$E = E_0 \exp\left\{2\pi fi\left[t - \frac{x}{v}\right]\right\} \qquad (4.6)$$

Where, (E_0) is the incident electric field vector, and

$\{2\pi fi[t-(x/v)]\}$ is displacement at time t after a disturbance, x, along the line of propagation.

Since the velocity of propagation through a solid of complex refractive index $N = n - ik$ is related to the speed of light in a vacuum, c, by

$$v = \frac{c}{N}, \qquad (4.7)$$

we have

$$\frac{1}{v} = \left(\frac{n}{c}\right) - \left(\frac{ik}{c}\right). \qquad (4.8)$$

If equation (4.8) is substituted in equation (4.6) we get

$$E = E_0 \exp(2\pi fti)\exp\left(\frac{-2\pi xni}{c}\right)\exp\left(\frac{-2\pi fkx}{c}\right) \qquad (4.9)$$

The term $\left(-2\pi\ \mathrm{fkx}/\mathrm{c}\right)$ is a measure of the damping factor, or extinction coefficient, *k*.

But power (*P*) or intensity of an incident wave through a solid is given by

$$P = \sigma \boldsymbol{E}^2 \qquad (4.10)$$

where σ, is conductivity of the solid, and ***E*** is the electric field vector.

Using the damping factor term, the fraction of the incident power that propagates from position (*o*) to a distance (*x*) through the material with conductivity (σ) is given by:

$$\frac{\mathrm{P}(\mathrm{x})}{\mathrm{P}(0)} = \frac{\sigma \mathrm{E}^2(\mathrm{x})}{\sigma \mathrm{E}^2(0)} = \exp\left(\frac{-4\pi\ \mathrm{fkx}}{\mathrm{c}}\right). \qquad (4.11)$$

Thus, absorption coefficient is given by,

$$\alpha = \frac{4\pi\ \mathrm{fk}}{\mathrm{c}} \qquad (4.12)$$

(e) Reflectivity

Most of this section you will do on your own. However, some definitions are hereby provided.

(ii) In optics, **reflectivity** is the **reflectance** that is, the ratio of reflected power to incident power.

(iii) Reflectivity is generally expressed in decibels.

Complete this section and make your notes. Include some examples.

(f) Transmissivity

Some of the information provided here are to help you make comprehensive notes on transmissivity

(i) Of importance, we talk about *external transmittance and internal transmittance*

o *External transmittance is the single-pass irradiance of an optical element, while Internal transmittance is the single-pas irradiance transmittance in the absence of any surface reflection losses (i.e., tranmittance of the material.*

(ii) External transmittance is of paramount importance when selecting optics for an image-forming lens system because external transmittance neglects multiple reflections between lens surfaces.

If T_e is the desired external irradiance transmittance, T_i the corresponding internal transmittance, t_1, the single-pass transmittance of the first surface, and t_2 the single-pass transmittance of the second surface, the

$$T_e = t_1 t_2 T_i = t_1 t_2 e^{-\mu t_c} \qquad (4.13)$$

μ is the absorption coefficient of the lens material, and t_c is the lens centre thickness.

- **Use the references provided and acoount for how equation (4.13) is derived.**

If both surfaces of the lens are not coated, then

$$t_1 t_2 = 1 - 2\gamma + \gamma^2 \qquad (4.14)$$

where $\gamma = \left(\frac{n-1}{n+1}\right)^2$

is the single-surface single-pass irradiance reflectance at normal incidence as given by Fresnel formula. Both refractive index, n and μ are fumnctions of wavelength.

***FOR completeness you can read more about this topic.*

Self-evaluation 4

1. Write short notes on:

   a) Valence band,
   b) Conduction band,
   c) Forbidden band gap,
   d) Sketch a diagram showing these bands in a metal.

2. (i) Use the diagram in Fig. 4.1 to compare the three materials.

   (ii) Explain how conduction takes place in a semiconductor when an electron is excited from the valence band to the conduction band.
   (iii) Differentiate between intrinsic and extrinsic semiconductors.
   (iv) What is meant by an impurity in semiconductor technology?

XI. Compiled list of all key concepts (glossary)

Anharmonic motion: Is a motion of a body subjected to a restoring force that is not directly proportional to the displacement from a fixed point in the line of motion.

Annealing: Is the process of heating a substance to a specific temperature lower than its melting point, maintaining that temperature for some time, and then cooling slowly. Slow crystallization thus takes place in the solid state under controlled temperature conditions. Annealing generally softens metals and stabilizes glas articles by allowing stresses produced during fabrication to disappear.

Atomic orbital: Is an allowed wave function of an electron in an atom obtained by solutions of SchÖdinger's wave equation.

Bands: In crystalline solids, atoms interact with their neighbors, and the energy levels of the electrons in isolated atoms turn into bands.

Coordination lattice: A crystal lattice in which each ion bears the same relation to the neighbouring ions in all directions, so that the identity of the molecules becomes abiguous.

Crystal structure: The specification both of the geometric framework to which the crystal may be referred, and of arrangement of atoms or electron-density distribution relative to that framework.

Degrees of freedom: The number of degrees of freedom of a mechanical system is equal to the number of independent variables needed to describe its configuration; e.g. a system consisting of two particles connected by a rigid bar has 5 degrees of freedom since 5 coordinates (3 of mass centre or of either particle, together with 2 angles) are needed to specify its state. The smallest number of coordinates needed to specify the state of the system is called its *generalized coordinates* and since these specify the state of the complete system, they also specify the state of any individual particle of the system. The generalized coordinates may be chosen in more than one way. The number of degrees of freedom depends only on the possibilities of motion of the various parts of the system and not on the actual motions. For monatomic gas the number is 3. For diatomic gas with rigid molecules, it is 6, made up of 3 degrees of freedom of the centre of gravity to move in space, 2 degrees of freedom of the line joining the two atoms to change direction in space and 1 for rotation about this axis.

Doping: Is the addition of impurities (*dopants)* to a semiconductor to achieve a desired n-conductivity or p-conductivity.

Equipartition of energy: The principle of equipartition of energy is based on the classical statistical mechanics and ennciated by Boltzmann, states that the mean energy of the molecules of a gas is equally divided among the various degrees of freedom of the molecules. The average energy of each degree of freedom is $\frac{1}{2}kT$, where k is the Boltmann's constant and T is the thermodynamic temperature.

Intrinsic conductivity: The conductivity of a semiconductor that is associated with the semiconductor itself and is not contributed by impurities. At any given tempeerature equal numbers of charge carriers –electrons and holes are thermally generated, and it is these that give rise to the intrinsic conductivity.

Lattice: A lattice Is a simplified geometry of a crystal in which the atoms are swept away leaving only a skeleton of mathematical points whereby each point replaces anything from one to several hundred of original atoms. Each group of these atoms is called the *basis.*

Molar heat capacity: Is the heat capacity of unit amount of substance of an element, compound, or material. It measured in joules per kelvin per mole.

The Mole:-A quantity which contains 6.02 x 10^{23}particles is the mole.

Pauli exclusion principle: Is the principle that no two identical fermions in any system can be in the same quantum state, that is have the same set of quantum numbers. The principle was first proposed in (1925) in the form that not more than two electrons in an atom could have the same set of quantum numbers. This hypothesis accounted for the main features of the structure of the atom and for the periodic table. With the introduction of the fourth quantum number it was seen that only one electron could be in a given state. An electron in an atom is characterized by four quantum numbers, n, l, m and s (where n, s, l and m are principal quantum number, spin quantum number, azimuthal quantum number, and magnetic spin respectively. A particular *atomic orbital* which has fixed values of n, l and m can thus contain a maximum of two electrons, since the spin quantum number s can be +½ or -½. Two electrons with opposing spins in an atomic orbital are said to be spin-paired.

Photons: A photon is the quantum of electromagnetic radiation. It has an energy of $h\nu$ where h is the Planck's constant and ν the frequency of radiation. For some purposes photons can be considered as elementary particles travelling at the speed of light (c) and having a momentum of $h\nu / c$. Photons can cause excitation of atoms and molecules and more energetic ones can cause ionization.

