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The Physics of Ferromagnetism



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The Physics of Ferromagnetism

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Preface

The field of magnetism has always steadily developed and new phenomena and/or new materials have appeared. These, we must study ourselves and teach to students. The time of lecture is limited, therefore we prefer to teach basic and fundamental matters rather than new ones. During the stay in the university as the faculty to teach magnetism to students, we realized the difficulty of teaching magnetism. After lecture hours we were asked by Dr. Ascheron, the editor of Springer, to write a book related to magnetism. At first we thought that we do have not enough ability to write a book of magnetism in English. But in recent years, all people are authors and the quality of the contents of a book are judged by the readers. In addition, due to having the co-authors, and not a single author, we accepted his proposal.

This book consists of three parts; part one gives the basis of magnetism, part two discusses magnetic materials and part three, spintronics. Part one includes chapters on magnetostatics, magnetism of atoms, magnetism of solids, exchange interactions, magnetic anisotropies, magnetostrictive effects, magnetic domain, and micromagnetism. Some relations of vector analysis, group theory, and second quantization, which are summarized in the corresponding appendices, are applied in some sections. Details of mathematical processes of some equations in the text are attached in the notes at the end of the section. To help readers who are not familiar with the objects, the relations in the appendices along with equations, figures, and tables in the text are referred in many parts of the text whenever they are used.

Part two is related to magnetic materials which are roughly classified as soft and hard magnetic materials. The fundamental properties of each are described. If both magnetic properties are understood well, we can apply them to individual materials.

Part three discusses spintronics, where the basic phenomena has been known for a long time, but the research field itself is new compared with parts one and two. Chapter 1 treats the history of magnetoresistance research and classification of magnetoresistance effect. Especially, theoretical and experimental treatments of magnetoresistance effect are described in detail. Chapter 2 focuses on the tunnel

magnetoresistance effect. After describing the historical background, development of MgO barrier tunnel magnetoresistance junction which triggered the giant tunnel magnetoresistance is described. Also, Heusler electrode tunnel junctions which are reported much after that is introduced. Chapter 3 is related to magnetic memory, especially the principle, development, and several issues about Magnetoresistive Random Access Memory (MRAM) research are described. In Chap. 4, accompanying technologies for the development of spintronics devices such as spin-polarization measurement and Gilbert damping constant, which are very important values in order to discuss the spin-dynamics of ferromagnets, are introduced.

This book can be used as a reference for researchers. Part one, which would also be useful for researchers, can be used as a textbook for post graduate students who have learned introductory magnetism, group theory, and advanced quantum mechanics. Being written at an advanced level we recommend undergraduate students who begin to learn magnetism to read a plainly written magnetic book first, such as *Physics of Ferromagnetism* (S. Chikazumi, Oxford university Press, 1997), before reading this part. Parts one and two, at least, would also be useful for engineers and technicians working in magnetic materials and devices.

Finally, we hope that this book will be much helpful for students who are beginners in the field of magnetism and also researchers who are now active in magnetic fields.

Sendai
Changchun

Terunobu Miyazaki
Hanmin Jin

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Part I

Foundation of Magnetism

This part introduces fundamental magnetic phenomena and theories. It consists of eight chapters: Basis of magnetism; Magnetism of atoms; Magnetism of solids; Exchange interaction; Magnetic anisotropy; Magnetostriction effects; Magnetic domain; and Micromagnetism. Temperature is in Kelvin (K) unit unless other unit is given explicitly.

Chapter 1

Basis of Magnetism

This chapter reviews mostly the basic macroscopic magnetism. It contains the sections of Basic magnetic laws and magnetic quantities; Magnetic Coulomb's law, static magnetic field, and magnetic circuit; Zeeman energy, magnetization energy, and magnetostatic energy; Thermodynamics for magnetic media; and Hamiltonian of an electric charged particle in static electric and magnetic fields; and Appendices 1 to 3.

1.1 Basic Magnetic Laws and Magnetic Quantities

1.1.1 Basic Laws of Magnetic Forces, Magnetic Induction Vector, and Magnetic Moment

A particle with electric charge q moving in a magnetic field with velocity $\vec{v}$ experiences the Lorentz force (1892)

$$\vec{f} = q\vec{v} \times \vec{B}. \quad (1.1)$$

This relation, called Lorentz force law, also defines the quantity of magnetic induction vector (often tersely called magnetic induction) $\vec{B}$ (T) characterizing the magnetic field. For example, the creatures on the Earth are protected from the solar wind, a stream of energetic particles of electrons, positrons, He^{+1} ions, etc by the magnetosphere, the Earth's magnetic field space extending tens of kilometers outward, which deflects away the charged particles by the Lorentz force. $B \sim 3 \times 10^{-5} \text{ T}$ on the surface of the Earth.

A particle in an inhomogeneous magnetic field $\vec{B}$ in vacuum experiences the force

$$\vec{f} = (\vec{p}_M \cdot \nabla) \vec{B}. \quad (1.2)$$

This relation also defines the quantity of magnetic moment $\vec{p}_M$ ($\text{A} \cdot \text{m}^2$) characterizing the magnetic property of the particle. The magnitude of the quantity per unit mass is called specific magnetization. The equipment of magnetic balance measures the value of magnetic moment directly by using (1.2) through measuring the force. Another application of (1.2) is magnetic separation. A gradient magnetic field produced by a permanent magnet or electromagnet separates large specific magnetization particles from small specific magnetization particles by attracting the former but leaving the latter to drop away freely.

1.1.2 Vectors of Magnetization, Magnetic polarization and Magnetic field, and Magnetic Polarization Moment

Define the vector sum of the magnetic moments per unit volume

$$\vec{M} = \lim_{v \rightarrow 0} \frac{\sum_v \vec{p}_M}{v} (\text{A/m}) \quad (v: \text{volume}) \quad (1.3)$$

magnetization vector (often tersely called magnetization).

The magnetic polarization moment $\vec{p}_J$ and magnetic polarization vector (often tersely called magnetic polarization) $\vec{J}$ is defined by the relation

$$\vec{p}_J = \mu_0 \vec{p}_M \quad (\text{Wb} \cdot \text{m}) \quad (1.4)$$

and

$$\vec{J} = \mu_0 \vec{M} (\text{T}), \quad (1.5)$$

respectively. Here $\mu_0 (\text{N/A}^2)$ is the magnetic constant (also called vacuum permeability). $\vec{p}_J$ and $\vec{p}_M$, and $\vec{J}$ and $\vec{M}$, respectively, describe the same magnetic quantity but with different units. Appropriate unit quantities are used in different cases to make the formulations succinct.

Magnetic field vector (often tersely called magnetic field) $\vec{H}$ is defined by the relation

$$\vec{H} = \frac{\vec{B}}{\mu_0} - \vec{M} (\text{A/m}). \quad (\vec{B} = \mu_0 \vec{H} + \vec{J} (\text{T})) \quad (1.6)$$

In vacuum, $\vec{J} = 0$, so $\vec{H} = \vec{B}/\mu_0$ and $\vec{B}$ describes the same magnetic field using different units.

1.1.3 Maxwell Equations

The Maxwell equations (1861–1862) are

$$\nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t}, \quad (\vec{E}: \text{electric field vector, } t: \text{time}) \quad (1.7)$$

$$\nabla \cdot \vec{D} = \rho, \quad (\rho: \text{free electric charge density}) \quad (1.8)$$

$$\nabla \times \vec{H} = \vec{j} + \frac{\partial \vec{D}}{\partial t}, \quad (\vec{j}: \text{conducting electric current density}) \quad (1.9)$$

$$\nabla \cdot \vec{B} = 0, \quad (1.10)$$

where $\vec{D} = \varepsilon \varepsilon_0 \vec{E}$ is electric displacement vector, ε relative permittivity (often tersely called permittivity), ε_0 electric constant (also called vacuum permittivity), and $\varepsilon \varepsilon_0$ permittivity.

1.1.4 Magnetic Vector Potential

Equation (1.10) shows that $\vec{B}$ is continuous everywhere, so it is a curl of a vector potential $\vec{A}$ (a3.14):

$$\vec{B} = \nabla \times \vec{A}. \quad (1.11)$$

$\vec{A}$ is called magnetic vector potential. The integration of it along a closed circuit l is the magnetic flux through the circuit surface:

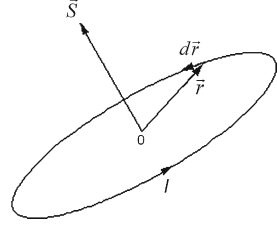
$$\oint_l \vec{A} \cdot d\vec{l} = \int \vec{B} \cdot d\vec{S} \text{ (Wb)}. \quad (\text{a3.27}) \quad (1.12)$$

The linear integration is along the right-hand direction about the circuit surface vector $\vec{S}$ direction (Fig. 1.1). Since

$$\nabla \times (\vec{A} + \nabla \Psi) = \nabla \times \vec{A} = \vec{B} \quad (\text{a3.10}) \quad (1.13)$$

for arbitrary function $\Psi(\vec{r})$, both $\vec{A} + \nabla \Psi$ and $\vec{A}$ depict the same $\vec{B}$, i.e., $\vec{A}$ can be represented by many different expressions. The expression will be restricted by the conditions that it does not include a gradient of any function and

$$\nabla \cdot \vec{A} = 0. \quad (1.14)$$

Fig. 1.1 Closed current coil

1.1.5 Magnetic Moment

In a static magnetic field in vacuum where no current flows, the relations

$$\frac{\partial B_\alpha}{\partial \beta} = \frac{\partial B_\beta}{\partial \alpha} \quad (\alpha, \beta = x, y, z, \nabla \times \vec{B} = \mu_0 \nabla \times \vec{H} = 0) \quad (1.15)$$

hold, and (1.2) can be reformulated to

$$\vec{f} = \sum_{\alpha, \beta}^{x, y, z} p_{M\beta} \frac{\partial B_\alpha}{\partial \beta} \vec{e}_\alpha = \sum_{\alpha, \beta}^{x, y, z} p_{M\beta} \frac{\partial B_\beta}{\partial \alpha} \vec{e}_\alpha = \sum_{\alpha}^{x, y, z} \frac{\vec{p}_M \cdot \partial \vec{B}}{\partial \alpha} \vec{e}_\alpha = \frac{\vec{p}_J \cdot \partial \vec{H}}{\partial \vec{r}}, \quad (1.16)$$

where $\vec{e}_\alpha$ represents the unit vector in the α direction.

Consider the magnetic polarization moment $\vec{p}_J$ and the magnetic field as a system. If $\vec{p}_J$ is shifted by $d\vec{r}$ under the action of the outside force $-\vec{f}$ counterbalancing the internal force of (1.16), the energy of the system E increases by

$$dE = -\vec{f} \cdot d\vec{r} = -\vec{p}_J \cdot d\vec{H}. \quad (1.17)$$

Therefore, $\vec{p}_J$ is related with E by

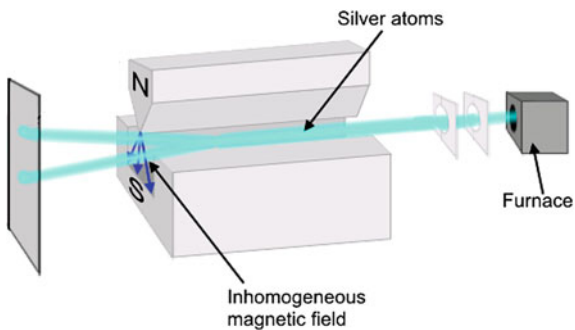
$$\vec{p}_J = -\frac{\partial E}{\partial \vec{H}}. \quad (1.18)$$

1.1.6 Magnetic Moment of Current Coil

One example of magnetic moment is the magnetic moment of a small current coil. Let

$$\vec{S} = \frac{1}{2} \oint_S \vec{r} \times d\vec{r} \quad (1.19)$$

Fig. 1.2 Stern-Gerlach experiment [1]



denote the surface vector of the coil (Fig. 1.1) and I the current flowing in the right-hand direction about the $\vec{S}$ direction. The Lorentz force sensed by the current coil in an inhomogeneous magnetic field is

$$\vec{f} = \frac{I\vec{S} \cdot \partial \vec{B}}{\partial \vec{r}}. \quad (\text{Note 1 of this section}) \quad (1.20)$$

Comparison of this relation with (1.16) reveals that the current coil has a magnetic moment of

$$\vec{p}_M = I\vec{S}. \quad (1.21)$$

1.1.7 Magnetic Moment of Electron Spin

Another example of magnetic moment is the magnetic moment of electron spin. Consider the Stern-Gerlach experiment (1922) in which a thin vapor beam of H, Li, Ag, or another atom of the s-block of the periodic table (group 1 and group 2), formed in a furnace and passing through successively two small apertures separated by certain distance, travels through an inhomogeneous magnetic field and reaches the detector. The magnetic field and its gradient directions are up and down perpendicular to the beam (Fig. 1.2). When the magnetic field is absent the beam does not deflect. If the magnetic field is applied, the beam splits up and down symmetrically under the action of the magnetic force of (1.16). The s-block atom has an s valence electron, and the atomic orbital magnetic moment is zero (Chap. 2). The experiments conclude that an electron has an intrinsic magnetic moment called electron spin magnetic moment, the projects of it in the field direction has only two components of same magnitude and different signs.

1.1.8 Magnetic Field Strength, Magnetic Induction, Magnetization, Permeability, and Susceptibility

The magnitude H of $\vec{H}$ is called magnetic field strength (often tersely called magnetic field), and the projection of $\vec{B}$, $\vec{J}$, and $\vec{M}$ in the direction of $\vec{H}$ B , J , and M is called magnetic induction, magnetic polarization, and magnetization, respectively.

$$\mu\mu_0 = \frac{B}{H} = \frac{J + \mu_0 H}{H} = (\chi + 1)\mu_0 \quad (\text{N/A}^2) \quad (1.22)$$

is called permeability, $\mu = \chi + 1$ is called relative permeability (often tersely called permeability), $\chi\mu_0 = J/H$ is called susceptibility, and $\chi = M/H$ is called relative susceptibility (often tersely called susceptibility).

Note 1

Exploiting the relations of

$$\vec{B}(\vec{r}) \approx \vec{B}(0) + \sum_{\alpha} \frac{\partial \vec{B}}{\partial \alpha} \bigg|_0 \alpha, \quad (1.23)$$

$$\frac{\partial \vec{B}}{\partial \alpha} \equiv \frac{\partial \vec{B}}{\partial \alpha} \bigg|_0 = \frac{\partial \vec{B}(\vec{r})}{\partial \alpha}, \quad (1.24)$$

and

$$\frac{\partial B_z}{\partial z} = - \left(\frac{\partial B_x}{\partial x} + \frac{\partial B_y}{\partial y} \right), \quad (1.10) \quad (1.25)$$

the component x of (1.20), for instance, is proved as

$$\begin{aligned} X &\equiv \frac{1}{I} \left(\vec{f} - \frac{I \vec{S} \cdot \vec{\partial} \vec{B}}{\partial \vec{r}} \right)_x = \left[\oint d\vec{r} \times \vec{B}(\vec{r}) - \frac{1}{2} \oint \frac{(\vec{r} \times d\vec{r}) \cdot \partial \vec{B}}{\partial \vec{r}} \right]_x \\ &= \oint \left[dy \left(\frac{\partial B_z}{\partial x} x + \frac{\partial B_z}{\partial y} y + \frac{\partial B_z}{\partial z} z \right) - dz \left(\frac{\partial B_y}{\partial x} x + \frac{\partial B_y}{\partial y} y + \frac{\partial B_y}{\partial z} z \right) \right] \\ &\quad - \frac{1}{2} \oint \left[(ydz - zdy) \frac{\partial B_x}{\partial x} + (zdx - xdz) \frac{\partial B_y}{\partial x} + (xdy - ydx) \frac{\partial B_z}{\partial x} \right] \\ &= \frac{1}{2} \frac{\partial B_z}{\partial x} \oint d(xy) + \frac{1}{2} \frac{\partial B_z}{\partial y} \oint (dy^2 - dz^2) - \frac{1}{2} \frac{\partial B_y}{\partial x} \oint d(xz) \\ &\quad - \frac{1}{2} \frac{\partial B_x}{\partial x} \oint d(yz) - \frac{\partial B_y}{\partial y} \oint d(yz) = 0. \end{aligned} \quad (1.26)$$

1.2 Magnetic Coulomb's law, Static Magnetic Field, and Magnetic Circuit

Consider a static magnetic system.