Phonons: In a solid the atoms do not vibrate independently but the oscillations are transmitted through the substance as acoustic waves of extremely high frequency, f , (typically of the order of 10^{12} Hz). The energy transmitted by the waves id quantized; the quantum is called a phonon and has a value hf , where is the Planck's constant. For many purposes the phonons can be treated as if they were gas molecules moving within the space occupied by the solid, the mean free path being limited by various scattering processes.

Plastic deformation: Microscopic investigations show that when a metal is plastically deformed, the deformation occurs by a slip of on a plane of closest packing along the direction of the line of closest packing in that plane.

Elasticity: Hooke's law is valid for compression as well as tension if the compressive stress is not too great and For many materials, Young's modulus has the same value for both tensile and compressive stresses, with the exception of composite materials such as concrete.

Insulators: Bands which are completely full of electrons cannot conduct electricity, because there is no state of nearby energy to which the electrons can jump. Materials in which all bands are full are called insulators

Metals:- Metals are good conductors because they have unfilled space in the valence energy band

Thermal conductivity conceptually can be thought of as the container for the medium-dependent properties which relate the rate of heat loss per unit area to the rate of change of temperature.

Heat transfer by conduction:- involves transfer of energy within a material without any motion of the material as a whole. The rate of heat transfer depends upon the temperature gradient and the thermal conductivity of the material.

In solid state physics, the electronic band structure (or simply band structure): of a solid describes ranges of energy that an electron is "forbidden" or "allowed" to have. The band structure determines a material's electronic properties, optical properties, and a variety of other properties

In optics, reflectivity:- is the reflectance (the ratio of reflected power to incident power, generally expressed in decibels or percentage) at the surface of a material so thick that the reflectance does not change with increasing thickness.

Yield point: A point on a graph of stress versus strain for material at which the strain becomes dependent on time and the material begins to flow.

XII. Compiled list of compulsory readings

Reading 1: Crystal Structure

Complete reference :
From Wikipedia.
URL : http://en.wikipedia.org/wiki/Crystal_structure
Accessed on the 20th April 2007

Abstract : This reading material briefly describes the unit cell, classification of crystals by symmetry, Physical properties of crystals and links are given to various sites within wikipedia and other sites.

Rationale: This reading material provides elaborated discussion on the contents of the first activity of the module.

Reading 2: Crystal Structure

Complete reference :
From University of Exeter
URL : http://newton.ex.ac.uk/teaching/resources/rjh/phy2009/
Accessed on the 20th April 2007

Abstract : In this article, crystal structure is described with well illustrated diagrams. The exercises in the article help the reader to consolidate the topics learnt.

Rationale: This article gives another way of looking at crystal structures. Further the sample tests and exercises given at the end provide good opportunity to use the theories and principles exercised from different perspectives.

Reading 3: Atomic Scale Structure of Materials

Complete reference :
From DoITPoMS Teaching and Learning Packages
URL :
Accessed on the 24th April 2007

Abstract : Various crystal types are described and worked example are given in topics of crystal and defects in crystal.

Rationale: This material is part of the DoITPoMS Teaching and Learning Packages. The packages are intended to be used interactively at a computer! This print-friendly extract is provided for convenience, but does not display all the content of the TLP. For example, any video clips and answers to questions are missing. If you have internet access take time to visit and interact with the exercises It supplements the second activity of the module.

Reading 4: Heat Capacity

Complete reference :
From Wikipedia, the free encyclopedia.
URL : http://en.wikipedia.org/wiki/Heat_capacity
Accessed on the 20th April 2007

Abstract : Heat capacity is defined and quantitatively described for compressible bodies. Specific heat capacity is defined and theoretical models are described. Heat capacity at various temperatures is described..

Rationale: This material supplements the thermal properties section of the third activity in the module. Links are provided for further reading.

Reading 5: Electrical Conductivity

Complete reference :
From Wikipedia, the free encyclopedia.
URL : http://en.wikipedia.org/wiki/Electrical_Conductivity
Accessed on the 24th April 2007

Abstract : Classification of materials by conductivity, Some typical electrical conductivities temperature dependence of conductivity are discussed. Links to other sides is also provided.

Rationale: This material supplements the electrical properties section of the third activity in the module. Links are provided for further reading..

XIII. Compliled List of (Optional) Multimedia Resources

Resource #1

Title: Electrons in Extrinsic Semiconductor Simulation

URL: http://www.collage.soe.ucsc.edu/JavaFiles/ElectronDopedSimulation.html

Description: Applet shows the motion of electrons in extrinsic semiconductor. The electric field the number of electrons and there is a mechanism to drag and drop an interstitial impurity.

Rationale: helps to visualize conduction is extrinsic semiconductors.

Resource #2

Title: Braggs law

URL: http://www.eserc.stonybrook.edu/ProjectJava/Bragg/

Description: The applet shows two rays incident on two atomic layers of a crystal, e.g., atoms, ions, and molecules, separated by the distance d. The layers look like rows because the layers are projected onto two dimensions and your view is parallel to the layers. The applet begins with the scattered rays in phase and interfering constructively. Bragg's Law is satisfied and diffraction is occurring. The meter indicates how well the phases of the two rays match. The small light on the meter is green when Bragg's equation is satisfied and red when it is not satisfied.

The meter can be observed while the three variables in Bragg's are changed by clicking on the scroll-bar arrows and by typing the values in the boxes. The d and q variables can be changed by dragging on the arrows provided on the crystal layers and scattered beam, respectively

Rationale: helps to visualize conduction is extrinsic semiconductors.

XIV. Compiled list of useful links

At least 10 relevant web sites. These useful links should help students understand the topics covered in the module. For each link, the complete reference (Title of the site, URL), as well as a 50 word description written in a way to motivate the learner to read the text should be provided. The rationale for the link provided should also be explained (maximum length : 50 words). A screen capture of each useful link is required.

Useful Link # 1

Title: Amorphous Solid

URL: http://www.britannica.com/eb/article-9110300/amorphous-solid

Screen Capture:

amorphous solid

any noncrystalline solid in which the atoms and molecules are not organized in a definite lattice pattern. Such solids include glass, plastic, and gel.

Solids and liquids are both forms of condensed matter;

Description: The online Encyclopaedia Britannica is one of the excellent online recourses to have introductory discursion nearly in all topics of interest. Although the site is not free there is a time limited access.

Rationale: A detailed account of solids is available.

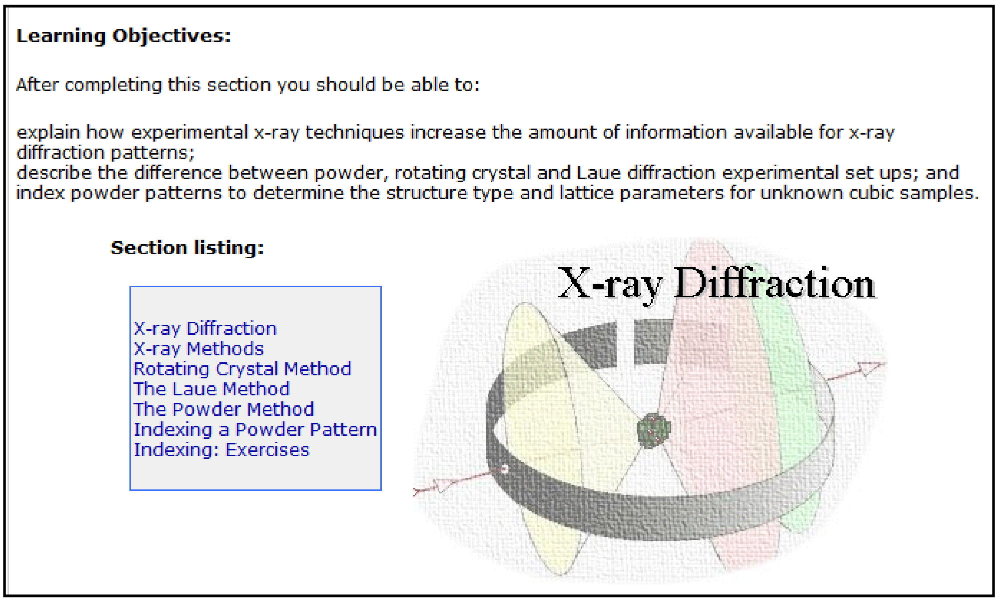
Date Consulted:-29th April 2007

Useful Link # 2

Title: X-Ray Diffraction

URL: http://galileo.physics.edu/classes/252 http://mhsweb.ci.manchester.ct.us/Library/webquests/atomicmodels.htm

Screen Capture:



Learning Objectives:

After completing this section you should be able to:

explain how experimental x-ray techniques increase the amount of information available for x-ray diffraction patterns;
describe the difference between powder, rotating crystal and Laue diffraction experimental set ups; and
index powder patterns to determine the structure type and lattice parameters for unknown cubic samples.

Section listing:

X-ray Diffraction
X-ray Methods
Rotating Crystal Method
The Laue Method
The Powder Method
Indexing a Powder Pattern
Indexing: Exercises

Description: This site has links to full description of diffraction and x-ray methods.

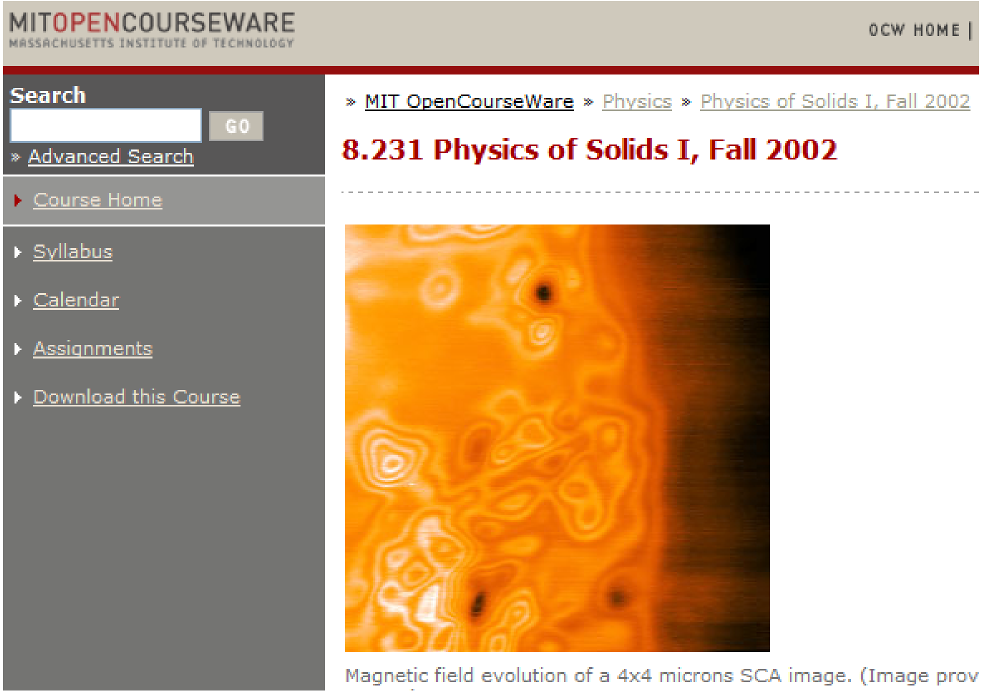
Date Consulted:- April 2007

Useful Link # 3

Title: http://galileo.physics.edu/classes/252 **MIT open courseware**

URL: http://ocw.mit.edu/OcwWeb/Physics/8-231Physics-of-Solids-IFall2002/CourseHome/index.htm

Screen Capture:



» MIT OpenCourseWare » Physics » Physics of Solids I, Fall 2002

8.231 Physics of Solids I, Fall 2002

Magnetic field evolution of a 4x4 microns SCA image. (Image prov

Description: The MIT Open Courseware is one of the world famous collections of course materials accessible worldwide. It is rich in video demonstrations and exercises. This collection has mirror sites in African universities like Addis Ababa University http://ocwmit.aau.edu.et/ and Nairobi University. .

Rationale: Very relevant to the module in general. .

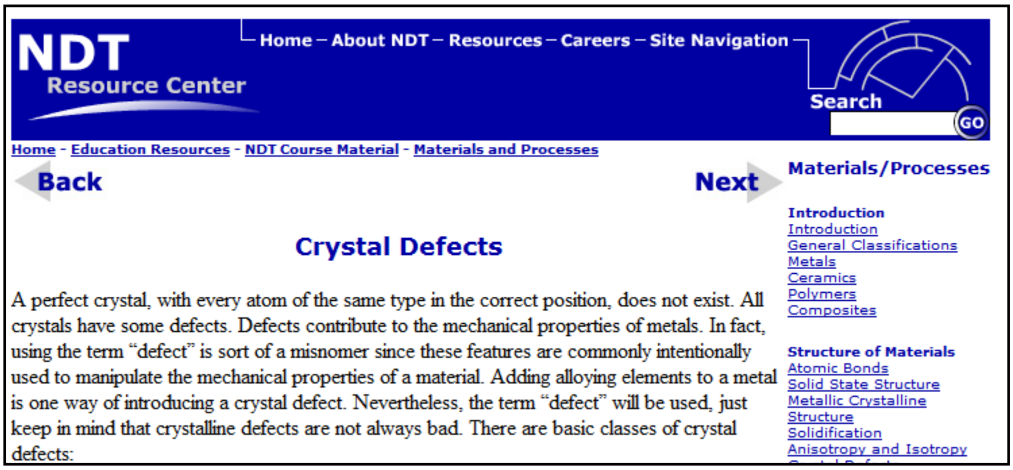
Date Consulted: April 2007.

Useful Link # 4

Title: http://galileo.physics.edu/classes/252 Defects in crystals

URL: http://www.ndt-ed.org/EducationResources/CommunityCollege/Materials/Structure/crystal_defects.htm http://mhsweb.ci.manchester.ct.us/Library/webquests/atomicmodels.htm

Screen Capture:



Crystal Defects

A perfect crystal, with every atom of the same type in the correct position, does not exist. All crystals have some defects. Defects contribute to the mechanical properties of metals. In fact, using the term "defect" is sort of a misnomer since these features are commonly intentionally used to manipulate the mechanical properties of a material. Adding alloying elements to a metal is one way of introducing a crystal defect. Nevertheless, the term "defect" will be used, just keep in mind that crystalline defects are not always bad. There are basic classes of crystal defects:

Description: This web page is part of the NDT Resource Center. This site was designed to be a comprehensive source of information and materials for NDT and NDE technical education. The site was created by NDT professionals and educators from around the world.

Rationale: A number of relevant links are provided and the basic sciences of crystal defects are discussed.

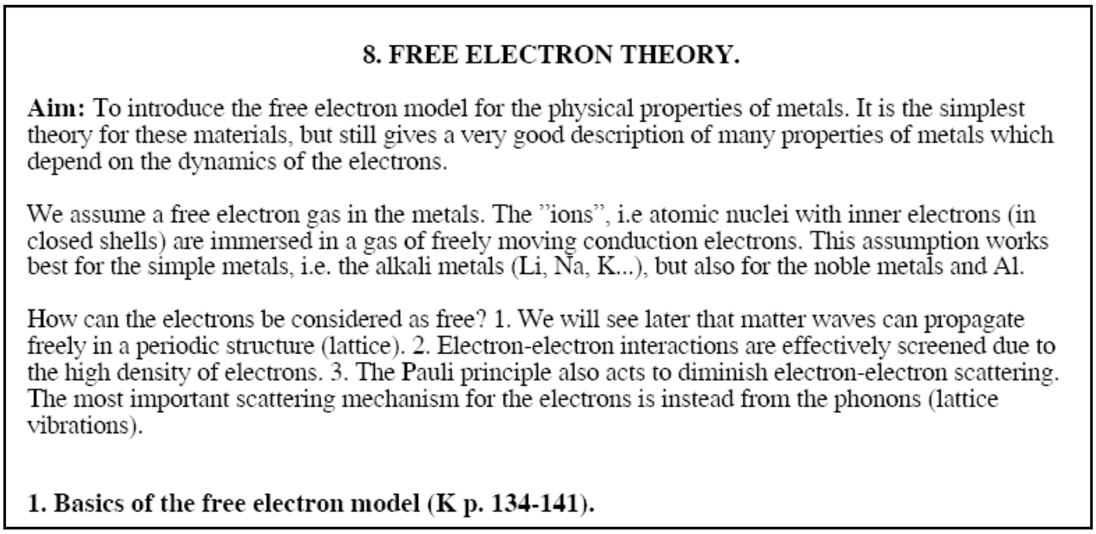
Date Consulted: May 2007

Useful Link # 5

Title: http://galileo.physics.edu/classes/252 Free Electron Theory

URL: http://www.teknik.uu.se/ftf/education/ftf1/forelasningar/overview/Freelectronmodel.pdf