1.2.1 Magnetic Charge and Magnetic Coulomb's Law

Define

$$\rho_m = -\nabla \cdot \vec{J} \quad (1.27)$$

as volume magnetic charge density. Inserting (1.6) and (1.27) into (1.10) we get

$$\nabla \cdot \vec{H} = \frac{\rho_m}{\mu_0}. \quad (1.28)$$

$\vec{H}$ is the sum of the magnetic field vectors produced by electric currents and magnetic media $\vec{H}_I$ and $\vec{H}_m$:

$$\vec{H} = \vec{H}_I + \vec{H}_m. \quad (1.29)$$

The Maxwell equations for $\vec{H}_I$ are

$$\nabla \times \vec{H}_I = \vec{j}, \quad \nabla \cdot \vec{H}_I = 0, \quad (1.30)$$

and the relations of $\vec{H}_I$ with the magnetic induction $\vec{B}_I$ and magnetic vector potential $\vec{A}_I$ both produced by electric current are

$$\vec{B}_I = \mu_0 \vec{H}_I = \nabla \times \vec{A}_I. \quad (1.31)$$

The Maxwell equations for $\vec{H}_m$ are completely the same in form with those of static electric field $\vec{E}$ in vacuum, that is

$$\nabla \times \vec{H}_m = 0, \quad \nabla \cdot \vec{H}_m = \frac{\rho_m}{\mu_0}, \quad (1.32)$$

$$\nabla \times \vec{E} = 0, \quad \nabla \cdot \vec{E} = \frac{\rho}{\varepsilon_0}, \quad (1.33)$$

in which $\vec{H}_m$, ρ_m , and μ_0 corresponds to $\vec{E}$, ρ and ε_0 , respectively. The left relations of (1.32) and (1.33) show that $\vec{H}_m$ as well as $\vec{E}$ are gradients of scalar potentials (a3.13),

$$\vec{H}_m = -\nabla V_m, \quad (1.34)$$

$$\vec{E} = -\nabla V. \quad (V: \text{electric potential}) \quad (1.35)$$

V_m is called magnetic scalar potential or tersely magnetic potential. The symmetrical relations of (1.32) with (1.33) and (1.34) with (1.35) reveal that the expressions of $\vec{H}_m$ and V_m produced by a magnetic point charge q_m at a position $\vec{r}$ from the charge are the same in form with those of $\vec{E}$ and V produced by an electric point charge q , that is

$$\vec{H}_m = \frac{q_m}{4\pi\mu_0 r^3} \vec{r}, \quad \vec{E} = \frac{q}{4\pi\epsilon_0 r^3} \vec{r}, \quad (1.36)$$

$$V_m = \frac{q_m}{4\pi\mu_0 r}, \quad V = \frac{q}{4\pi\epsilon_0 r}. \quad (1.37)$$

In vacuum, the force experienced by a magnetic body in an applied magnetic field $\vec{H}$ is

$$\vec{f} = \int (\vec{J} \cdot \nabla) \vec{H} dv = \oint \vec{H} \sigma_m dS + \int \vec{H} \rho_m dv, \quad (\text{Note 1 of this section}) \quad (1.38)$$

where

$$\sigma_m \equiv \vec{J} \cdot \frac{d\vec{S}}{dS} \quad (1.39)$$

is the surface magnetic charge density on the surface of the magnetic body and $d\vec{S}$ is the differential surface vector normal to the surface and directed outward. Equation (1.38) shows that a magnetic point charge $q_m (= \sigma_m dS \text{ or } = \rho_m dv)$ senses a force

$$\vec{f} = q_m \vec{H}. \quad (1.40)$$

In the case where $\vec{H}$ is the magnetic field produced by a magnetic point charge q'_m (1.36) apart r from q_m , (1.40) becomes the magnetic Coulomb's law

$$\vec{f} = \frac{q_m q'_m \vec{r}}{4\pi\mu_0 r^3}. \quad (1.41)$$

This law had been found experimentally in 1785 and has ever been the fundamental law of magnetism until up to the end of the following century. Correspondingly, the magnetic charge and magnetic field vector had been the fundamental magnetic quantities. According to modern magnetism, the fundamental laws are (1.1) and (1.2) and Maxwell equations (1.7)–(1.10). Correspondingly, the fundamental magnetic quantities are magnetic induction vector and magnetic moment.

The above arguments show that the behaviors of q_m and $\vec{H}_m$ are completely the same with those of q and $\vec{E}$. The magnetic Coulomb's law is very useful as is demonstrated below.

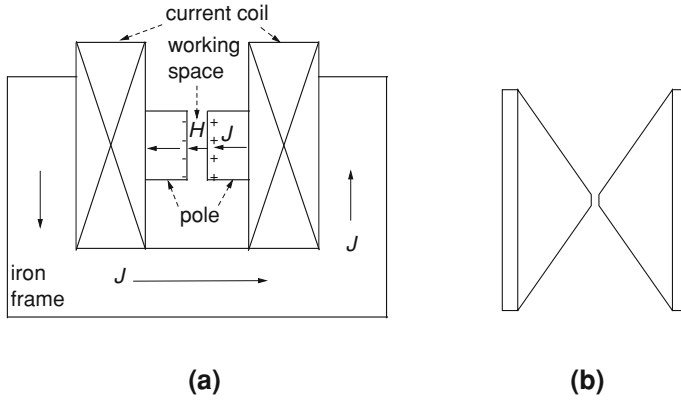


Fig. 1.3 **a** Flat pole surface electromagnet; **b** Cone-shaped pole

1.2.2 Examples of Application of Magnetic Coulomb's Law

1.2.2.1 Magnetic Field of Electromagnet

Consider an electromagnet (Fig. 1.3).

The pure Fe metal core is magnetized by the current coils wrapped around the poles. The magnetic field in the work space between the pole faces is mainly produced by the positive and negative magnetic charges on the vis-a-vis pole faces. The field produced by the current coil is much smaller. Usually Fe-35%Co alloy, which has the largest value of saturation magnetic polarization of $J_s = 2.46$ T at room temperature (R.T.), is used as the pole material. Approximately 2%V is added in the alloy to improve the mechanical strength. If a flat pole (Fig. 1.3a) is used and the gap between the pole faces is narrow, the magnetic induction in the space is $\mu_0 H = J$ T and its upper limit is $J_s = 2.46$ T. The attraction between the two pole surfaces can reach as large as $J_s^2/2\mu_0 = 2.4 \times 10^6$ N/m². If the pole is made appropriately cone shaped with small flat top surface (Fig. 1.3b), the upper limit of the field at the center of the space can reach as large as ~ 4 T but at the expense of much smaller work space.

1.2.2.2 Magnetic Moment of Magnetic Dipole

Consider a tiny columnar magnetic bar of length l and cross-section area S with the magnetic polarization vector $\vec{J}$ in the length direction $\vec{l}$. The magnetic charges $q_m = JS$ and $-q_m$ appear on the two base surfaces which constitute a magnetic dipole in the same way as an electric dipole constituted by a pair of positive and negative electric charges $\pm q$. The magnetic dipole in an inhomogeneous field senses a force of

$$\vec{f} = q_m \left[\vec{H}(\vec{r}_{q_m}) - \vec{H}(\vec{r}_{-q_m}) \right] = (q_m \vec{l} \cdot \nabla) \vec{H}. \quad (1.42)$$

Comparison of (1.42) with (1.2) reveals that magnetic dipole $q_m \vec{l}$ has a magnetic polarization moment of

$$\vec{p}_J = q_m \vec{l}. \quad (1.43)$$

1.2.2.3 Torque Sensed by a Magnetic Moment in a Magnetic Field

The magnetic dipole in the field $\vec{H}$ is under action of torque

$$\vec{L} = \vec{l} \times q_m \vec{H} = \vec{p}_J \times \vec{H}. \quad (1.44)$$

The last of the above equation is the general expression of the torque sensed by a magnetic moment in a magnetic field.

1.2.2.4 Magnetic Field Produced by a Magnetic Moment

V_m and $\vec{H}_m$ produced by a magnetic moment of magnetic dipole at $\vec{r} (r \gg l)$ from the dipole are

$$V_m = \frac{q_m}{4\pi\mu_0 r_{q_m}} - \frac{q_m}{4\pi\mu_0 r_{-q_m}} = \frac{\vec{p}_M \cdot \vec{r}}{4\pi r^3},$$

(r_{q_m} : the distance from magnetic charge q_m)

$$(1.45)$$

$$\vec{H}_m = -\nabla V_m = \frac{1}{4\pi} \left[\frac{3(\vec{p}_M \cdot \vec{r}) \vec{r}}{r^5} - \frac{\vec{p}_M}{r^3} \right]. \quad (1.46)$$

The last expressions of (1.45) and (1.46) are the general expressions of V_m and $\vec{H}_m$ produced by a magnetic moment. Since

$$\nabla \cdot \vec{H}_m(\vec{r}) = 0, \quad ((1.32), \rho_m = 0) \quad (1.47)$$

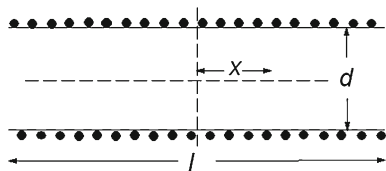
it holds

$$\mu_0 \vec{H}_m = \nabla \times \vec{A}_m(\vec{r}). \quad (1.48)$$

$\vec{A}_m(\vec{r})$ produced by $\vec{p}_J$ is

$$\vec{A}_m(\vec{r}) = \frac{\vec{p}_J \times \vec{r}}{4\pi r^3} = \frac{1}{4\pi} \nabla \times \frac{\vec{p}_J}{r}. \quad (\text{Note 2 of this section}) \quad (1.49)$$

For a uniformly magnetized sphere, (1.45) through (1.49) holds strictly at any position outside the magnet (Note 3 of this section).

Fig. 1.4 Solenoid

1.2.3 Magnetic Field Produced by Electric Current

$\vec{A}_I$ produced by an electric current distribution of current density $\vec{j}$ is (Note 4 of this section)

$$\vec{A}_I = \frac{\mu_0}{4\pi} \int \frac{\vec{j}}{r} dv. \quad (r: \text{distance between the observation point and } \vec{j} dv) \quad (1.50)$$

$\vec{H}_I$ produced by current I flowing in the circuit l is

$$\begin{aligned} \vec{H}_I &= \frac{1}{\mu_0} \nabla \times \vec{A}_I = \frac{I}{4\pi} \oint \nabla \times \frac{d\vec{l}}{r} = \frac{I}{4\pi} \oint (\nabla \frac{1}{r}) \times d\vec{l} \\ &= \frac{I}{4\pi} \oint \frac{d\vec{l} \times \vec{r}}{r^3} \quad (r: \text{distance between the observation point and } d\vec{l}, \text{ (a3.18)}) \end{aligned} \quad (1.51)$$

which is just the Biot-Savart law.

A solenoid is used to produce a field within it. The magnetic field on the axis in a solenoid of length l , diameter d , number of coil per unit length n , and current I (Fig. 1.4) is in the axis direction, and the strength at distant x from the center of the solenoid is

$$H_I = n \frac{I}{2} \left[\frac{l + 2x}{\sqrt{d^2 + (l + 2x)^2}} + \frac{l - 2x}{\sqrt{d^2 + (l - 2x)^2}} \right], \quad (1.52)$$

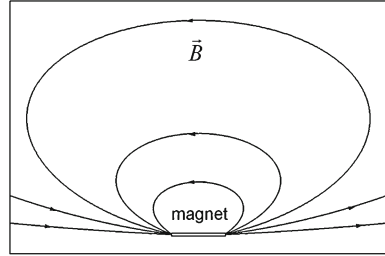
and if $l \gg d$, the magnetic field is very uniform in a wide range of space near the center of the solenoid with the value

$$H_I = nI. \quad (1.53)$$

The upper limit of the field is restricted by the increase of the temperature of the solenoid caused by the Joule heat, and in usual $\mu_0 H$ is smaller than ~ 0.2 T.

A small number of high magnetic field laboratories around the world can produce as high as 30 T static fields by tremendously powerful cooling of the solenoid. A superconductor solenoid (also called superconducting magnet) has no electric

Fig. 1.5 Magnetic induction lines in the space produced by a magnetic bar



resistance below the critical current of superconductivity. The current can be very large which can produce as high as 30 T static magnetic field.

As large as over 100 T pulse magnetic field can be produced in a coil by instantly discharging the electric charge stored in a very large capacitance. The upper limit of the field is restricted by mechanical destruction of the coil under the strong repulsing forces between the current segments.

1.2.4 Volume Integral of Scalar Products of $\vec{H}_m$ with $\vec{H}_I$, $\vec{B}_m$, and $\vec{B}$

If static magnetic media and electric currents are distributed in a finite space, it holds

$$\int_{\infty} \vec{H}_I \cdot \vec{H}_m dv = \int_{\infty} \vec{B}_m \cdot \vec{H}_m dv = \int_{\infty} \vec{B} \cdot \vec{H}_m dv = 0. \quad (\text{Note 5 of this section}) \quad (1.54)$$

1.2.5 Magnetic Circuit

Consider the space distribution of $\vec{B}$ produced by a thin uniformly magnetized bar in the axis direction (Fig. 1.5). The total magnetic flux emitted from the bar into the space is

$$\Phi = \int d\Phi = \int_S \vec{B} \cdot d\vec{S}. \quad \left(\int_S \text{ is over the central section of the bar} \right) \quad (1.55)$$

A locus of $\vec{B}$ forms a closed magnetic induction line (Fig. 1.5). A magnetic flux tube is formed with the induction lines covering the tube surface surrounding a small magnetic flux $\Delta\Phi = B dS$ passing through the section. A pair of magnetic charges

is formed on the two base surfaces of the bar and the integration of H in the space along the induction line l in a flux tube between the two bases is

$$\int_{+base}^{-base} H dl = \Delta \Phi \int_{+base}^{-base} \frac{dl}{\mu \mu_0 dS} = \Delta \Phi r_m = \Delta V_m. \quad (1.56)$$

$\frac{dl}{\mu \mu_0 dS}$ is called the magnetic resistance of the segment and $r_m = \int_{+base}^{-base} \frac{dl}{\mu \mu_0 dS}$ the magnetic resistance of the tube between the two bases. The values of the potential difference ΔV_m are the same for all parallel connected tubes. These parallel connected magnetic circuits completely correspond to the parallel electric circuits, (1.55) corresponds to the electric counterpart of Kirchhoff's current law that the total current of a parallel connected circuit system is the sum of the currents of the circuits, and (1.56) corresponds to the Ohm's law. Here ΔV_m , $\Delta \Phi$, and r_m correspond to the electric potential difference, a current flowing in a parallel connected circuit and the electric resistance of the circuit, respectively. Equation (1.56) shows that under a given ΔV_m , smaller the magnetic resistance of a magnetic circuit larger the magnetic flux in the circuit. One application of the above concept is magnetic shielding. The work space is covered by a wall made up by a large μ ($\sim 10^5$) magnetic material. The magnetic flux of the field of the Earth ($\mu_0 H \sim 3 \times 10^{-5}$ T) and the other field near the work space are drawn into the wall thus decreasing the field in the work space by several orders. In this way, for instance, an extremely low magnetic field space is constructed for the research of human body magnetic field of $10^{-13} \sim 10^{-8}$ T [2].