Screen Capture:



8. FREE ELECTRON THEORY.

Aim: To introduce the free electron model for the physical properties of metals. It is the simplest theory for these materials, but still gives a very good description of many properties of metals which depend on the dynamics of the electrons.

We assume a free electron gas in the metals. The ”ions”, i.e atomic nuclei with inner electrons (in closed shells) are immersed in a gas of freely moving conduction electrons. This assumption works best for the simple metals, i.e. the alkali metals (Li, Na, K...), but also for the noble metals and Al.

How can the electrons be considered as free? 1. We will see later that matter waves can propagate freely in a periodic structure (lattice). 2. Electron-electron interactions are effectively screened due to the high density of electrons. 3. The Pauli principle also acts to diminish electron-electron scattering. The most important scattering mechanism for the electrons is instead from the phonons (lattice vibrations).

1. Basics of the free electron model (K p. 134-141).

Description: This link provides a pdf document on free electron theory..

Rationale: Relevant to the third activity of this module.

Date Consulted: May 19, 2007

Useful Link # 6

Title: http://galileo.physics.edu/classes/252 Optical Properties of Solids

URL: http://web.missouri.edu/~speckan/witch-stuff/Research/chapter4/node2.html
http://mhsweb.ci.manchester.ct.us/Library/webquests/atomicmodels.htm

Screen Capture:

- Introduction
- Physical optics
    - Classical electromagnetic theory
    - Acoustic and optical modes
    - Electrical properties of matter
- The complex refractive indices of material media
    - Scattering
    - Simulating the Particulate Spectra: Mie Theory
    - Experimental Determination of Optical Constants
- A problem with the laboratory spectra
    - Thin film vs. KBr-dispersion spectra
        - Laboratory techniques and results for thin-film samples
        - Comparison with dispersed-sample results
- Kramers-Kronig dispersion relations
    - About this document ...

Description: A detailed description of optical properties is available at this site and links there..

Rationale: Advanced treatment of the content for curious reader..

Date Consulted: May 20, 2007

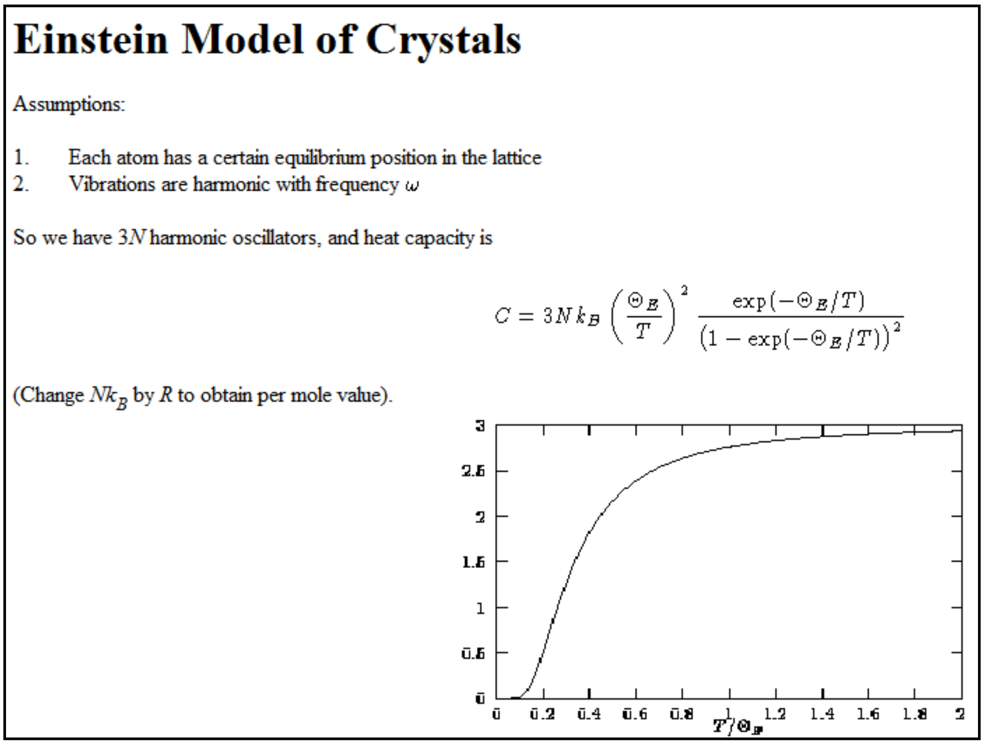
Useful Link #7

Title: http://galileo.physics.edu/classes/252 Einstein Model of Crystals

URL: http://www.plmsc.psu.edu/~www/matsc597c-1997/systems/Lecture4/node3.html

http://mhsweb.ci.manchester.ct.us/Library/webquests/atomicmodels.htm

Screen Capture:



Einstein Model of Crystals

Assumptions:

1. Each atom has a certain equilibrium position in the lattice
2. Vibrations are harmonic with frequency ω

So we have $3N$ harmonic oscillators, and heat capacity is

$$C = 3N k_B \left(\frac{\Theta_E}{T}\right)^2 \frac{\exp(-\Theta_E/T)}{\left(1 - \exp(-\Theta_E/T)\right)^2}$$

(Change Nk_B by R to obtain per mole value).

Description: Einstein model is described. Links are available for the Debye model, solid state and harmonic oscillator as well..

Rationale: supplements a topic in activity three of this module.

Date Consulted: May 20, 2007

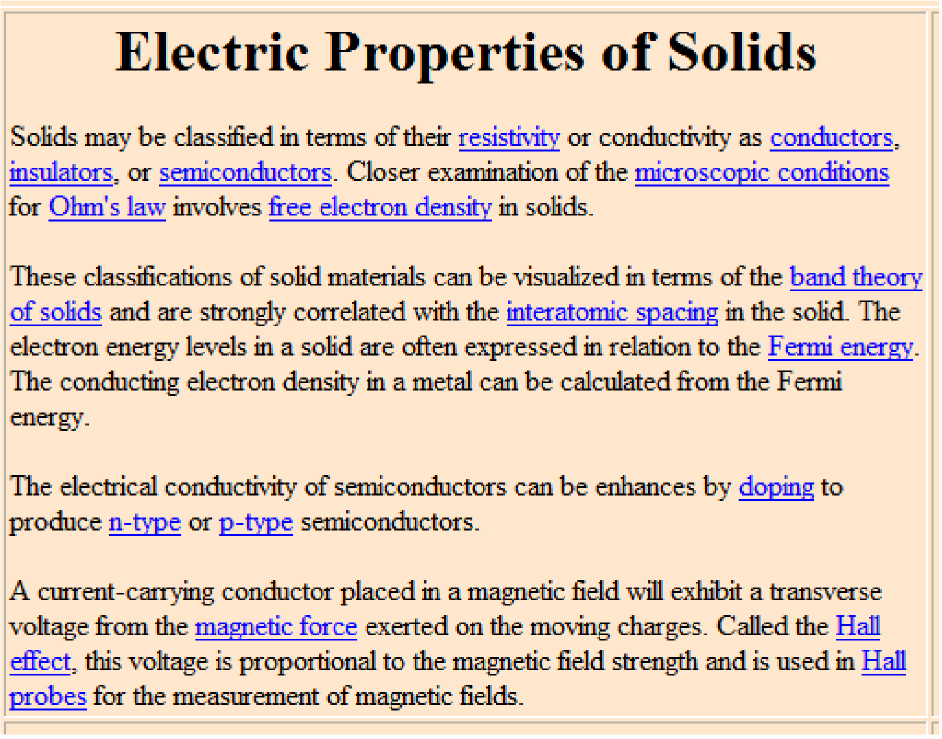
Useful Link # 8

Title: http://galileo.physics.edu/classes/252 Electric properties of Solids

URL: http://hyperphysics.phy-astr.gsu.edu/hbase/solids/elpro.html#c1

http://mhsweb.ci.manchester.ct.us/Library/webquests/atomicmodels.htm

Screen Capture:



Electric Properties of Solids

Solids may be classified in terms of their resistivity or conductivity as conductors, insulators, or semiconductors. Closer examination of the microscopic conditions for Ohm's law involves free electron density in solids.