Note 1

The α component of the force is

$$\begin{aligned} f_\alpha &= \int \vec{J} \cdot \nabla H_\alpha dv & (1.2) \\ &= \int [\nabla \cdot (H_\alpha \vec{J}) - H_\alpha \nabla \cdot \vec{J}] dv & (a3.16) \\ &= \oint H_\alpha \sigma_m dS + \int H_\alpha \rho_m dv. & ((a3.25), (1.39), (1.27)) \quad (1.57) \end{aligned}$$

Note 2

$$\begin{aligned} \mu_0 \vec{H}_m &= \nabla \times \vec{A}_m(\vec{r}) \\ &= -\mu_0 \nabla V_m(\vec{r}) = -\nabla \left(\frac{\vec{p}_J \cdot \vec{r}}{4\pi r^3} \right) & ((1.48), (1.46), (1.45)) \\ &= -\vec{p}_J \times \left(\nabla \times \frac{\vec{r}}{4\pi r^3} \right) - (\vec{p}_J \cdot \nabla) \frac{\vec{r}}{4\pi r^3} & (a3.15) \end{aligned}$$

$$\begin{aligned}
&= \left(\nabla \cdot \frac{\vec{r}}{4\pi r^3} \right) \vec{p}_J - (\vec{p}_J \cdot \nabla) \frac{\vec{r}}{4\pi r^3} \quad \left(\nabla \times \frac{\vec{r}}{r^3} = \nabla \cdot \frac{\vec{r}}{r^3} = 0 \quad (r \neq 0) \right) \\
&= \nabla \times \left(\vec{p}_J \times \frac{\vec{r}}{4\pi r^3} \right) \\
&= \nabla \times \left[\left(\nabla \frac{1}{4\pi r} \right) \times \vec{p}_J \right] \quad (\text{a3.19}) \\
&= \nabla \times \left(\nabla \times \frac{\vec{p}_J}{4\pi r} \right). \quad (\text{a3.18}) \quad (1.58)
\end{aligned}$$

Note 3

V_m satisfies the Laplace equation axially symmetrical around the magnetization direction:

$$\nabla^2 V_m = \frac{1}{r^2} \left[\frac{\partial}{\partial r} \left(r^2 \frac{\partial V_m}{\partial r} \right) + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial V_m}{\partial \theta} \right) \right] = 0, \quad (\text{a3.23}) \quad (1.59)$$

where θ is the angle between $\vec{r}$ and the magnetization direction. Inserting

$$V_m(r, \theta) = R(r)\Theta(\theta) \quad (1.60)$$

into (1.59) we get

$$\frac{1}{R(r)} \frac{d}{dr} \left[r^2 \frac{dR(r)}{dr} \right] = - \frac{1}{\Theta(\theta) \sin \theta} \frac{d}{d\theta} \left[\sin \theta \frac{d\Theta(\theta)}{d\theta} \right]. \quad (1.61)$$

The left of the equation is the function of r , and the right is the function of θ , so they should equal to a constant λ . A solution of (1.61) is $\lambda = l(l+1)$ ($l = 0$ or a positive integer),

$$R_l(r) = a_l r^l + \frac{b_l}{r^{l+1}}, \quad (a_l, b_l: \text{constants}) \quad (1.62)$$

$$\Theta_l(\theta) = P_l(\cos \theta) = \frac{1}{2^l l!} \frac{d^l}{d(\cos \theta)^l} (\cos^2 \theta - 1)^l, \quad (1.63)$$

where $P_l(\cos \theta)$ is the Legendre polynomial. The common solution of (1.59) is

$$V_m(r, \theta) = \sum_l^{0,1,2,\dots} \left(a_l r^l + \frac{b_l}{r^{l+1}} \right) P_l(\cos \theta). \quad (1.64)$$

Applying the boundary conditions of

$$V_m(r \gg r_0, \theta) = \frac{\vec{p}_M \cdot \vec{r}}{4\pi r^3} = \frac{p_M}{4\pi r^2} P_1(\cos \theta), \quad (r_0: \text{radius of the magnet}) \quad (1.65)$$

$$V_m(\vec{r}_{0-}) = \frac{1}{3} M r_0 \cos \theta = V_m(\vec{r}_{0+}) = \sum_l^{0,1,2,\dots} \left(a_l r_0^l + \frac{b_l}{r_0^{l+1}} \right) P_l(\cos \theta), \quad (1.66)$$

where $V_m(\vec{r}_{0-})$ and $V_m(\vec{r}_{0+})$ are the magnetic potentials on the magnet surface in and out of the magnet, we get the final solution of

$$V_m(r, \theta) = \frac{\vec{p}_M \cdot \vec{r}}{4\pi r^3}, \quad (r \geq r_0) \quad (1.67)$$

The above expression being the same with the last expression of (1.45), the expressions of $\vec{H}_m$ (1.46) and $\vec{A}_m$ (1.49) also hold anywhere outside the spherical magnet.

Note 4

$$\begin{aligned} \nabla \times \vec{B}_I &= \mu_0 \nabla \times \vec{H}_I = \nabla \times \nabla \times \vec{A}_I = \nabla \nabla \cdot \vec{A}_I - \nabla^2 \vec{A}_I = -\nabla^2 \vec{A}_I = \mu_0 \vec{j}. \\ &((1.30), (1.31), (a3.12), (1.14)) \end{aligned} \quad (1.68)$$

The last relation of the above equation has the same form with

$$\nabla^2 V = -\frac{\rho}{\varepsilon_0} \quad (1.69)$$

for the electric potential V in vacuum. Here $\vec{A}_I$, $\vec{j}$, and μ_0 correspond to V , ρ , and $1/\varepsilon_0$, respectively. The solution of (1.69) being well known as

$$V = \frac{1}{4\pi \varepsilon_0} \int \frac{\rho dv}{r}, \quad (1.70)$$

the solution of the last relation of (1.68) is obtained directly as (1.50).

Note 5

$$\mu_0 \int_{\infty} \vec{H}_I \cdot \vec{H}_m dv = \int_{\infty} (\nabla \times \vec{A}_I) \cdot \vec{H}_m dv \quad (1.31)$$

$$= \int_{\infty} \left[\vec{A}_I \cdot (\nabla \times \vec{H}_m) + \nabla \cdot (\vec{A}_I \times \vec{H}_m) \right] dv \quad (a3.17)$$

$$= \oint_{\infty} (\vec{A}_I \times \vec{H}_m) \cdot d\vec{S} = 0. \quad ((1.32), (a3.25),$$

$$\vec{A}_I(r \rightarrow \infty) \propto \oint_l \frac{d\vec{l}}{r} = \int d\vec{S}_{\text{coil}} \times \nabla \frac{1}{r} \propto \frac{1}{r^2} \quad (a3.24),$$

$$H_m(r \rightarrow \infty) \propto \frac{1}{r^3} \quad (1.46), S(r \rightarrow \infty) \propto r^2 \quad (1.71)$$

$$\begin{aligned} \int_{\infty} \vec{B}_m \cdot \vec{H}_m dv &= \int_{\infty} (\nabla \times \vec{A}_m) \cdot \vec{H}_m dv \\ &= \frac{1}{\mu_0} \int_{\infty} \left[\vec{A}_m \cdot (\nabla \times \vec{H}_m) + \nabla \cdot (\vec{A}_m \times \vec{H}_m) \right] dv \quad (a3.17) \end{aligned}$$

$$= \oint_{\infty} (\vec{A}_m \times \vec{H}_m) \cdot d\vec{S} = 0. \quad ((1.32), (a3.25),$$

$$\vec{A}_m(\vec{r} \rightarrow \infty) \propto \frac{1}{r^2} \quad (1.49) \quad (1.72)$$

$$\int_{\infty} \vec{B} \cdot \vec{H}_m dv = \int_{\infty} (\vec{B}_m + \mu_0 \vec{H}_I) \cdot \vec{H}_m dv = 0. \quad (1.73)$$

1.3 Zeeman Energy, Magnetization Energy, and Magnetostatic Energy

1.3.1 Zeeman Energy

Assume that a static magnetic field is distributed in a finite space into which a magnetic moment is brought to position $\vec{r}$ in vacuum from infinite distance. The magnetic polarization moment at the position is $\vec{p}_J(\vec{r})$. The work done by the outside force which is the change in the energy of the system consisted of the field and the magnetic moment is

$$E = - \int_{\infty}^{\vec{r}} \frac{\vec{p}_J \cdot \partial \vec{H}}{\partial \vec{r}} \cdot d\vec{r} = - \int_0^{\vec{H}(\vec{r})} \vec{p}_J \cdot d\vec{H} \quad (1.16)$$

$$= -\vec{p}_J(\vec{r}) \cdot \vec{H}(\vec{r}) + \int_{\vec{p}_J(\infty)}^{\vec{p}_J(\vec{r})} \vec{H} \cdot d\vec{p}_J. \quad (1.74)$$

If $\vec{p}_J(\vec{r})$ remains unchanged during the process, the work done is

$$- \vec{p}_J(\vec{r}) \cdot \vec{H}(\vec{r}), \quad (1.75)$$

which is the interaction energy between $\vec{p}_J(\vec{r})$ and $\vec{H}(\vec{r})$, that is, the potential energy of the magnetic polarization moment in the field. This kind of potential energy is called Zeeman energy.

1.3.2 Magnetization Energy

The last expression in (1.74) also includes the integral of

$$\vec{H} \cdot d\vec{p}_J. \quad (1.76)$$

Apparently $\vec{H} \cdot d\vec{p}_J$ is the work done to change the magnetic polarization moment by $d\vec{p}_J$ in the field $\vec{H}$, which is called magnetization energy.

1.3.3 Magnetostatic Energy

1.3.3.1 Magnetic Energy in an Electromagnetic System

Assume that a system of electromagnetic media, electric sources, and steady electric currents are distributed within a finite space. It holds

$$\begin{aligned} & \int_{\infty} \left[\vec{E} \cdot \left(\vec{j} + \frac{\partial \vec{D}}{\partial t} \right) + \vec{H} \cdot \frac{\partial \vec{B}}{\partial t} \right] dv \\ &= \int_{\infty} \left[\vec{E} \cdot (\nabla \times \vec{H}) - \vec{H} \cdot (\nabla \times \vec{E}) \right] dv \quad ((1.9), (1.7)) \\ &= \int_{\infty} \nabla \cdot (\vec{H} \times \vec{E}) dv \end{aligned}$$

$$= \oint_{S=\infty} (\vec{H} \times \vec{E}) \cdot d\vec{S} = 0, \quad ((a3.17), (a3.25)) \quad (1.77)$$

$$\vec{j} = \sigma (\vec{E} + \vec{E}_S), \quad (1.78)$$

where σ is electric conductivity and $\vec{E}_S$ is the equivalent electric field of electromotive force $\oint_l \vec{E}_S \cdot d\vec{l}$ of non-electric origin. The energy $\int \int \vec{j} \cdot \vec{E}_S dv dt$ provided by the electric source transforms to three kinds of energy as

$$\int \int \vec{j} \cdot \vec{E}_S dv dt = \int \int \vec{j} \cdot \left(\frac{\vec{j}}{\sigma} - \vec{E} \right) dv dt \quad (1.78)$$

$$= \int \int \frac{j^2}{\sigma} dv dt + \int \int \vec{E} \cdot d\vec{D} dv + \int \int \vec{H} \cdot d\vec{B} dv. \quad (1.77) \quad (1.79)$$

The first, second, and third terms in the last expression are the Joule heat, the change in electric energy, and magnetic energy.

1.3.3.2 Magnetic Field Energy

The magnetic energy $\int \int \vec{H} \cdot d\vec{B} dv$ can be broken down into two parts:

$$\int \int \vec{H} \cdot d\vec{B} dv = \int \int \vec{H} \cdot d\vec{J} dv + \int \frac{\mu_0 H^2}{2} dv. \quad (1.80)$$

The first term in the right is the magnetization energy. The second term is the magnetic field energy which is the sum of the magnetic field energy of the field produced by currents and that produced by magnetic media:

$$\int \frac{\mu_0 H^2}{2} dv = \int \frac{\mu_0 H_I^2}{2} dv + \int \frac{\mu_0 H_m^2}{2} dv. \quad ((1.29), (1.54)) \quad (1.81)$$

1.3.3.3 Magnetic Moment Interaction Energy, Magnetic Charge Interaction Energy, and Magnetostatic Energy

The magnetic field energy produced by magnetic moments can be reformulated as

$$\int \frac{\mu_0 H_m^2}{2} dv = -\frac{1}{2} \int \vec{J} \cdot \vec{H}_m dv = \frac{1}{2} \left(\int \rho_m V_m dv + \oint \sigma_m V_m dS \right). \quad (\text{Note 1 of this section}) \quad (1.82)$$

The second expression of the above equation represents the interaction energy between magnetic moments. The third expression represents the interaction energy between magnetic charges. In brief summary, all of the field energy of the field produced by magnetic moments, the interaction energy between magnetic moments, and the interaction energy between magnetic charges refer to the same energy. The only differences between them are the physical pictures, and they are called magnetostatic energy.

Note 1

Since

$$\int \vec{B} \cdot \vec{H}_m dv = \int \left[\mu_0 \left(\vec{H}_I + \vec{H}_m \right) + \vec{J} \right] \cdot \vec{H}_m dv = 0, \quad (1.54) \quad (1.83)$$

it holds

$$\begin{aligned} \int \frac{\mu_0 H_m^2}{2} dv &= -\frac{1}{2} \int \vec{J} \cdot \vec{H}_m dv & (1.54) \\ &= \frac{1}{2} \int \vec{J} \cdot (\nabla V_m) dv = \frac{1}{2} \int \left[-(\nabla \cdot \vec{J}) V_m + \nabla \cdot (\vec{J} V_m) \right] dv \\ &\quad ((1.34), (a3.16)) \\ &= \frac{1}{2} \left(\int \rho_m V_m dv + \oint \sigma_m V_m dS \right). \\ &\quad ((1.27), (a3.25), (1.39)) & (1.84) \end{aligned}$$

1.4 Thermodynamics for Magnetic Media

1.4.1 Principles of Thermodynamics for Magnetic Media

The increase in internal energy of a system dU equals to the sum of the heat supplied to the system δQ and the work done on the system $\sum_i X_i dx_i$:

$$dU = \delta Q + \sum_i X_i dx_i. \quad (1.85)$$

Here X_i and x_i are a generalized force and coordinate,

$$\delta Q \leq T dS, \quad (1.86)$$

where T and S are the temperature and entropy. The equal and non-equal relation of (1.86) applies to reversible and irreversible processes, respectively.