These classifications of solid materials can be visualized in terms of the band theory of solids and are strongly correlated with the interatomic spacing in the solid. The electron energy levels in a solid are often expressed in relation to the Fermi energy. The conducting electron density in a metal can be calculated from the Fermi energy.

The electrical conductivity of semiconductors can be enhances by doping to produce n-type or p-type semiconductors.

A current-carrying conductor placed in a magnetic field will exhibit a transverse voltage from the magnetic force exerted on the moving charges. Called the Hall effect, this voltage is proportional to the magnetic field strength and is used in Hall probes for the measurement of magnetic fields.

Description: This is part of a large collection of articles on solid state physics. If you click http://hyperphysics.phy-astr.gsu.edu/hbase/solcon.html you will get how the content is structured at this site and use it on other topics as well..

Rationale: Very relevant to the course here.

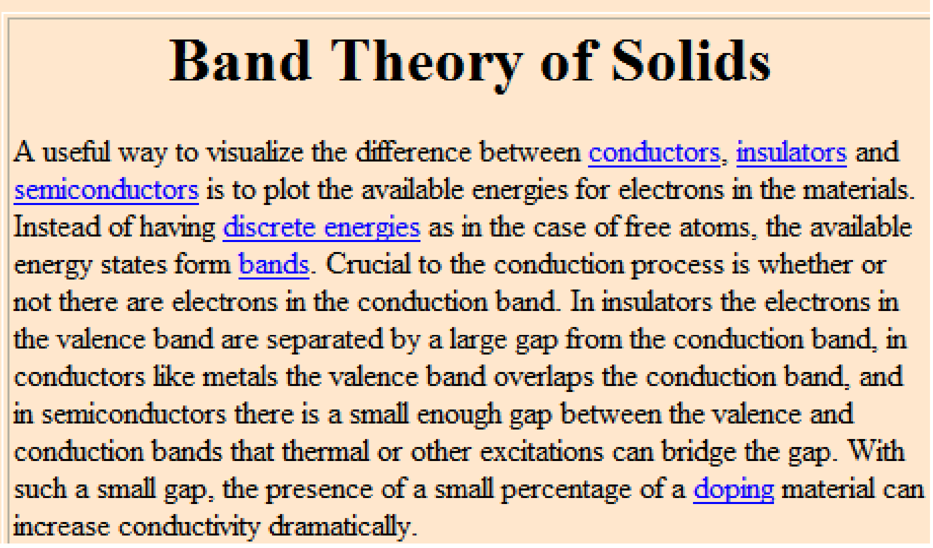
Date Consulted: April 2007

Useful Link #9:

Title: http://galileo.physics.edu/classes/252 Band Theory of Solids

URL: http://hyperphysics.phy-astr.gsu.edu/hbase/solids/band.html#c6

Screen Capture:



Band Theory of Solids

A useful way to visualize the difference between conductors, insulators and semiconductors is to plot the available energies for electrons in the materials. Instead of having discrete energies as in the case of free atoms, the available energy states form bands. Crucial to the conduction process is whether or not there are electrons in the conduction band. In insulators the electrons in the valence band are separated by a large gap from the conduction band, in conductors like metals the valence band overlaps the conduction band, and in semiconductors there is a small enough gap between the valence and conduction bands that thermal or other excitations can bridge the gap. With such a small gap, the presence of a small percentage of a doping material can increase conductivity dramatically.

Description: A good collection of theories and java applets is available at this link..

Rationale: Complements Activity 4

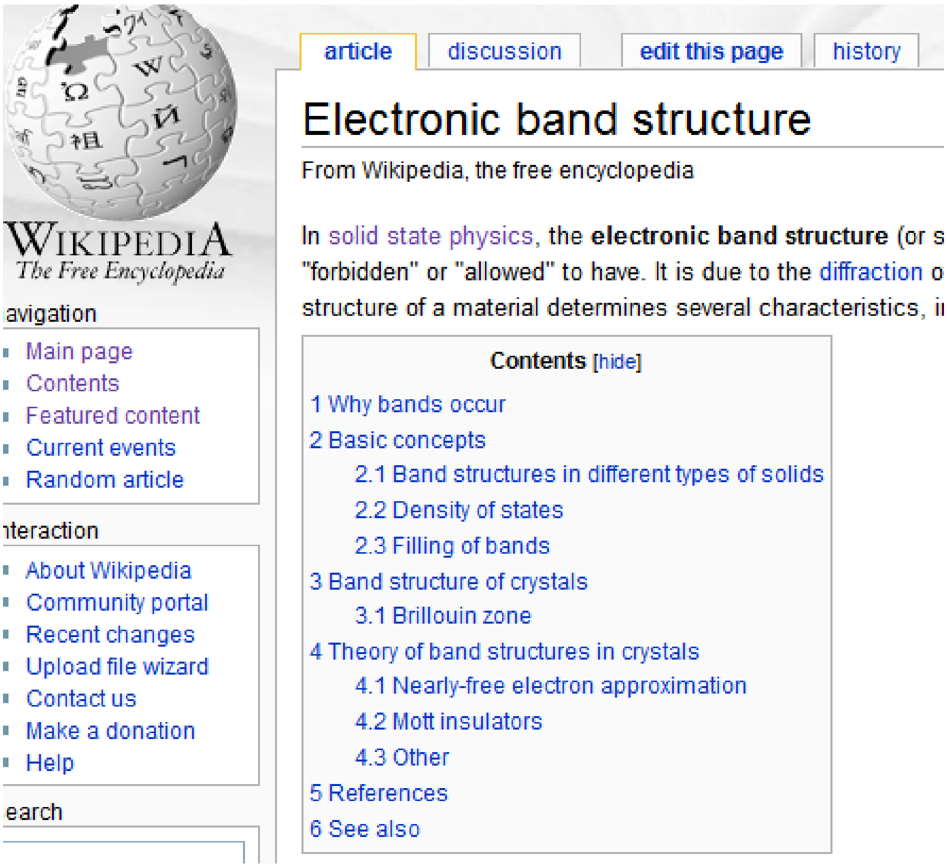
Date Consulted: April 2007

Useful Link #10:

Title: http://galileo.physics.edu/classes/252 Electronic Band Structure

URL: http://en.wikipedia.org/wiki/Electronic_band_structure

Screen Capture:



Electronic band structure

From Wikipedia, the free encyclopedia

In solid state physics, the **electronic band structure** (or s "forbidden" or "allowed" to have. It is due to the diffraction o structure of a material determines several characteristics, ii

Contents [hide]

1 Why bands occur
2 Basic concepts
    2.1 Band structures in different types of solids
    2.2 Density of states
    2.3 Filling of bands
3 Band structure of crystals
    3.1 Brillouin zone
4 Theory of band structures in crystals
    4.1 Nearly-free electron approximation
    4.2 Mott insulators
    4.3 Other
5 References
6 See also

Description: A Clear explanation of Insulator Energy Bands; Semiconductor Energy Bands Conductor Energy Bands; Semiconductor, Dopants are provided.