The entropy of an isolated system increases steadily during an irreversible process and reaches a maximum when the system stabilizes.

In the following a unit volume of an infinite magnetic medium of uniform magnetization under the atmospheric pressure is considered as the system in order to exclude magnetostatic energy from consideration. During a reversible process, the change of the internal energy is

$$\begin{aligned} dU &= TdS + \sum_i X_i dx_i = TdS + \vec{H} \cdot d\vec{J} + \sum_i^{X_i dx_i \neq \vec{H} \cdot d\vec{J}} X_i dx_i \\ &= TdS + HdJ + \sum_i^{X_i dx_i \neq HdJ} X_i dx_i, \end{aligned} \quad (1.87)$$

where $\sum_i^{X_i dx_i \neq HdJ} X_i dx_i$ is the work other than HdJ .

1.4.2 Free Energy and Thermal Potential

The free energy (Helmholtz free energy) F , thermal potential (Gibbs's free energy) G , and their differentials are

$$F \equiv U - TS, \quad (1.88)$$

$$dF = -SdT + \vec{H} \cdot d\vec{J} + \sum_i^{X_i dx_i \neq \vec{H} \cdot d\vec{J}} X_i dx_i = -SdT + HdJ + \sum_i^{X_i dx_i \neq HdJ} X_i dx_i, \quad (1.89)$$

$$G \equiv F - \sum_i X_i x_i = F - \vec{H} \cdot \vec{J} - \sum_i^{X_i x_i \neq \vec{H} \cdot \vec{J}} X_i x_i = F - HJ - \sum_i^{X_i x_i \neq HJ} X_i x_i, \quad (1.90)$$

$$\begin{aligned} dG &= -SdT - \sum_i x_i dX_i = -SdT - \vec{J} \cdot d\vec{H} - \sum_i^{x_i dX_i \neq \vec{J} \cdot d\vec{H}} x_i dX_i \\ &= -SdT - JdH - \sum_i^{x_i dX_i \neq JdH} x_i dX_i. \end{aligned} \quad (1.91)$$

$-\vec{H} \cdot \vec{J} = -HJ$ in (1.90) is the potential energy of the magnetization in the field, i.e., the interaction energy between the system and the field applied from outside. If the system is selected to include the field, $-\vec{H} \cdot \vec{J} = -HJ$ becomes a part of the

energy of the system and G of (1.90) is no longer the thermal potential but becomes the free energy of the system.

1.4.3 Stabilization Conditions for a System at Constant Temperature

Suppose X_i and x_i other than H and J remain constant. The stabilization conditions for a system at constant temperature are:

In the absence of magnetic field, $\vec{J}$ takes the value and direction to make the F minimum.

In the presence of magnetic field, $\vec{J}$ takes the value and direction to make the G minimum (Note 1 of this section).

With the above characteristics of F and G , they are often tersely called energy.

It can be deduced from $dF = 0$ (1.89) and $dG = 0$ (1.91) that at an equilibrium state under a constant temperature the following relations hold:

$$\vec{H} - \frac{\partial F}{\partial \vec{J}} = 0, \quad H - \frac{\partial F}{\partial J} = 0. \quad (1.92)$$

$$\vec{J} = -\frac{\partial G}{\partial \vec{H}}, \quad J = -\frac{\partial G}{\partial H}. \quad (1.93)$$

The relations of (1.92) are the equilibrium conditions of the forces that the sum of the force acting on the system $\vec{H}$ (or H) and internal force $-\frac{\partial F}{\partial \vec{J}}$ (or $-\frac{\partial F}{\partial J}$) equals zero. Equation (1.93) shows that $\vec{J}$ (or J) equals to $-\frac{\partial G}{\partial \vec{H}}$ (or $-\frac{\partial G}{\partial H}$). For a system consisting of N same magnetic ions, G is a function of the distribution function Z :

$$G = -k_B T N \ln Z. \quad (k_B: \text{Boltzmann constant}) \quad (1.94)$$

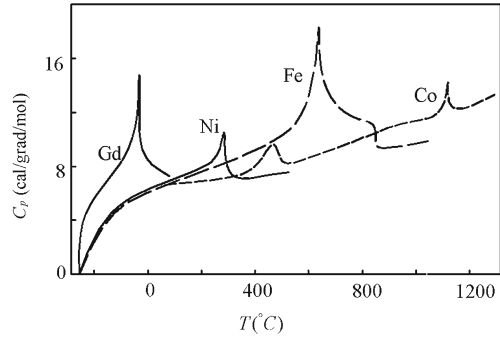
The localized magnetic ions being distinguishable the classic statistics is applicable and Z is

$$Z = \sum_n \exp\left(-\frac{E_n}{k_B T}\right), \quad (1.95)$$

where E_n is the n^{th} eigenenergy of the ion. If $\{E_n\}$ is known, J can be calculated from the relation of

$$J = -\frac{\partial G}{\partial H} = -\frac{N}{Z} \sum_n \frac{\partial E_n}{\partial H} \exp\left(-\frac{E_n}{k_B T}\right). \quad (1.96)$$

Fig. 1.6 Specific heat vs temperature for Fe, Co, Ni, and Gd metals [3]



1.4.4 First- and Second-Order Transformations

First consider the crystal structure transformation. The thermal potential of the crystal and its differential are

$$G = F + pv - \sum_i^{X_i x_i \neq -pv} X_i x_i, \quad (1.97)$$

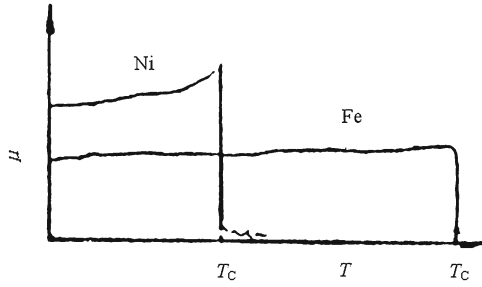
$$dG = vdp - SdT, \quad \left(\sum_i^{x_i dX_i \neq -vd p} x_i dX_i = 0 \right) \quad (1.98)$$

where p is the pressure in the system and v is the volume of the crystal. The transformation accompanies discontinuous change of the volume $v = \partial G / \partial p$ and absorption or release of the latent heat caused by rearrangement of the atoms. The latent heat is the product of the change of the entropy and the phase transformation temperature which remains constant. Therefore, $S = -\partial G / \partial T$ also changes discontinuously. Such a transformation for which the first partial derivatives of G with respect to temperature and general force change discontinuously with temperature is called first-order transformation. This kind of transformation has some hysteresis phenomenon, i.e., the phase transformation temperatures are somewhat different for the opposite phase transformations.

Magnetic transformation, such as ferromagnetism $\leftrightarrow$ paramagnetism, is different from the first-order transformation. The first-order partial derivatives of G with respect to temperature and general force, $S = -\partial G / \partial T$ and $J = -\partial G / \partial H$, change continuously. But the specific heat $C_p = T \partial S / \partial T = -T \partial^2 G / \partial T^2$ and differential susceptibility $\partial J / \partial H = -\partial^2 G / \partial H^2$ which are the second-order partial derivatives change discontinuously (Figs. 1.6 and 1.7). Such kind of transformation is called second-order transformation.

A small number of magnetic media abruptly and markedly change J through crystal structure or magnetic transformation, such as from monoclinic to orthorhombic

Fig. 1.7 AC permeability (0.16 kA/m, 5 kHz) vs temperature for Fe and Ni metals [4]



or from ferrimagnetic to ferromagnetic transformation, when H is changed. Such kind of transition induced by magnetic field is called metamagnetic transition.

1.4.5 Magneto-Caloric Effect

Let

$$U' = U - HJ. \quad (1.99)$$

During a reversible process

$$dU' = TdS - JdH. \quad (1.100)$$

Take T and H as the independent variables. During an adiabatic process dS is zero:

$$dS = \frac{1}{T} \left[\frac{\partial U'}{\partial T} dT + \left(\frac{\partial U'}{\partial H} + J \right) dH \right] = 0, \quad (1.100) \quad (1.101)$$

where

$$\frac{\partial U'}{\partial T} = T \frac{\partial S}{\partial T} = C_H \quad (1.102)$$

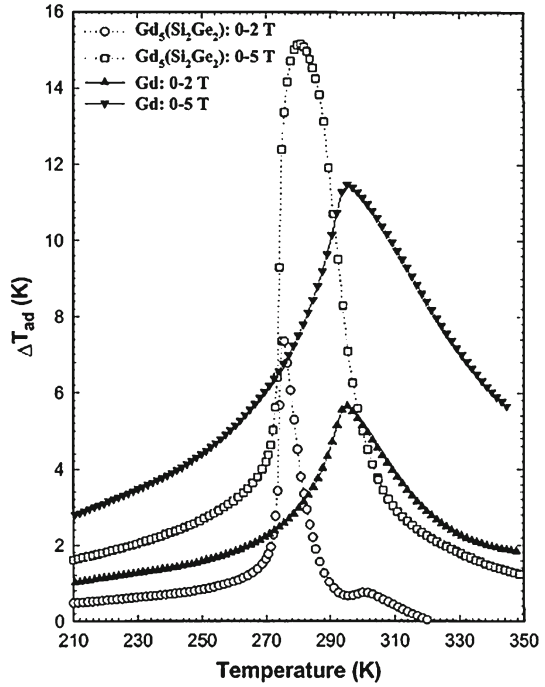
is the specific heat in a constant magnetic field and

$$\frac{\partial U'}{\partial H} + J = T \frac{\partial S}{\partial H} = -T \frac{\partial}{\partial H} \frac{\partial G}{\partial T} = T \frac{\partial J}{\partial T}. \quad (1.103)$$

Inserting (1.102) and (1.103) into the second relation of (1.101) and then integrating the latter we get the change of temperature ΔT_{ad} induced by application of magnetic field as,

$$\Delta T_{ad} = - \int_0^H \frac{T}{C_H} \frac{\partial J}{\partial T} dH. \quad (1.104)$$

Fig. 1.8 ΔT_{ad} vs T for Gd metal ($T_C=293$ K) and $Gd_5Si_2Ge_2$ ($T_C = 276 \sim 299$ K). $\mu_0 H$ is varied between 0 and 2 T and 0 and 5 T [5]



This phenomenon is called magneto-caloric effect. The effect has been widely applied in the cooling at low temperatures.

In recent years the exploration of magneto-caloric materials for cooling around R.T. is active. These materials should be able to produce large ΔT_{ad} at around R.T. by applying a not very large magnetic field. To satisfy these conditions, the material should have a large value of $\partial J/\partial T$, i.e., a large J_s and Curie temperature near R. T.. Gd metal satisfies these conditions relatively well. A large ΔT_{ad} can also be obtained by use of metamagnetic materials with metamagnetic transition temperature near R.T.. $Gd_5Si_2Ge_2$ belongs to such kind of materials. Figure 1.8 demonstrates the ΔT_{ad} as a function of temperature for Gd and $Gd_5Si_2Ge_2$ under the variation of H .

Note 1

Let δS and δS_0 denote the change of entropy of the magnetic medium and the infinitely large isothermal heat source, respectively, after an irreversible process. According to the second law of thermodynamics, the total entropy increases:

$$\delta S + \delta S_0 > 0. \quad (1.105)$$

Under the condition of constant temperature, the exchange of heat is reversible for the infinite isothermal heat source, so

$$\delta S_0 = -\frac{\delta Q}{T}. \quad (1.106)$$

When $H = 0$, the heat transferred to the medium is $\delta Q = \delta U$ and hence $\delta S_0 = -\delta U/T$. Inserting this relation into (1.105), we get

$$T\delta S - \delta U = -\delta F > 0, \quad (1.107)$$

that is, F decreases until it reaches a minimum.

Under the conditions of constant temperature and applied magnetic field,

$$\delta S_0 = -\frac{\delta Q}{T} = -\frac{\delta(U - HJ)}{T}. \quad (1.108)$$

Inserting the above relation into (1.105), we get

$$T\delta S - \delta(U - HJ) = -\delta(U - TS - HJ) = -\delta G > 0, \quad (1.109)$$

that is, G decreases until it reaches a minimum.

1.5 Hamiltonian of an Electric Charged Particle in Static Electric and Magnetic Fields

Let m and e denote the mass and electric charge of the particle.

1.5.1 Hamiltonian and Momentum in Classical Mechanics

In the classical mechanics the Hamiltonian of a particle is defined by

$$H(\vec{q}, \vec{p}; t) \equiv \left[\dot{\vec{q}} \cdot \vec{p} - L(\vec{q}, \dot{\vec{q}}; t) \right]_{\dot{\vec{q}} \rightarrow \vec{p}}, \quad \left(\dot{\vec{q}} \equiv \frac{d\vec{q}}{dt}, t : \text{time} \right) \quad (1.110)$$

where $\vec{q}$ is the generalized coordinate and $\vec{p}$ is the generalized momentum conjugates to the coordinate $\vec{q}$ defined by

$$\vec{p} \equiv \frac{\partial L(\vec{q}, \dot{\vec{q}}; t)}{\partial \dot{\vec{q}}}. \quad (1.111)$$

Here L is the Lagrangian which satisfies the Lagrange's equation

$$\frac{d}{dt} \frac{\partial L(\vec{q}, \dot{\vec{q}}; t)}{\partial \dot{\vec{q}}} - \frac{\partial L(\vec{q}, \dot{\vec{q}}; t)}{\partial \vec{q}} = 0. \quad (1.112)$$

The $\vec{p}$, L , and H in static electric and magnetic fields are

$$\vec{p} = m\dot{\vec{q}} + e\vec{A}(\vec{q}), \quad (\vec{A}: \text{magnetic vector potential}) \quad (1.113)$$

$$L(\vec{q}, \dot{\vec{q}}; t) = \frac{1}{2}m\dot{\vec{q}}^2 - e[V(\vec{q}) - \dot{\vec{q}} \cdot \vec{A}(\vec{q})], \quad (1.114)$$

$$H(\vec{q}, \vec{p}; t) = \frac{1}{2m} [\vec{p} - e\vec{A}(\vec{q})]^2 + eV(\vec{q}) = \frac{(m\dot{\vec{q}})^2}{2m} + eV. \quad (1.115)$$

Above relations show that $\vec{p}$ is the usual momentum $m\dot{\vec{q}}$ in the absence of magnetic field but is not in a magnetic field, and the Hamiltonian is the total energy irrelevant to the magnetic field.

1.5.2 Hamiltonian and Momentum in Quantum Mechanics

In quantum mechanics the Hamiltonian is an operator $\hat{H}$ which has the same form of (1.115) of classical mechanics and also represents the total energy. The operator of generalized momentum $\vec{p}$ is

$$\hat{\vec{p}} = -i\hbar\nabla. \quad (\hbar: \text{reduced Planck constant}) \quad (1.116)$$

Here $\hat{\vec{p}}$ rather than $m\dot{\vec{q}}$ is considered the momentum. Thus, in contrast to the Hamiltonian of classical mechanics (1.115), it includes not only the kinetic energy $\hat{\vec{p}}^2/2m$ and electric potential energy eV but also the energy related to the magnetic field.