Rationale: This site provides simple reading on band theory. This is very important for one to develop a firm foundation in the topic. The important topics include: why bands occur; basic concepts, band structure of crystals, among others .

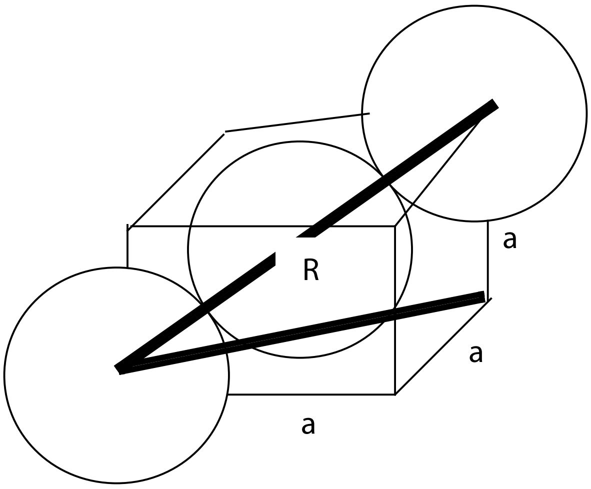
Date Consulted: May 20, 2007

Solutions to self evaluation 1

1. At room temperature, ionic compounds are usually solids and have high melting points.They are good electrical insulators in solid state since the electrons are nearly all firmly bound to particular ions and few are available for conduction. In molten state, some ionic bonds are broken and conduction is possible.
2. The lattice formed is a *square*. Each point represents three atoms.
3. (i) A rectangular lattice has a two-fold symmetry

   ii) An equilateral crystal has a three-fold symmetry
4. All lattices possess the property of translational symmetry: because the lattice transforms into itself (i.e. remains the same) when moved through integer numbers of lattice vectors
5. We cannot find a lattice that goes into itself under rotation such as 2π/5 or 2π/7. This is because the lattice undergoing such a rotation would overlap. A five-fold axis of symmetry cannot exist in a lattice because it is not possible to fill all space with connected array of pentagons.

7 P<u>acking fraction in a bcc</u>



Calculation of radius of atomSketch diagram showing relative positions of atoms in a BCC

For a bcc, the atoms touch along the diagonal as shown in Fig. 1.21. If the radius of the atom is *r* then

$$R^2 = 2a^2 + a^2 = 3a^2$$

But R = 4*r*

$$\Rightarrow 16r^2 = 3a^2$$

OR $r^2 = \frac{3a^2}{16} \Leftrightarrow r = \frac{a}{4}\sqrt{3}$

Next, lets determine the number of lattice points in a bcc

Each atom at the corner is shared by 8 cells, just like in the case of a sc. Thus number of lattice points due to atoms at the corner is one.

In addition to this, there in one atom within the cell. This means that in a bcc, there are two lattice points.

Thus, volume occupied by the lattice points is

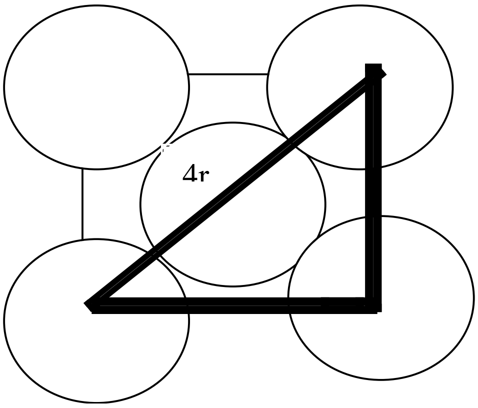
$$\frac{4}{3}\pi r^3 \times 2$$

Packing fraction = $\frac{\text{volume occupied by lattice points}}{\text{Volume occupied by unit cell}}$

$$= \frac{\frac{4}{3}\pi r^3 \times 2}{a^3} = 68\%.$$

This means that only 32% of the space in a bcc is empty, while 68% is filled with atoms.

(ii) *Determine a packing fraction in a fcc.*



Packing fraction in a crystal

In the fcc the atoms touch one another on the face along the diagonal as shown in Fig. 1.22. If the lattice parameter is *a and the radius of each atom is r* then

$$(4r)^2 = 2a^2 \Leftrightarrow r^2 = \frac{a^2}{8}.$$

Determining the number of lattice points.

This is due to the atom at the face and those at the corners.

The atoms on the faces are shared by two cells, while those at the corners are shared by 8 cells.

$$\begin{aligned}\text{Thus, number of lattice points} &= \frac{1}{2}\times 6 + \frac{1}{8}\times 8 \\ &= 4.\end{aligned}$$

$$\text{Thus, packing fraction} = \frac{\frac{4\pi}{3}\left(\frac{a}{2\sqrt{2}}\right)^3 \times 4}{a^3} = 74\%.$$

8. When X-rays hit an atom, they make the electronic cloud move as does any electromagnetic wave. The movement of these charges re-radiates waves with the same frequency (blurred slightly due to a variety of effects); this phenomenon is known as the Rayleigh scattering (or elastic scattering). These re-emitted wave fields interfere with each other either constructively or destructively, producing a diffraction pattern on a detector or film. The resulting wave interference pattern is the basis of diffraction analysis. The X-ray wavelength iscomparable with inter-atomic distances (~150 pm) and thus are an excellent probe for this length scale.

   The interference is constructive when the phase shift is proportional to 2π ; this condition can be expressed by Bragg's law:

   $$n\lambda = 2d\sin\theta.$$

where

n is an integer,

λ is the wavelength of X-rays,

d is the spacing between the planes in the atomic lattice, and

θ is the angle between the incident ray and the scattering planes.

Solutions to Self Assessment 2

Solution to Q1.

Substitutional impurities cause some distortion around the point where they are

found. Further, The presence of defects increases the disorder of the crystal, i.e. it increases its entropy. There is therefore a tendency for more defects to be present at higher temperatures.

- Around a vacancy for example, there is a tendency for atomic arrangement to readjust slightly and causing the crystal lattice to be distorted.. The presence of vacancies provides a mean for atoms to diffuse fairly easily from one point to another since an atom can move to a vacancy thereby leaving its own site vacant without producing too much disruption of the existing crystal i.e. *very little energy is required.* This implies that diffusion can be thought of as migration of vacancies in the opposite direction.
- Complexes can also form between different kinds of point defects. For example, if a vacancy encounters an impurity, the two may bind together if the impurity is too large for the lattice. Interstitials can form 'split interstitial' or 'dumbbell' structures where two atoms effectively share an atomic site, resulting in neither atom actually occupying the site.

Solution to section 2.1.2

The presence of a vacancy at a positive-ion site upsets the electrical neutrality of the region and so the vacancy has an effective negative charge associated with it as effectively illustrated by the enclosed surface in the disgram.

(i) This increases the electrostatic energy of the crystal, hence in order to maintain electrical neutrality there is a tendency for positive and negative ion vacancies to be produced.

(ii) The presence of vacancies also enhance ordinary diffusion in an ionic crystal, but in the presence of applied electric field, the increased diffusion due to vacancies will also assist the electrical conduction.

Solution to section 2.1.5 (c)

In a bcc crystals slip occur along the six equivalent [110}

Solution to Q1(b) Planar defects

The possible effects of planar defects are:

Grain boundaries occur where the crystallographic direction of the lattice abruptly changes. This commonly occurs when two crystals begin growing separately and then meet.

Anti phase boundaries occur in ordered alloys: in this case, the crystallographic direction remains the same, each side of the boundary has an opposite phase: For example if the ordering is usually ABABABAB, an anti phase boundary takes the form of ABABBABA.

Stacking faults occur in a number of crystal structures, but the common example is in close packed structures. face centered cubic (fcc) structures differ from hexagonal close packed (hcp) structures only in stacking order: both structures have close packed atomic planes with six fold symmetry -- the atoms form equilateral triangles. When stacking one of these layers on top of another, the atoms are not directly on top of one another -- the first two layers are identical for hcp and fcc, and labelled AB. If the third layer is placed so that its atoms are directly above those of the first layer, the stacking will be ABA -- this is the hcp structure, and it continues ABABABAB. However there is another location for the third layer, such that its atoms are not above the first layer. Instead, the fourth layer is placed so that its atoms are directly above the first layer. This produces the stacking ABCABCABC, and is actually a cubic arrangement of the atoms. A stacking fault is a one or two layer interruption in the stacking sequence, for example if the sequence ABCABABCAB were found in an fcc structure.

Self Evaluation 3

Solution to Q1

(i) Heat capacity is an extensive quantity because it is sensitive to the size of the object (for example, a bathtub of water has a greater heat capacity than a cup of water). Dividing heat capacity by the body's

(ii) Specific heat capacity is an intensive quantity because it is no longer dependent on amount of material, but more dependent on the type of material, as well as the physical conditions of heating.

Solution to Exercise 1(c) in 3.1.3

- One of the reasons for this phenomenon is the quantization of vibrational, and to a lesser extent, rotational states.
- When assumed that the molecules remain in their lowest vibrational energy state due to large inter-level energy spacings, the predicted molar constant volume heat capacity for a diatomic molecule becomes

$$C_{V,m} = \frac{3R}{2} + R = 2.5R$$

- This is a fairly close approximation of the heat capacities of the lighter molecules.

- If the quantum harmonic ocillator approximation (READ ABOUT THIS) is made, it turns out that the quantum vibrational energy level spacings are inversely proportional to the square root of the reduced mass(READ ABOUT THIS) of the atoms composing the diatomic molecule.

  Thus, in the case of the heavier diatomic molecules, the quantum vibrational energy level spacings become finer, which allows more excitations into higher vibrational levels at a fixed temperature

Solution to Q2

Both the Einstein model and the Debye model provide a *functional form* for the heat capacity. They are *models*, and no model is without a scale. The scale of the Einstein model, is given by

$$C_V = 3Nk\left(\frac{\varepsilon}{kT}\right)^2 \frac{e^{\varepsilon/kT}}{(e^{\varepsilon/kT}-1)^2}$$

is ε / *k*. And the scale of the Debye model is T_D, the Debye temperature.

-Einstein and Debye scales are **not** the same, that is to say,

$$\frac{\varepsilon}{k} \neq T_D$$

which means that plotting them on the same set of axes is not appropriate. They are two models of the same thing, but of different scales. If **Einstein temperature** is defined as

$$T_E \underline{\underline{\text{def} \frac{\varepsilon}{k}}}$$

then one can say $T_E \neq T_D$, and to relate the two, one must seek the relation $\frac{T_E}{T_D}$.

The Einstein solid is composed of single-frequency, $\varepsilon = hw = hv$. This frequency would be related to the speed of sound, although there is no sound in Einstein solid, one can imagine the propagation of sound as a sequence of atoms *hitting* one another If this is so, the frequency of oscillation must correspond to the minimum wavelength sustainable by the atomic lattice, $\lambda_{\min}$

$$v = \frac{c_s}{\lambda} = \frac{c_s\sqrt[3]{N}}{2L} = \frac{c_s}{2}\sqrt[3]{\frac{N}{V}}$$, *L* is dimension of a cube.

which makes the Einstein temperature

$$T_E = \frac{\varepsilon}{k} = \frac{hv}{k} = \frac{hc_s}{2k}\sqrt[3]{\frac{N}{V}} \ .$$

and therefore the ratio is

$$\frac{T_E}{T_D} = \sqrt{\frac{\pi}{6}}$$

Now both models can be plotted on the same graph.

Solution to Q4

(i) Electrical conductivity is more or less strongly dependent on temperature.

(ii) In metals, electrical conductivity decreases with increasing temperature, whereas in semiconductors, electrical conductivity increases with increasing temperature.

(iii Over a limited temperature range, the electrical conductivity can be approximated as being directly proportinal to temperature.

(iv) In order to compare electrical conductivity measurements at different temperatures, they need to be standardized to a common temperature. This dependence is often expressed as a slope in the conductivity-vs-temperature graph, and can be used:

$$\sigma_{T'} = \frac{\sigma_T}{1 + \alpha\left(T - T'\right)}$$

where

$\sigma_{T'}$ is the electrical conductivity at a common temperature, T' ,
σ_T is the electrical conductivity at a measured temperature, T
α is the temperature compensation slope of the material,
T is the measured temperature,
T' is the common temperature.

Solution to section 3.1.5 (c) (i)

(ii) Metals are good conductors because they have unfilled space in the valence energy band. In the absence of an electric field, there exist electrons travelling in all directions and many different velocities up to the Fermi velocity (the velocity of electrons at the Fermi energy).

(iii) When an electric field is applied, a slight imbalance develops and mobile electrons flow.

(iv) Electrons in this band can be accelerated by the field because there are plenty of nearby unfilled states in the band.

Solution to Q5

(i) Heat transfer by conduction involves transfer of energy within a material without any motion of the material as a whole. The rate of heat transfer depends upon the temperature gradient and the thermal conductivity of the material.

(ii) Gases transfer heat by direct collisions between molecules, and therefore, their thermal conductivity is low compared to most solids since they are dilute media. Non-metallic solids transfer heat by lattice vibrations so that there is no net motion of the media as the energy propagates through. Such heat transfer is often described in terms of «phonons», quanta of lattice vibrations. Metals are much better thermal conductors than non-metals because the same mobile electrons which participate in electrical conduction also take part in the transfer of heat.

(iii) For non-metallic solids, the heat transfer is view as being transferred via lattice vibrations, as atoms vibrating more energetically at one part of a solid transfer that energy to less energetic neighboring atoms. This can be enhanced by cooperative motion in the form of propagating lattice waves, which in the quantum limit are quantized as phonons. Practically, there is so much variability for non-metallic solids that we normally just characterize the substance with a measured thermal conductivity when doing ordinary calculations.

Solutions to Self Assessment 4

Solution to Q1

(a) The valence band

This is the band made up of the occupied molecular orbitals and is lower in energy than the conduction band. It is generally completely full in semiconductors. When heated, the electrons from this band, jump out of the band across the band gap and into the conduction band, making the material conductive.

(b) The conduction band

It is the band that accepts the electrons from the valence band. In insulators the electrons in the valence band are separated by a large gap from the conduction band, in conductors like metals the valence band overlaps the conduction band, thus making the valence electrons free, and in semiconductors there is a small enough gap between the valence and conduction bands that thermal or other excitations can bridge the gap.

Solution to Q2

(i)

- The important thing about conduction is whether or not there are electrons in the conduction band.
- In insulators the electrons in the valence band are separated by a large gap from the conduction band,
- In conductors like metals the valence band overlaps the conduction band, and
- In semiconductors there is a small enough gap between the valence and conduction bands that thermal or other excitations can bridge the gap. With such a small gap, the presence of a small percentage of a doping material can increase conductivity dramatically.

(ii)

- When electrons are excited to the conduction band they leave behind electron holes, or unoccupied states in the valence band.
- Both the conduction band electrons and the valence band holes contribute to electrical conductivity.
- The holes themselves don't actually move, but a neighbouring electron can move to fill the hole, leaving a hole at the place it has just come from, and in this way the holes appear to move, and the holes behave as if they were actual positively charged particles.

(iii) A semiconductor whose electrical properties depend upon the presence of certain impurities is referred to as extrinsic semiconductor; while an intrinsic semiconductor is a pure semiconductor containing no impurity atoms.

(iv) In semiconductor technology, a material such as boron, phosphorus or arsenic added in small quantities to a crystal to produce an excess of electrons (donor impurity) or holes (acceptor impurity) is referred to as an impurity.