Corresponding to $\vec{p}_J = -\partial E/\partial \vec{H}$ (1.18) of classical mechanics, the operator of magnetic polarization moment in quantum mechanics is

$$\hat{\vec{p}}_J = -\frac{\partial \hat{H}}{\partial \vec{H}}. \quad (1.117)$$

In the classical mechanics the total energy being irrelevant to magnetic field, derivative of the energy with respect to magnetic field is zero, and the magnetic moment is independent of magnetic field and is always zero. This result contradicts with reality, which reveals that the classical mechanics cannot explain magnetic phenomena of media. This fact is called Bohr-van Leeuwen theorem [6].

In quantum mechanics $\hat{H}$ being related with magnetic field, the magnetic moment may not be zero. In fact, magnetism of media is quantum phenomena.

Introducing some results of quantum mechanics, such as a magnetic atom has an intrinsic magnetic moment and there exists exchange interactions between electron spins, into the frame of classical mechanics, however, many magnetic phenomena can be explained successfully with convenience. Such method is used widely.

Appendix 1: Physical constants

Table a1.1 Physical constants [7]

Physical quantity		SI unit	CGS unit
Avogadro constant	N_A	$6.022,142 \times 10^{23} \text{ mol}^{-1}$	$6.022,142 \times 10^{23} \text{ mol}^{-1}$
Bohr magneton	$\mu_B = \mu_0 e \hbar / (2m)$ $= e \hbar / (2m)$	$1.165,406 \times 10^{-29} \text{ J} \cdot \text{m/A}$ $9.274,009 \times 10^{-24} \text{ J/T}$	$9.274,009 \times 10^{-21} \text{ erg/Oe}$
Boltzmann constant	k_B	$1.380,649 \times 10^{-23} \text{ J/K}$	$1.380,649 \times 10^{-16} \text{ erg/K}$
Electron charge	e	$-1.602,176,6 \times 10^{-19} \text{ C}$	$-4.803,204 \times 10^{-10} \text{ esu}$
Electron rest mass	m	$9.109,382 \times 10^{-31} \text{ kg}$	$9.109,382 \times 10^{-28} \text{ g}$
Reduced Planck constant	$\hbar$	$1.054,571,7 \times 10^{-34} \text{ J} \cdot \text{s}$	$1.054,571,7 \times 10^{-27} \text{ erg} \cdot \text{s}$
Magnetic constant	μ_0	$4\pi \times 10^{-7} \text{ N/A}^2$	1
Speed of light in vacuum	c	$2.997,924,58 \times 10^8 \text{ m/s}$	$2.997,924,58 \times 10^{10} \text{ cm/s}$
Electric constant	$\varepsilon_0 = 1/(\mu_0 c^2)$	$8.854,187,817 \times 10^{-12} \text{ F/m}$	1

Appendix 2: Units and Their Conversions

Table a2.1 Formulae

SI	CGS
$\vec{B} = \mu_0 (\vec{H} + \vec{M}), \quad \vec{J} = \mu_0 \vec{M}$	$\vec{B} = \vec{H} + 4\pi \vec{M}$
$f = \frac{q_{m1} q_{m2}}{4\pi \mu_0 r^2}$	$f = \frac{q_{m1} q_{m2}}{r^2}$
$\int \vec{H} \cdot d\vec{B}$	$\frac{1}{4\pi} \int \vec{H} \cdot d\vec{B}$
$\nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t}$	$\nabla \times \vec{E} = -\frac{1}{c} \frac{\partial \vec{B}}{\partial t}$
$\nabla \times \vec{H} = \vec{j} + \frac{\partial \vec{D}}{\partial t}$	$\nabla \times \vec{H} = \frac{4\pi}{c} \vec{j} + \frac{1}{c} \frac{\partial \vec{D}}{\partial t}$
$\nabla \cdot \vec{B} = 0$	$\nabla \cdot \vec{B} = 0$
$\nabla \cdot \vec{D} = \rho$	$\nabla \cdot \vec{D} = 4\pi \rho$

Table a2.2 Units and Their Conversions

Magnetic quantity	SI		CGS		Unit conversion
Magnetic field	H	A/m	H	Oe	$1\text{Oe} = 10^3/4\pi\text{A/m}$
Magnetic induction	B	$\text{T} = \text{Wb/m}^2$	B	Gs	$1\text{Gs} = 10^{-4}\text{T}$
Magnetic polarization moment	p_J	$\text{Wb}\cdot\text{m}$		emu	$1\text{emu} = 4\pi \times 10^{-10}\text{Wb}\cdot\text{m}$
Magnetic moment	p_M	$\text{A}\cdot\text{m}^2$		emu	$1\text{emu} = 1 \times 10^{-3}\text{A}\cdot\text{m}^2$
Magnetization	M	A/m	M	Gs	$1\text{Gs} = 10^3\text{A/m}$
Magnetic polarization	J	T	$4\pi M$	Gs	$1\text{Gs} = 10^{-4}\text{T}$
Magnetic energy product	$(BH)_{\max}$	J/m^3	$(BH)_{\max}$	Gs·Oe	$1\text{Gs}\cdot\text{Oe} = 0.1/4\pi\text{J/m}^3$
Magnetic flux	ϕ	Wb	ϕ	Mx	$1\text{Mx} = 10^{-8}\text{Wb}$
Magnetic constant	μ_0	$\text{N/A}^2 = \text{H/m}$			

Appendix 3: Selections From Vector Analysis

Vector Algebra

$$\vec{a} \cdot \vec{b} = \sum_{\alpha}^{x,y,z} a_{\alpha} b_{\alpha}. \quad (\text{a3.1})$$

$$\vec{a} \times \vec{b} = \begin{vmatrix} \vec{e}_x & \vec{e}_y & \vec{e}_z \\ a_x & a_y & a_z \\ b_x & b_y & b_z \end{vmatrix} = (a_y b_z - a_z b_y) \vec{e}_x + (a_z b_x - a_x b_z) \vec{e}_y + (a_x b_y - a_y b_x) \vec{e}_z. \quad (\text{a3.2})$$

($\vec{e}_{\alpha}$: unit vector in the α direction)

$$\vec{a} \cdot (\vec{b} \times \vec{c}) = \vec{b} \cdot (\vec{c} \times \vec{a}) = \vec{c} \cdot (\vec{a} \times \vec{b}) = \begin{vmatrix} a_x & a_y & a_z \\ b_x & b_y & b_z \\ c_x & c_y & c_z \end{vmatrix}. \quad (\text{a3.3})$$

$$\vec{a} \times (\vec{b} \times \vec{c}) = \vec{b}(\vec{a} \cdot \vec{c}) - \vec{c}(\vec{a} \cdot \vec{b}). \quad (\text{a3.4})$$

Del, Gradient, Divergence, and Curl Operators

$$\nabla \equiv \sum_{\alpha}^{x,y,z} \vec{e}_{\alpha} \frac{\partial}{\partial \alpha}. \quad (\text{Del or Nabla operator}) \quad (\text{a3.5})$$

$$\nabla \cdot \nabla = \nabla^2 = \sum_{\alpha}^{x,y,z} \frac{\partial^2}{\partial \alpha^2}. \quad (\text{Laplace operator}) \quad (\text{a3.6})$$

$$\nabla \varphi \equiv \left(\frac{d\varphi}{d\vec{l}} \right)_{\max} = \sum_{\alpha}^{x,y,z} \frac{\partial \varphi}{\partial \alpha} \vec{e}_{\alpha}. \quad (\text{gradient of } \varphi) \quad (\text{a3.7})$$

$$\nabla \cdot \vec{a} \equiv \lim_{v \rightarrow 0} \frac{\oint \vec{a} \cdot d\vec{S}}{v} = \sum_{\alpha}^{x,y,z} \frac{\partial a_{\alpha}}{\partial \alpha}. \quad (\text{divergence of } \vec{a}, v : \text{volume surrounded by the closed surface } S) \quad (\text{a3.8})$$

$$\nabla \times \vec{a} \equiv \lim_{S \rightarrow 0} \left(\frac{\oint \vec{a} \cdot d\vec{l}}{S} \right)_{\max} = \begin{vmatrix} \vec{e}_x & \vec{e}_y & \vec{e}_z \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ a_x & a_y & a_z \end{vmatrix}. \quad (\text{curl of } \vec{a}, S: \text{area of the closed curve } l) \quad (\text{a3.9})$$

$$\nabla \times \nabla \varphi = 0. \quad (\text{a3.10})$$

$$\nabla \cdot \nabla \times \vec{a} = 0. \quad (\text{a3.11})$$

$$\nabla \times \nabla \times \vec{a} = \left(\nabla \nabla \cdot - \nabla^2 \right) \vec{a}. \quad (\text{a3.12})$$

If $\nabla \times \vec{a} = 0$ in region D, $\vec{a}$ is a divergence of a scalar in D:

$$\vec{a} = \nabla \varphi. \quad (\text{a3.13})$$

If $\nabla \cdot \vec{a} = 0$ in region D, $\vec{a}$ is a curl of a vector in D:

$$\vec{a} = \nabla \times \vec{A}. \quad (\text{a3.14})$$

Del Operations on Products of Two Functions

$$\nabla(\vec{a} \cdot \vec{b}) = \vec{a} \times (\nabla \times \vec{b}) + \vec{b} \times (\nabla \times \vec{a}) + (\vec{a} \cdot \nabla) \vec{b} + (\vec{b} \cdot \nabla) \vec{a}. \quad (\text{a3.15})$$

$$\nabla \cdot (\varphi \vec{a}) = (\nabla \varphi) \cdot \vec{a} + \varphi \nabla \cdot \vec{a}. \quad (\text{a3.16})$$

$$\nabla \cdot (\vec{a} \times \vec{b}) = (\nabla \times \vec{a}) \cdot \vec{b} - \vec{a} \cdot (\nabla \times \vec{b}). \quad (\text{a3.17})$$

$$\nabla \times (\varphi \vec{a}) = (\nabla \varphi) \times \vec{a} + \varphi \nabla \times \vec{a}. \quad (\text{a3.18})$$

$$\nabla \times (\vec{a} \times \vec{b}) = (\vec{b} \cdot \nabla) \vec{a} - (\vec{a} \cdot \nabla) \vec{b} + (\nabla \cdot \vec{b}) \vec{a} - (\nabla \cdot \vec{a}) \vec{b}. \quad (\text{a3.19})$$

Del Operations in Spherical Coordinate System

$$\nabla \varphi = \frac{\partial \varphi}{\partial r} \vec{e}_r + \frac{1}{r} \frac{\partial \varphi}{\partial \theta} \vec{e}_\theta + \frac{1}{r \sin \theta} \frac{\partial \varphi}{\partial \phi} \vec{e}_\phi. \quad (\text{a3.20})$$

$$\nabla \cdot \vec{a} = \frac{1}{r^2} \frac{\partial (a_r r^2)}{\partial r} + \frac{1}{r \sin \theta} \frac{\partial (a_\theta \sin \theta)}{\partial \theta} + \frac{1}{r \sin \theta} \frac{\partial a_\phi}{\partial \phi}. \quad (\text{a3.21})$$

$$\begin{aligned} \nabla \times \vec{a} = & \frac{1}{r \sin \theta} \left[\frac{\partial (a_\phi \sin \theta)}{\partial \theta} - \frac{\partial a_\theta}{\partial \phi} \right] \vec{e}_r + \frac{1}{r} \left[\frac{1}{\sin \theta} \frac{\partial a_r}{\partial \phi} - \frac{\partial (a_\phi r)}{\partial r} \right] \vec{e}_\theta \\ & + \frac{1}{r} \left[\frac{\partial (a_\theta r)}{\partial r} - \frac{\partial a_r}{\partial \theta} \right] \vec{e}_\phi. \end{aligned} \quad (\text{a3.22})$$

$$\nabla^2 \varphi = \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial \varphi}{\partial r}) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial \varphi}{\partial \theta}) + \frac{1}{(r \sin \theta)^2} \frac{\partial^2 \varphi}{\partial \phi^2}. \quad (\text{a3.23})$$

Integral Relations

$$\int d\vec{S} \times \nabla \varphi = \oint \varphi d\vec{l}. \quad (\text{a3.24})$$

$$\int \nabla \cdot \vec{a} dv = \oint \vec{a} \cdot d\vec{S}. \quad (\text{a3.25})$$

$$\int \nabla \times \vec{a} dv = \oint d\vec{S} \times \vec{a}. \quad (\text{a3.26})$$

$$\int (\nabla \times \vec{a}) \cdot d\vec{S} = \oint \vec{a} \cdot d\vec{l}. \quad (\text{a3.27})$$

$$\int [\psi \nabla^2 \varphi + (\nabla \psi) \cdot (\nabla \varphi)] dv = \oint \psi (\nabla \varphi) \cdot d\vec{S}. \quad (\text{a3.28})$$

$$\int (\psi \nabla^2 \varphi - \varphi \nabla^2 \psi) dv = \oint (\psi \nabla \varphi - \varphi \nabla \psi) \cdot d\vec{S}. \quad (\text{a3.29})$$

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Chapter 2

Magnetism of Atoms

The magnetic moments of magnetic materials originate from magnetic moments of the atoms. The hyperfine interactions have important applications in magnetism. This chapter introduces the basic theories relating to atomic magnetism and hyperfine interactions in atom. It contains the sections of Electron configuration of atom; Term and multiplet; Intrinsic magnetic moment and gyromagnetic ratio of atom; Paramagnetism and diamagnetism of atom; Exchange interaction in He atom; Exchange interaction in H_2 molecule; and Hyperfine interactions in atom; and Appendices 4 to 6. The eigenfunctions are assumed orthonormalized.

2.1 Electron Configuration of Atom

Intrinsic atomic magnetic moment is decided by the state of the electrons. Consider an atom or an ion of atomic number Z which has N electrons.

2.1.1 Electron Spin

An electron has an intrinsic angular momentum called spin angular momentum, or tersely spin. The operators of its projections on the x , y and z axes (z axis = quantum axis) are

$$\hat{s}_\alpha \equiv \frac{\hbar}{2} \hat{\sigma}_\alpha, \quad (\alpha = x, y, z), \quad (2.1)$$

where $\hat{\sigma}_\alpha$ is the Pauli spin matrices,

$$\hat{\sigma}_x \equiv \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \hat{\sigma}_y \equiv \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \hat{\sigma}_z \equiv \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad \hat{\sigma}_\alpha^2 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \quad (2.2)$$

Let $|s, m_s\rangle$ denote the simultaneous eigenfunction (eigenstate) of $\hat{s}^2$ and $\hat{s}_z$:

$$\hat{s}^2 |s, m_s\rangle = \hbar^2 s(s+1) |s, m_s\rangle, \quad (s = 1/2: \text{spin quantum number}) \quad (2.3)$$

$$\hat{s}_z |s, m_s\rangle = \hbar m_s |s, m_s\rangle, \quad (m_s = \pm s: \text{spin projection quantum number}) \quad (2.4)$$

$$|s, s\rangle \equiv \chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad (2.5)$$

$$|s, -s\rangle \equiv \chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \quad (2.6)$$

$$\langle \chi_\sigma | \chi_{\sigma'} \rangle \equiv \chi_\sigma^+ \chi_{\sigma'} = \delta(\sigma, \sigma'). \quad (\sigma, \sigma' = \pm) \quad (2.7)$$

Here χ_σ^+ is the conjugate transpose of χ_σ such as $\chi_+^+ = (1, 0)$, and $\delta(\alpha, \beta)$ is the Kronecker delta which is equal to 1 if $\sigma = \sigma'$ and 0 if $\sigma \neq \sigma'$.