XV. Synthesis of the Module

In the first activity we learnt of many things. This included learning about properties of crystalline and amorphous solids and how they can be distinguished from one another. Identification of lattices were done and we able to derive an equation such as

$$\cos\alpha = \frac{3 + p - m}{2}$$

which enabled us to calculate the possible allowed rotation. In the activity we learnt how Miller indices are calculated, including how different planes can be sketched. Further learning included how packing density for sc, bcc and fcc are calculated. You learnt about X-rays diffraction. This included how Bragg's law equation is derived and applied to numerical problems. The concept of X-ray diffraction also included treatment involving reciprocal lattice space where Ewald sphere was constructed in order to determine the planes responsible for X-rays diffraction.

In the second activity crystal defects and mechanical properties formed most of the activty. You should now be able to differentiate between the different types of crystal defects including how they affect thermal, physical and electrical properties of solids. The basic difinitions learnt is that, point defects are very localised and are of atomic size, while dislocation is a disorder which extend beyond the volume of one or two atoms. The effects of these defects on mechanical, and electrical properties have all been discussed and learnt. The learning activity has enabled you to derive and apply expression for Young's modulus. This also includes expression for shear modulus and yield stress by simultaneous slip of atoms.

Basically in activity three you able to derive expressions for heat capacitybat constant volume and constant presure. Linked to this, explanations of variation of heat capacity with temperature based on the classical, Einstein and Debye models were made. In addition the use free electron theory to explain high thermal and electrical conductivities of metals and derivation and application the Wiedermann-Frantz law were topics you learnt. That is, you learnt that Wiedemann-Franz law is derived by treating the electrons like a classical gas and you able to compare the resultant thermal conductivity to the electrical conductivity. The expressions for thermal and electrical conductivity drived is that

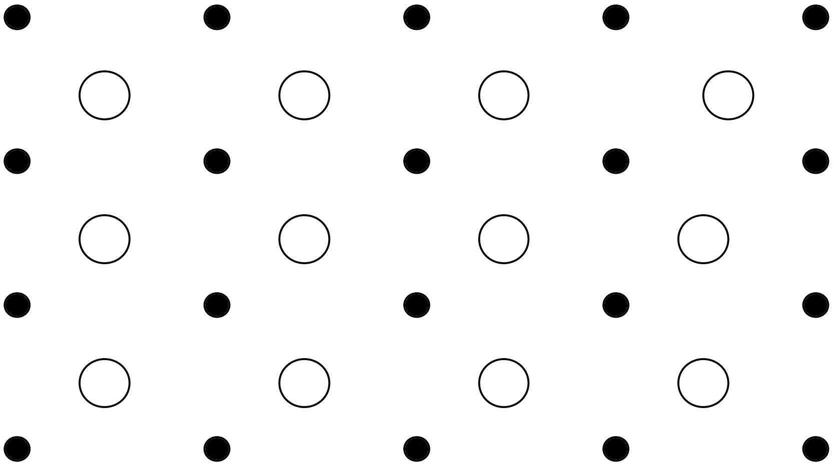
$$\text{conductivities} \quad \underbrace{\kappa = \frac{n\langle v\rangle \lambda k}{2}}_{\textit{Thermal}} \qquad \underbrace{\sigma = \frac{ne^2\lambda}{m\langle v\rangle}}_{\textit{Electrical}}$$

Finally, in activity four, you learnt about band theory and this enabled you to explain the differences between conductors, semiconductors and insulators. The concept further enabled you to explain the differences between intrinsic and extrinsic semiconductors in relation to the role of doping. At the end of it all, you used the concepts of the interaction of electromagnetic waves (light) and materials to explain optical absorption, reflectivity and Transmissivity.

XVI. Summative Evaluation

1) Answere the following questions based on the figure below.

   a) Define the lattice.
   b) Describe how a primitive cell may be chosen by a Wigner- Seitz Procedure.
   c) Identify the lattice given below and state the number of atoms per lattice point.



   d) Derive an expression for an allowed rotation, α , in a periodic lattice and show how the possible solutions to the equation are obtained**.**

2)

   a) Define Coordination number and give an illustration
   b) Determine whether the following directions are coplanar

$$\left[1\bar{1}0\right],\ \left[1\bar{2}1\right],\ \left[2\bar{1}\bar{1}\right]$$

   c) Derive an expression for the packing fraction for a bcc lattice. Explain the meaning of the expression.
   d) Derive an expression for Bragg's law and state the conditions required

3) A linear chain of alternating masses M and m are interconnected to neighbouring masses by springs having a force constant α. The frequencies υ of the vibrational modes of this system are given by the expression

$$4\pi^2 v^2 = \left(\frac{\alpha}{Mm}\left[M + m \pm \left(M^2 + m^2 + 2mM\cos qA\right)^{1/2}\right]\right)$$

where A is the length of the repeat unit, and q is the magnitude of the wavevector.

a) Reduce the above expression to that appropriate for a chain of like particles interconnected by identical springs.

b) Sketch the dispersion relations of both systems to the same scale. Derive expressions for key points and discuss the similarities and differences between the two diagrams

c) Give sketches of the densities of modes for both systems.

4) Suppose a crystal has N normal sites and N_I interstitials sites

a) Show that the number of ways of arranging N_f atoms on interstitial sites and N-N_f atoms on normal sites is given by

$$W = \frac{N!}{N_f!\left(N - N_f\right)!}\cdot\frac{N_I!}{N_f!\left(N_I - N_f\right)!}$$

b) If E_f is the energy required to move an atom from a normal site to an interstitial site show that the free energy is a minimum when

$$\frac{\left(N - N_f\right)\left(N_I - N_f\right)}{N_f^2} = e^{\beta E_f}$$

$$\frac{\left(N - N_f\right)\left(N_I - N_f\right)}{N_f^2} = e^{\beta E_f}$$

c) Show that the number of Frenkel defects, N_f ,is given by

$$N_f = \left(NN_I\right)^{1/2} .e^{-\beta E_f/2}$$

If N_f is much smaller than N and N_I .

5)

a) Explain the meaning of the following; *valence band; conduction band,* and the *Fermi level* in relation to solids.

b) Derive an expression for the energy ε_n of a free particle in a cubical box of volume V in terms of quantum number *n,* the mass *m* of the particle and other usual constants

hence show that the energy corresponding to the momentum p_i is given by

$$\varepsilon_j = n_j^2 \frac{h^2}{8mL^2}$$

L is the side length of the cube

6)

a) Explain the meaning of the followings: *electronic, orientational and ionic polarization*

b) Describe how points defects may be formed and explain their effects on the properties of crystals

c) Show that shear stress, τ has a maximum value of $\frac{G}{2\pi}$ when it causes a particular plane to move. G is the shear (or rigidity) modulus.

XVII. References

Steadman R, 1982, Crystallography, Van Nostrand Reinhold (UK) Co. Ltd, Norfolk.

Blakemore J.S. 1974, Solid State Physics 2nd ed., Cambridge University Press, Cambridge

C. Kittel, Introduction to Solid State Physics, 5th Ed., New York:Wiley, 1976.

Sears F.W & Salinger Gerhard L, (1975), Thermodynamics, Kinetic Theory, and Statistical Thermodynamics, 3rd ed., Addison-Wesley Publishing Company, Reading..

H.P Myers, (1997), Introductory Solid State Physics, CRC Pr I Llc

Laszlo Mihaly & Michael C. Martin, (1996), Solid State Physics: Problems and Solutions (Paperback), John Wiley

Wilson J. & M.N Rudden, (1993), Elements of Solid State Physics John Wiley & Sons Inc

Myers H.P., (1997), Introductory Solid State Physics, CRC Pr I Llc

Keer, H.V. (1993), Principles of the Solid State, John Wiley & Sons Inc

Richard Christman J, (1998), Fundamentals of Solid State Physics, John Wiley & Sons Inc

Hans Luth & Harald Ibach, (1995), Solid-State Physics: An Introduction to Principles of Materials Science, Springer Verlag.

John R. Hook & Henry Edgar Hall. Solid State Physics (The Manchester Physics Series); John Wiley and Sons Ltd; 2Rev Ed edition (31 Jan 1995)

XVIII. Main Author of the Module

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XIX. File Structure

The module is given in doc file format: Solid State Physics.doc

Compulsory Readings are given in pdf format: Compulsory readings.pdf