2.1.2 Hartree-Fock Equations

By taking into account only the Coulomb interactions, the Hamiltonian of the electron system of an atom is the sum of one-particle Hamiltonian $\hat{H}_1$ and two-particle Hamiltonian $\hat{H}_2$:

$$\hat{H}(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \hat{H}_1 + \hat{H}_2, \quad (\vec{r}_i: \text{position of } i^{\text{th}} \text{ electron relative to the nucleus}) \quad (2.8)$$

$$\hat{H}_1(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \sum_i^{1, \dots, N} \hat{h}(\vec{r}_i). \quad (2.9)$$

$$\hat{h}(\vec{r}) = \frac{\hat{p}^2(\vec{r})}{2m} - \frac{Ze^2}{4\pi\epsilon_0 r}, \quad (m: \text{electron rest mass}) \quad (2.10)$$

$$\hat{H}_2(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \frac{1}{2} \sum_{i,j}^{1, \dots, N; i \neq j} g(\vec{r}_i, \vec{r}_j). \quad (2.11)$$

$$g(\vec{r}_1, \vec{r}_2) = \frac{e^2}{4\pi\epsilon_0 r_{12}}. \quad (e: \text{electron charge}, r_{ij} \equiv |\vec{r}_i - \vec{r}_j|) \quad (2.12)$$

By solving the Schrödinger equation (1926)

$$\hat{H}\Psi(\vec{r}_1, \sigma(1), \vec{r}_2, \sigma(2), \dots, r_N, \sigma(N)) = E\Psi(\vec{r}_1, \sigma(1), \vec{r}_2, \sigma(2), \dots, r_N, \sigma(N)) \quad (2.13)$$

the eigenfunctions $\{\Psi\}$ and eigenvalues $\{E\}$ of the system can be obtained. Here σ is the variable of spin which takes $+(m_s = s)$ or $-(m_s = -s)$. Equation (2.13) for multi-electron system is very difficult to solve. The method which has long been used to approximately solve is to approximate Ψ by a Slater determinant:

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(\vec{r}_1)\chi_{\sigma_1}(1) & \varphi_2(\vec{r}_1)\chi_{\sigma_2}(1) & \dots & \varphi_N(\vec{r}_1)\chi_{\sigma_N}(1) \\ \varphi_1(\vec{r}_2)\chi_{\sigma_1}(2) & \varphi_2(\vec{r}_2)\chi_{\sigma_2}(2) & \dots & \varphi_N(\vec{r}_2)\chi_{\sigma_N}(2) \\ \dots & \dots & \dots & \dots \\ \varphi_1(\vec{r}_N)\chi_{\sigma_1}(N) & \varphi_2(\vec{r}_N)\chi_{\sigma_2}(N) & \dots & \varphi_N(\vec{r}_N)\chi_{\sigma_N}(N) \end{vmatrix}. \quad (2.14)$$

Here $\varphi_\alpha(\vec{r}_i)$ and $\chi_{\sigma_\alpha}(i)$ are the orbital and spin state of the i^{th} electron occupying the orbit α . $\psi_{\alpha, \sigma_\alpha}(i) = \varphi_\alpha(\vec{r}_i)\chi_{\sigma_\alpha}(i)$ is called spin orbital. The best set of $\{\varphi_\alpha(\vec{r})\}$ could be obtained by invoking the variational principle $\delta\langle\Psi|\hat{H}|\Psi\rangle = 0$ under the condition of orthonormality of $\{\varphi_\alpha(\vec{r})\}$. The $\{\varphi_\alpha(\vec{r})\}$ satisfies the N -coupled Hartree–Fock equations (1930–1935)

$$\left[\hat{h}(\vec{r}) + \sum_{\beta}^{1, \dots, N} \int |\varphi_\beta(\vec{r}')|^2 g(\vec{r}, \vec{r}') d\mathbf{v}' - \sum_{\beta}^{1, \dots, N} \delta(\sigma_\alpha, \sigma_\beta) \int \varphi_\beta^*(\vec{r}') g(\vec{r}, \vec{r}') \varphi_\alpha(\vec{r}') \frac{\varphi_\beta(\vec{r})}{\varphi_\alpha(\vec{r})} d\mathbf{v}' \right] \varphi_\alpha(\vec{r}) = \varepsilon_\alpha \varphi_\alpha(\vec{r}).$$

($\alpha = 1, 2, \dots, N$. Note 1 of this section) (2.15)

Thus, the many-body problem transforms to the problem to solve N -coupled one-electron equations. The above method is called Hartree–Fock approximation. More widely, such kind of approach to solve a many-body problem by use of one-electron equations is called one-electron method. In the left of (2.15), the first term in the bracket is the sum of the kinetic energy and Coulomb potential in the electric field produced by the nucleus (2.10); the second term is the Coulomb potential in the average electric field produced by all the electrons; and the third term the average exchange potential. Those of $\beta = \alpha$ in the second and third terms cancel each other. Equation (2.15) shows that an electron moves around in the potential consisted of the Coulomb potential of the nucleus, average Coulomb potential, and average exchange field produced by the electrons. Therefore, Hartree–Fock approximation is a mean field approximation. Here the space distribution of $\varphi_\beta(\vec{r}')$ is not affected by the variation of position $\vec{r}$ of the α electron.

2.1.3 Central Field Approximation

The total potential in the bracket of the left of (2.15) is spherically asymmetric and is slightly different for different $\varphi_\alpha(\vec{r})$. By averaging the potentials for all $\varphi_\alpha(\vec{r})$ and approximating it by its spherically symmetrical part $u(r)$, the N -coupled Hartree–Fock equations simplify to a single equation of

$$\left[\frac{\hat{p}^2(\vec{r})}{2m} + u(r) \right] \varphi_\alpha(\vec{r}) = \varepsilon_\alpha \varphi_\alpha(\vec{r}), \quad (2.16)$$

where $u(r)$ is common for all $\varphi_\alpha(\vec{r})$. Such approximation is called central field approximation.

The solution of (2.16) is

$$\begin{aligned} \varphi_\alpha(\vec{r}) &= \varphi_{nlm_l}(r, \theta, \phi) = R_{nl}(r) Y_{lm_l}(\theta, \phi), \\ (n &= 1, 2, \dots; l = 0, 1, \dots, n-1; m_l = -l, -l+1, \dots, l) \end{aligned} \quad (2.17)$$

where θ and ϕ is the zenith angle of $\vec{r}$ from the positive z axis direction and azimuth angle from the positive x axis direction, respectively, and n , l , and m_l are the principal quantum number, orbital angular quantum number (or azimuthal quantum number), and magnetic quantum number. $Y_{lm_l}(\theta, \phi)$ is the spherical harmonics,

$$\begin{aligned} Y_{lm_l}(\theta, \phi) &= (-1)^{\frac{m_l+|m_l|}{2}} \sqrt{\frac{2l+1}{4\pi}} \sqrt{\frac{(l-|m_l|)!}{(l+|m_l|)!}} \\ &\times P_l^{|m_l|}(\cos \theta) \exp(im_l \phi), \text{ (Table 2.1)} \end{aligned} \quad (2.18)$$

$$P_l^{|m_l|}(\xi) = (1 - \xi^2)^{\frac{|m_l|}{2}} \frac{d^{|m_l|}}{d\xi^{|m_l|}} P_l(\xi), \quad (2.19)$$

where $P_l^{|m_l|}(\xi)$ is the associated Legendre function and $P_l(\xi)$ is the Legendre polynomial (1.63). The orbital angular momentum operator of an electron is

$$\hat{\vec{l}} = \vec{r} \times \hat{\vec{p}} = -i\hbar \vec{r} \times \nabla, \quad (1.116) \quad (2.20)$$

and $Y_{lm_l}(\theta, \phi)$ is the simultaneous eigenfunction of $\hat{l}^2$ and $\hat{l}_z$:

$$\hat{l}^2 Y_{lm_l}(\theta, \phi) = \hbar^2 l(l+1) Y_{lm_l}(\theta, \phi), \quad (2.21)$$

$$\hat{l}_z Y_{lm_l}(\theta, \phi) = \hbar m_l Y_{lm_l}(\theta, \phi). \quad (2.22)$$

Table 2.1 Expressions of spherical harmonics $Y_{lm_l}(\theta, \phi)$ and $Y_{lm_l}(x/r, y/r, z/r)$

l	m_l	$Y_{lm_l}(\theta, \phi)$	$Y_{lm_l}(x/r, y/r, z/r)$
0	0	$\sqrt{\frac{1}{2\pi}} \sqrt{\frac{1}{2}}$	$\sqrt{\frac{1}{2\pi}} \sqrt{\frac{1}{2}}$
1	0	$\sqrt{\frac{1}{2\pi}} \sqrt{\frac{3}{2}} \cos \theta$	$\sqrt{\frac{1}{2\pi}} \sqrt{\frac{3}{2}} \frac{z}{r}$
	± 1	$\mp \sqrt{\frac{1}{2\pi}} \sqrt{\frac{3}{4}} \sin \theta \exp(\pm i\phi)$	$\mp \sqrt{\frac{1}{2\pi}} \sqrt{\frac{3}{4}} \frac{x \pm iy}{r}$
2	0	$\sqrt{\frac{1}{2\pi}} \sqrt{\frac{5}{8}} (3 \cos^2 \theta - 1)$	$\sqrt{\frac{1}{2\pi}} \sqrt{\frac{5}{8}} \frac{3z^2 - r^2}{r^2}$
	± 1	$\mp \sqrt{\frac{1}{2\pi}} \sqrt{\frac{15}{4}} \cos \theta \sin \theta \exp(\pm i\phi)$	$\mp \sqrt{\frac{1}{2\pi}} \sqrt{\frac{15}{4}} \frac{z(x \pm iy)}{r^2}$
	± 2	$\sqrt{\frac{1}{2\pi}} \sqrt{\frac{15}{16}} \sin^2 \theta \exp(\pm 2i\phi)$	$\sqrt{\frac{1}{2\pi}} \sqrt{\frac{15}{16}} \frac{(x \pm iy)^2}{r^2}$
3	0	$\sqrt{\frac{1}{2\pi}} \sqrt{\frac{7}{8}} \cos \theta (5 \cos^2 \theta - 3)$	$\sqrt{\frac{1}{2\pi}} \sqrt{\frac{7}{8}} \frac{z(5z^2 - 3r^2)}{r^2}$
	± 1	$\mp \sqrt{\frac{1}{2\pi}} \sqrt{\frac{21}{32}} (5 \cos^2 \theta - 1) \sin \theta \exp(\pm i\phi)$	$\mp \sqrt{\frac{1}{2\pi}} \sqrt{\frac{21}{32}} \frac{(5z^2 - r^2)(x \pm iy)}{r^3}$
	± 2	$\sqrt{\frac{1}{2\pi}} \sqrt{\frac{105}{16}} \cos \theta \sin^2 \theta \exp(\pm 2i\phi)$	$\sqrt{\frac{1}{2\pi}} \sqrt{\frac{105}{16}} \frac{z(x \pm iy)^2}{r^3}$
	± 3	$\mp \sqrt{\frac{1}{2\pi}} \sqrt{\frac{35}{32}} \sin^3 \theta \exp(\pm i3\phi)$	$\mp \sqrt{\frac{1}{2\pi}} \sqrt{\frac{35}{32}} \frac{(x \pm iy)^3}{r^3}$

The spherical harmonic addition theorem

$$Y_{l0}(\theta_{12}, 0) = \sqrt{\frac{4\pi}{2l+1}} \sum_m^{-l, -l+1, \dots, l} Y_{lm}^*(\theta_1, \phi_1) Y_{lm}(\theta_2, \phi_2) = \sqrt{\frac{2l+1}{4\pi}} P_l(\cos \theta_{12}) \quad (2.23)$$

holds, where θ_{12} is the angle between $\vec{r}(\theta_1, \phi_1)$ and $\vec{r}(\theta_2, \phi_2)$ directions. The function

$$U_{m_l}^l \equiv \sqrt{\frac{4\pi}{2l+1}} Y_{lm_l} \quad (2.24)$$

is used instead of Y_{lm_l} in some cases for convenience.

The radial function $R_{nl}(r)$ (2.17) satisfies the radial equation

$$\left\{ \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) - \frac{l(l+1)}{r^2} + \frac{2m}{\hbar^2} [\varepsilon_\alpha - u(r)] \right\} R_{nl}(r) = 0. \quad (2.25)$$

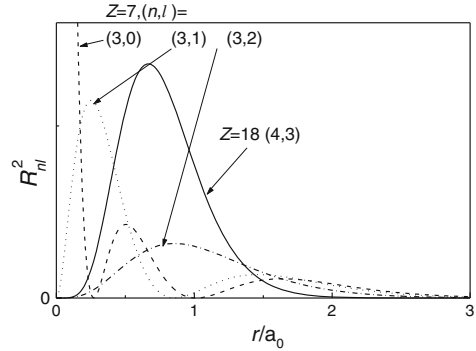
A general characteristics of $R_{nl}(r)$ can be seen from the analytical solutions for the simple case of nuclear Coulomb potential $u(r) = -Ze^2/4\pi\varepsilon_0 r$ (Table 2.2, Fig. 2.1). It has $n - l - 1$ spherical surfaces of $R_{nl}(r) = 0$, and

$$R_{n0}(0) \neq 0, \quad R_{n,l \neq 0}(0) = 0. \quad (2.26)$$

Table 2.2 Expressions of $R_{nl}(r)$ for $u(r) = -Ze^2/4\pi\epsilon_0 r$

n	l	$R_{nl}(r)$ ($a_0 \equiv 4\pi\epsilon_0\hbar^2/me^2$: Bohr radius)
1	0	$\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} 2 \exp\left(-\frac{Zr}{a_0}\right)$
2	0	$\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \frac{1}{\sqrt{2}} \left(1 - \frac{Zr}{2a_0}\right) \exp\left(-\frac{Zr}{2a_0}\right)$
	1	$\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \frac{1}{2\sqrt{6}} \frac{Zr}{a_0} \exp\left(-\frac{Zr}{2a_0}\right)$
3	0	$\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \frac{2}{3\sqrt{3}} \left[1 - \frac{2Zr}{3a_0} + \frac{2}{27} \left(\frac{Zr}{a_0}\right)^2\right] \exp\left(-\frac{Zr}{3a_0}\right)$
	1	$\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \frac{8}{27\sqrt{6}} \frac{Zr}{a_0} \left(1 - \frac{Zr}{6a_0}\right) \exp\left(-\frac{Zr}{3a_0}\right)$
	2	$\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \frac{4}{81\sqrt{30}} \left(\frac{Zr}{a_0}\right)^2 \exp\left(-\frac{Zr}{3a_0}\right)$
4	3	$\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \frac{1}{768\sqrt{35}} \left(\frac{Zr}{a_0}\right)^3 \exp\left(-\frac{Zr}{4a_0}\right)$

Fig. 2.1 r/a_0 dependences of some R_{nl}^2 of R_{nl} given in Table 2.2



The eigenvalue $\varepsilon_\alpha = \varepsilon_{nl}$ of (2.25) is related with n and l but not with m_l .

To get the solution of $R_{nl}(r)$, $u(r)$ should be known in advance, but $u(r)$ is a function of the set of $\{R_{nl}(r)\}$ including $R_{nl}(r)$ itself. Therefore, it should be solved by means of an iterative method called self-consistent field method. First assume a set of $\{R_{nl}(r)\}$ with which $u(r)$ is calculated. A set of solutions $\{R_{nl}(r)\}$ is solved using this $u(r)$. Calculate $u(r)$ by using the new set of $\{R_{nl}(r)\}$. Repeat this process until the set of $\{R_{nl}(r)\}$ for the calculation of $u(r)$ becomes essentially the same with those solutions solved using the $u(r)$. In this way, we get the eigenstates $\{\varphi_{nlm_l}(\vec{r}) = R_{nl}(r)Y_{lm_l}(\theta, \phi)\}$ and the eigenvalues $\{\varepsilon_{nl}\}$.

2.1.4 Electron Configuration of Atom

The energy degeneracy of the energy level ε_{nl} is $2(2l + 1)$. According to the Pauli's exclusion principle, the N electrons have different spin-orbitals. The arrangement of the electrons in the electronic orbital subshells $\{(n, l)\}$ is called atomic orbital electron configuration or tersely electron configuration, and the total energy is called the energy of the configuration. If the electrons fill the lowest energy levels, we get the ground state electron configuration, otherwise an excited state configuration. The energy gaps between the excited state energy levels and ground state energy level are so large that the probability of occupation of excited states is extremely small under usual magnetic experimental conditions, and the effect of them on the magnetic properties can be neglected. Thus, the magnetic properties of an atom are related only to the ground state configuration. At the ground configuration, the inner electron subshells are fully filled and only the outermost subshell may be filled partially for the atoms of $Z \leq 18$ ($Z = 18$ for Ar atom). For example, the electron configuration of oxygen atom ($Z = 8$) is $1s^2 2s^2 2p^4$ which is often tersely denoted by $2p^4$ by omitting the fully filled subshell symbols. Here s, p, d, f, ... stands for $l = 0, 1, 2, 3, \dots$, and $2p^4$ refers to that the electron subshell of $n = 2$ and $l = 1$ is filled by four electrons.

Most important magnetic atoms and ions for magnetic materials are $\text{Fe}(3d^6)$, $\text{Co}(3d^7)$, and $\text{Ni}(3d^8)$ of 3d transition elements ($3d^k 4s^2$) and $\text{Pr}^{+3}(4f^2 5s^2 5p^6)$, $\text{Nd}^{+3}(4f^3 5s^2 5p^6)$, $\text{Sm}^{+3}(4f^5 5s^2 5p^6)$, $\text{Tb}^{+3}(4f^8 5s^2 5p^6)$, and $\text{Dy}^{+3}(4f^9 5s^2 5p^6)$ of 4f transition (rare-earth) ions ($4f^k 5s^2 5p^6$). Their atomic magnetic moments originate from the partially filled 3d subshell enclosed by the fully filled outer subshell $4s^2$ for the 3d atoms, and partially filled 4f subshell enclosed by the fully filled outer subshells of $5s^2 5p^6$ for the 4f transition ions.

2.1.5 Angular Momentum Operators

For succinctness of expressions hereafter all angular momentum operators will be formulated in $\hbar$ unit. Thus, (2.1), (2.3), (2.4), and (2.20)–(2.22) become

$$\hat{s}_\alpha \equiv \frac{1}{2} \hat{\sigma}_\alpha, \quad (2.27)$$

$$\hat{s}^2 |s, m_s\rangle = s(s + 1) |s, m_s\rangle, \quad (2.28)$$

$$\hat{s}_z |s, m_s\rangle = m_s |s, m_s\rangle, \quad (2.29)$$

$$\hat{l} = -i\vec{r} \times \nabla, \quad (2.30)$$

$$\hat{l}^2 Y_{lm_l}(\theta, \phi) = l(l+1)Y_{lm_l}(\theta, \phi), \quad (2.31)$$

$$\hat{l}_z Y_{lm_l}(\theta, \phi) = m_l Y_{lm_l}(\theta, \phi). \quad (2.32)$$

Any angular momentum operator $\hat{J}$ satisfies the following relations.

$$\hat{J}_{\pm} \equiv \hat{J}_x \pm i\hat{J}_y, \quad (\text{called raising and lowering operators}) \quad (2.33)$$

$$\hat{J} \times \hat{J} = i\hat{J}, \quad (2.34)$$

$$\hat{J}^2 |J, M_J\rangle = J(J+1)|J, M_J\rangle, \quad (J: \text{angular momentum quantum number}) \quad (2.35)$$

$$\hat{J}_z |J, M_J\rangle = M_J |J, M_J\rangle, \quad (M_J: \text{magnetic quantum number}) \quad (2.36)$$

$$\begin{aligned} \hat{J}_{\pm} |J, M_J\rangle &= \sqrt{J(J+1) - M_J(M_J \pm 1)} |J, M_J \pm 1\rangle. \\ (M_J &= -J, -J+1, \dots, J) \end{aligned} \quad (2.37)$$

Here $|J, M_J\rangle$ is the simultaneous eigenfunction of $\hat{J}^2$ and $\hat{J}_z$. If

$$\hat{J} = \hat{J}_1 + \hat{J}_2, \quad (2.38)$$

$$J = |j_1 - j_2|, |j_1 - j_2| + 1, \dots, j_1 + j_2. \quad (2.39)$$

Note 1

Define the Coulomb, exchange, and Fock operators $\hat{K}_{\alpha}(\vec{r})$, $\hat{A}_{\alpha}(\vec{r})$, and $\hat{F}(\vec{r})$ by the relations of

$$\hat{K}_{\alpha}(\vec{r})\varphi_{\beta}(\vec{r}) \equiv \int \varphi_{\alpha}^*(\vec{r}') g(\vec{r}, \vec{r}') \varphi_{\alpha}(\vec{r}') d\vec{r}' \varphi_{\beta}(\vec{r}), \quad (2.40)$$

$$\hat{A}_{\alpha}(\vec{r})\varphi_{\beta}(\vec{r}) \equiv \int \varphi_{\alpha}^*(\vec{r}') g(\vec{r}, \vec{r}') \varphi_{\beta}(\vec{r}') d\vec{r}' \varphi_{\alpha}(\vec{r}), \quad (2.41)$$

$$\hat{F}(\vec{r})\varphi_{\alpha}(\vec{r}) \equiv \left[\hat{h}(\vec{r}) + \sum_{\beta}^{1, \dots, N} [\hat{K}_{\beta}(\vec{r}) - \delta(\sigma_{\alpha}, \sigma_{\beta}) \hat{A}_{\beta}(\vec{r})] \right] \varphi_{\alpha}(\vec{r}). \quad (2.42)$$

Equation (2.42) is the left of the Hartree–Fock equation (2.15).

$$\begin{aligned}
E &= \langle \Psi | \hat{H} | \Psi \rangle = \langle N, \dots, 2, 1 | \sum_{\mu, \nu} h_{\mu\nu} \hat{a}_{\mu}^{\dagger} \hat{a}_{\nu} \\
&\quad + \frac{1}{2} \sum_{\mu, \nu, \gamma, \delta} g_{\mu\nu\gamma\delta} \hat{a}_{\mu}^{\dagger} \hat{a}_{\nu}^{\dagger} \hat{a}_{\gamma} \hat{a}_{\delta} | 1, 2, \dots, N \rangle \\
&= \sum_{\alpha}^{1, \dots, N} h_{\alpha\alpha} + \frac{1}{2} \sum_{\alpha, \beta}^{1, \dots, N} [g_{\alpha\beta\beta\alpha} - \delta(\sigma_{\alpha}, \sigma_{\beta}) g_{\alpha\beta\alpha\beta}], \quad (\text{Appendix 5}) \quad (2.43)
\end{aligned}$$

$$h_{\alpha\beta} \equiv \int \varphi_{\alpha}^* \hat{h} \varphi_{\beta} dv = \int \varphi_{\beta} \hat{h} \varphi_{\alpha}^* dv, \quad (\text{a4.8}) \quad (2.44)$$

$$g_{\alpha\beta\gamma\delta} \equiv \int \varphi_{\alpha}^*(\vec{r}_1) \varphi_{\beta}^*(\vec{r}_2) g(\vec{r}_1, \vec{r}_2) \varphi_{\gamma}(\vec{r}_2) \varphi_{\delta}(\vec{r}_1) dv_1 dv_2, \quad (2.45)$$

$$\delta h_{\alpha\alpha} = \int \delta \varphi_{\alpha}^* \hat{h} \varphi_{\alpha} dv + \int \varphi_{\alpha}^* \hat{h} \delta \varphi_{\alpha} dv = \int \delta \varphi_{\alpha}^* \hat{h} \varphi_{\alpha} dv + \int \delta \varphi_{\alpha} \hat{h} \varphi_{\alpha}^* dv, \quad (2.46)$$

$$\begin{aligned}
\delta g_{\alpha\beta\beta\alpha} &= \int \delta \varphi_{\alpha}^*(\vec{r}_1) \varphi_{\beta}^*(\vec{r}_2) g(\vec{r}_1, \vec{r}_2) \varphi_{\beta}(\vec{r}_2) \varphi_{\alpha}(\vec{r}_1) dv_1 dv_2 \\
&\quad + \int \varphi_{\alpha}^*(\vec{r}_1) \delta \varphi_{\beta}^*(\vec{r}_2) g(\vec{r}_1, \vec{r}_2) \varphi_{\beta}(\vec{r}_2) \varphi_{\alpha}(\vec{r}_1) dv_1 dv_2 \\
&\quad + \int \varphi_{\alpha}^*(\vec{r}_1) \varphi_{\beta}^*(\vec{r}_2) g(\vec{r}_1, \vec{r}_2) \delta \varphi_{\beta}(\vec{r}_2) \varphi_{\alpha}(\vec{r}_1) dv_1 dv_2 \\
&\quad + \int \varphi_{\alpha}^*(\vec{r}_1) \varphi_{\beta}^*(\vec{r}_2) g(\vec{r}_1, \vec{r}_2) \varphi_{\beta}(\vec{r}_2) \delta \varphi_{\alpha}(\vec{r}_1) dv_1 dv_2 \\
&= \int \delta \varphi_{\alpha}^* \hat{K}_{\beta} \varphi_{\alpha} dv + \int \delta \varphi_{\beta}^* \hat{K}_{\alpha} \varphi_{\beta} dv + \int \delta \varphi_{\beta} \hat{K}_{\alpha}^* \varphi_{\beta}^* dv + \int \delta \varphi_{\alpha} \hat{K}_{\beta}^* \varphi_{\alpha}^* dv, \quad (2.47)
\end{aligned}$$

$$\begin{aligned}
\delta g_{\alpha\beta\alpha\beta} &= \int \delta \varphi_{\alpha}^*(\vec{r}_1) \varphi_{\beta}^*(\vec{r}_2) g(\vec{r}_1, \vec{r}_2) \varphi_{\alpha}(\vec{r}_2) \varphi_{\beta}(\vec{r}_1) dv_1 dv_2 \\
&\quad + \int \varphi_{\alpha}^*(\vec{r}_1) \delta \varphi_{\beta}^*(\vec{r}_2) g(\vec{r}_1, \vec{r}_2) \varphi_{\alpha}(\vec{r}_2) \varphi_{\beta}(\vec{r}_1) dv_1 dv_2 \\
&\quad + \int \varphi_{\alpha}^*(\vec{r}_1) \varphi_{\beta}^*(\vec{r}_2) g(\vec{r}_1, \vec{r}_2) \delta \varphi_{\alpha}(\vec{r}_2) \varphi_{\beta}(\vec{r}_1) dv_1 dv_2 \\
&\quad + \int \varphi_{\alpha}^*(\vec{r}_1) \varphi_{\beta}^*(\vec{r}_2) g(\vec{r}_1, \vec{r}_2) \varphi_{\alpha}(\vec{r}_2) \delta \varphi_{\beta}(\vec{r}_1) dv_1 dv_2 \\
&= \int \delta \varphi_{\alpha}^* \hat{A}_{\beta} \varphi_{\alpha} dv + \int \delta \varphi_{\beta}^* \hat{A}_{\alpha} \varphi_{\beta} dv + \int \delta \varphi_{\alpha} \hat{A}_{\beta}^* \varphi_{\alpha}^* dv + \int \delta \varphi_{\beta} \hat{A}_{\alpha}^* \varphi_{\beta}^* dv, \quad (2.48)
\end{aligned}$$

$$\begin{aligned}
\delta E &= \sum_{\alpha}^{1,\dots,N} \delta h_{\alpha\alpha} + \frac{1}{2} \sum_{\alpha,\beta}^{1,\dots,N} [\delta g_{\alpha\beta\beta\alpha} - \delta(\sigma_{\alpha}, \sigma_{\beta}) \delta g_{\alpha\beta\alpha\beta}] \\
&= \sum_{\alpha}^{1,\dots,N} \left(\int \delta \varphi_{\alpha}^* \hat{h} \varphi_{\alpha} dv + \int \delta \varphi_{\alpha} \hat{h} \varphi_{\alpha}^* dv \right) \\
&\quad + \frac{1}{2} \sum_{\alpha,\beta}^{1,\dots,N} \left\{ \int \delta \varphi_{\alpha}^* \hat{K}_{\beta} \varphi_{\alpha} dv + \int \delta \varphi_{\beta}^* \hat{K}_{\alpha} \varphi_{\beta} dv \right. \\
&\quad + \int \delta \varphi_{\beta} \hat{K}_{\alpha}^* \varphi_{\beta}^* dv + \int \delta \varphi_{\alpha} \hat{K}_{\beta}^* \varphi_{\alpha}^* dv \\
&\quad - \delta(\sigma_{\alpha}, \sigma_{\beta}) \left[\int \delta \varphi_{\alpha}^* \hat{A}_{\beta} \varphi_{\alpha} dv + \int \delta \varphi_{\beta}^* \hat{A}_{\alpha} \varphi_{\beta} dv \right. \\
&\quad \left. \left. + \int \delta \varphi_{\alpha} \hat{A}_{\beta}^* \varphi_{\alpha}^* dv + \int \delta \varphi_{\beta} \hat{A}_{\alpha}^* \varphi_{\beta}^* dv \right] \right\} \\
&= \sum_{\alpha}^{1,\dots,N} \left[\int \delta \varphi_{\alpha}^* \hat{F} \varphi_{\alpha} dv + \int \delta \varphi_{\alpha} \hat{F}^* \varphi_{\alpha}^* dv \right]. \tag{2.49}
\end{aligned}$$

Suppose $\{\varphi_{\alpha}\}$ is orthonormal. Let $\{\lambda_{\alpha\beta}\}$ denote the Lagrange multipliers.

$$S_{\alpha\beta} \equiv \int \varphi_{\alpha}^* \varphi_{\beta} dv = \delta(\alpha, \beta), \tag{2.50}$$

$$\sum_{\alpha,\beta}^{1,\dots,N} \lambda_{\alpha\beta} \delta S_{\alpha\beta} = \sum_{\alpha,\beta}^{1,\dots,N} \lambda_{\alpha\beta} \left(\int \delta \varphi_{\alpha}^* \varphi_{\beta} dv + \int \varphi_{\alpha}^* \delta \varphi_{\beta} dv \right) = 0, \tag{2.51}$$

$$\begin{aligned}
\delta E - \sum_{\alpha,\beta}^{1,\dots,N} \lambda_{\alpha\beta} \delta S_{\alpha\beta} &= \sum_{\alpha}^{1,\dots,N} \left[\int \delta \varphi_{\alpha}^* (\hat{F} \varphi_{\alpha} - \sum_{\beta}^{1,\dots,N} \lambda_{\alpha\beta} \varphi_{\beta}) dv \right. \\
&\quad \left. + \int \delta \varphi_{\alpha} (\hat{F}^* \varphi_{\alpha}^* - \sum_{\beta}^{1,\dots,N} \lambda_{\beta\alpha} \varphi_{\beta}^*) dv \right] = 0. \tag{2.52}
\end{aligned}$$

$\delta \varphi_{\alpha}^*$ and $\delta \varphi_{\alpha}$ ($\alpha = 1, 2, \dots, N$) being independent, (2.52) means

$$\hat{F} \varphi_{\alpha} = \sum_{\beta}^{1,\dots,N} \lambda_{\alpha\beta} \varphi_{\beta}, \quad (\alpha, \beta = 1, 2, \dots, N) \tag{2.53}$$

$$\hat{F}^* \varphi_\alpha^* = \sum_{\beta}^{1, \dots, N} \lambda_{\beta\alpha} \varphi_\beta^*, \quad \hat{F} \varphi_\alpha = \sum_{\beta}^{1, \dots, N} \lambda_{\beta\alpha}^* \varphi_\beta. \quad (2.54)$$

From (2.53) and the second relation of (2.54) we get

$$\sum_{\beta}^{1, \dots, N} (\lambda_{\alpha\beta} - \lambda_{\beta\alpha}^*) \varphi_\beta = 0, \quad (2.55)$$

$$\lambda_{\alpha\beta} = \lambda_{\beta\alpha}^*, \quad (2.56)$$

that is, (λ) is a Hermitian matrix which can be diagonalized by an appropriate unitary matrix (A4.2.4) and the diagonal elements $\lambda_{\alpha\alpha} = \varepsilon_\alpha$ are real numbers. Equation (2.15) is (2.53) of diagonalized (λ) .

2.2 Term and Multiplet

2.2.1 Residual Coulomb Interaction and Term

If electron subshells $\{(n, l)\}$ are fully filled, the wave function of the atom Ψ is solely determined, and the configuration energy is nondegenerate. Take atom Ca($1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$) as an example. All of the subshell 1s, 2s, 2p, 3s, 3p, and 4s are fully filled and the spin-orbitals for each subshells are unique such as they are $\{R_{21} Y_{1m_1} \chi_\sigma\} (m_1 = 0, \pm 1; \sigma = \pm)$ for the 2p subshell. The situation is different if one of the subshell is partly filled. Take atom Ti($3d^2 4s^2$) of two more electrons as an example. The situation of the full subshells is the same with that of atom Ca. Another two electrons are in the 3d subshell which has ten different spin-orbital states $\{R_{32} Y_{2m_2} \chi_\sigma\} (m_2 = 0, \pm 1, \pm 2; \sigma = \pm)$. Therefore, there are $10 \times (10 - 1)/2! = 45$ different spin-orbitals for the two 3d electrons. The radial wave function R_{32} of them being the same, they have the same energy, that is, the configuration energy level is 45-fold degenerate.

The above results are obtained under the central field approximation which approximates the potential $\frac{1}{2} \sum_{i,j}^{1, \dots, N; i \neq j} \frac{e^2}{4\pi \varepsilon_0 r_{ij}} - \sum_i^{1, 2, \dots, N} \frac{Ze^2}{4\pi \varepsilon_0 r_i}$ (2.8)–(2.12) by $\sum_i^{1, 2, \dots, N} u(r_i)$ (2.16). Take the neglected residual Coulomb interaction

$$\hat{H}'_2 = \frac{1}{2} \sum_{i,j}^{1, \dots, N; i \neq j} \frac{e^2}{4\pi \varepsilon_0 r_{ij}} - \sum_i^{1, 2, \dots, N} \frac{Ze^2}{4\pi \varepsilon_0 r_i} - \sum_i^{1, 2, \dots, N} u(r_i) \quad (2.57)$$

as perturbation and solve the perturbation secular equation

$$|\langle \Psi_\beta | \hat{H}'_2 | \Psi_\gamma \rangle - \varepsilon \delta(\beta, \gamma)| = 0, \quad (\beta, \gamma = 1, 2, \dots, d. \text{ Appendix 6}) \quad (2.58)$$

where $\{\Psi_\beta\}$ is the configuration wave functions, d the degeneracy of the configuration energy level, and ε the perturbation energy. Let n denote the number of the electrons partially filling the subshell. Each sum of the orbital angular momenta and spin angular momenta of full electron subshells being zero, the orbital and spin angular momenta of the atom are

$$\hat{L} = \sum_i^{1, \dots, n} \hat{l}_i, \quad (2.59)$$

$$\hat{S} = \sum_i^{1, \dots, n} \hat{s}_i. \quad (2.60)$$

$\hat{H}'_2$ being irrelevant to spins, Ψ_β is a product of the functions of positions and spins $\Phi_\beta(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) |S, M_S\rangle$.

$\hat{H}'_2$ is invariant under the rotation–reflection operations (Note 1 of this section) and $\{|L, M_L\rangle\}$ is the basis vectors of irreducible representation of rotation–reflection group (A4.4.2). Therefore, under the $|\alpha, L, M_L\rangle$ representation of $\{\Phi_\beta\}$ the perturbation secular equation

$$|\langle \alpha, L, M_L | \hat{H}'_2 | \alpha, L', M_{L'} \rangle - \varepsilon \delta(L, L') \delta(M_L, M_{L'})| = 0$$

(α : quantum numbers other than L and M_L) (2.61)

is diagonalized (A4.7), and the eigenstates are $\{|\alpha, L, M_L, S, M_S\rangle = |\alpha, L, M_L\rangle |S, M_S\rangle\}$ which have definite values of L and S . The energy being irrelevant to M_S and M_L the degeneracy of each eigenenergy is $(2L + 1) \times (2S + 1)$.

Take atom $\text{Ti}(3d^2 4s^2)$ as an example. Under the residual Coulomb interaction the 45-fold degenerate configuration energy level splits to five energy levels of ^3F , ^1D , ^3P , ^1G , and ^1S (Fig. 2.2, Note 2 of this section). Here S, P, D, F, and G represent the orbital state of $L = 0, 1, 2, 3$, and 4, respectively, and the superscript on the left is the multiplicity $2S + 1$ of total spin. ^{2S+1}L represents a set of degenerate states called a term. ^3F and ^3P have the largest value of S , among which ^3F has the largest value of L . So according to the Hund's first and second rules (Note 3 of this section) ^3F is the ground term. In general, the energy gaps of excited term energy levels with the ground state term energy level are very large so that the excited terms affect magnetic properties of atom little. Hereafter, the excited terms will be neglected unless otherwise mentioned.

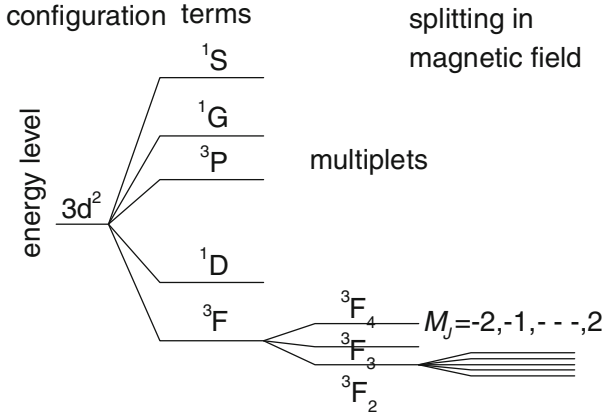


Fig. 2.2 Energy levels of the ground configuration, terms, multiplets, and the split of the ground multiplet energy level in a magnetic field for atom Ti

2.2.2 Spin-Orbit Interaction and Multiplet

An electron in an atom circumrotates around the nucleus, thus the nucleus circumrotates relatively around the electron and produces a magnetic field. This magnetic field interacts with the electron spin magnetic moment. This interaction belongs to a relativity effect and is called spin-orbit interaction. The spin-orbit interaction operator could be obtained from the relativistic Dirac equation (1928) [1]. The Hamiltonian of the electron in a single-electron atom in this equation is

$$\hat{H}_D = \frac{(\hat{\vec{p}} - e\vec{A})^2}{2m + (E' - eV)/c^2} + eV - \frac{e\hbar\hat{\vec{\sigma}} \cdot \vec{B}}{2m + (E' - eV)/c^2} + \frac{ie\hbar}{[2m + (E' - eV)/c^2]^2 c^2} \vec{E} \cdot [(\hat{\vec{p}} - e\vec{A}) + i(\hat{\vec{p}} - e\vec{A}) \times \hat{\vec{\sigma}}], \quad (2.62)$$

$$eV = u(r), \quad (2.63)$$

$$\vec{E} = \frac{E_r \vec{r}}{r} = -\frac{1}{e} \frac{du(r)}{dr} \frac{\vec{r}}{r}, \quad (2.64)$$

where c is the speed of light in vacuum, m the electron rest mass, $E' = E - mc^2$ the eigenenergy not including the rest-mass energy mc^2 , $\vec{A}$, $\vec{B}$, V , and $\vec{E}$ the magnetic vector potential, magnetic induction, electric potential, and electric field produced by the nucleus. The spin-orbit interaction is the term in the right of (2.62) which includes the product of $\hat{\vec{\sigma}}$ and $\hat{\vec{p}}$, that is,

$$\hat{H}_{LS} = \frac{ie\hbar}{[2m + (E' - eV)/c^2]^2 c^2} \vec{E} \cdot (i\hat{\vec{p}} \times \hat{\vec{\sigma}})$$

$$= \frac{\hbar^2}{2m^2c^2} \frac{1}{r} \frac{du(r)}{dr} \hat{l} \cdot \hat{s} \equiv \xi(r) \hat{l} \cdot \hat{s}. \quad ((E' - eV)/c^2 \ll 2m, \quad (\text{a3.3})) \quad (2.65)$$

The spin-orbit interactions in a multiple electron atom is

$$\hat{H}_{LS} = \sum_i^{1, \dots, n} \xi(r_i) \hat{l}_i \cdot \hat{s}_i, \quad (2.66)$$

where $\xi(r_i)$ is given by the last relation of (2.65) but with the central field $u(r_i)$ produced by both of the nucleus and the other electrons. $\hat{H}_{LS}$ for a term can be formulated simply as

$$\hat{H}_{LS} = \lambda \hat{L} \cdot \hat{S}. \quad (\text{Note 4 of this section}) \quad (2.67)$$

λ is called spin-orbit coupling constant.

The non-relativistic Hamiltonian for an atom including the spin-orbit interaction is $\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{H}_{LS}$. $\hat{H}$ is invariant under the rotation-reflection operations (Note 1 of this section). $\hat{J} = \hat{L} + \hat{S}$ is the total angular momentum of the atom. The simultaneous eigenfunction $|J, M_J\rangle$ of $\hat{J}^2$ and $\hat{J}_z$ is a basis vector of the irreducible representation of rotation-reflection group (A4.4.2). Therefore, under the representation of $|\alpha, L, S, J, M_J\rangle$ the secular equation

$$|\langle \alpha, L, S, J, M_J | \hat{H} | \alpha, L, S, J', M_{J'} \rangle - \varepsilon \delta(J, J') \delta(M_J, M_{J'})| = 0 \quad (2.68)$$

is diagonalized (A4.7) and the eigenstate is $|\alpha, L, S, J, M_J\rangle$ ($J = |L - S|, |L - S| + 1, \dots, L + S$). The perturbation energy of $\hat{H}_{LS}$ is

$$\begin{aligned} \varepsilon_{LS} &= \lambda \langle \alpha, L, S, J, M_J | \hat{L} \cdot \hat{S} | \alpha, L, S, J, M_J \rangle \\ &= \frac{1}{2} \lambda [J(J+1) - L(L+1) - S(S+1)], \end{aligned} \quad (2.69)$$

which is independent of M_J and is $2J + 1$ fold degenerate. Under the spin-orbit interaction the energy level of the term ^{2S+1}L splits into energy levels of $\{^{2S+1}L_J\}$ ($J = |L - S|, |L - S| + 1, \dots, L + S$). Here $^{2S+1}L_J$ represents the set of the eigenstates $\{|\alpha, L, S, J, M_J\rangle\}$ ($M_J = -J, -J + 1, \dots, J$) which is called multiplet. If the partially filled subshell is filled less than half or more than half, λ is positive or negative (Note 5 of this section), and J of the ground multiplet is $|L - S|$ or $L + S$. The last result is just the Hund's third rule (Note 3 of this section). The energy gap between the neighboring multiplets is

$$\varepsilon_{LS}(\alpha, L, S, J) - \varepsilon_{LS}(\alpha, L, S, J - 1) = \lambda J. \quad (2.70)$$

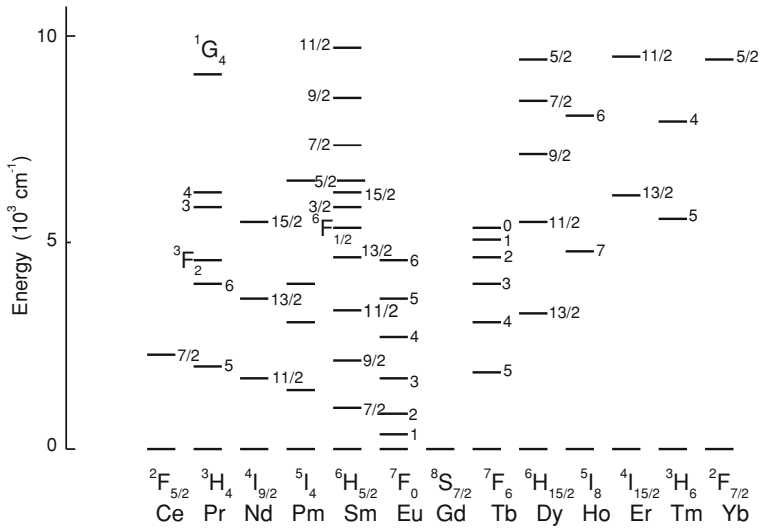


Fig. 2.3 The observed multiplet energy levels of the R (rare-earth) ions in RCl₂

Take atom Ti(3d²4s²) as an example. Under the spin-orbit interaction, the energy level of the ground term ³F splits into the energy levels of ³F₂, ³F₃, and ³F₄ multiplets. The 3d subshell is filled less than a half and hence ³F₂ is the ground state (Fig. 2.2).

In most cases, the energy gaps between excited multiplet energy levels and the ground multiplet energy level are still very large. Figure 2.3 demonstrates the multiplet energy levels of the rare-earth ions R observed in RCl₂ [2]. Take ion Nd⁺³(4f³) as an example. The energy gap between the first excited multiplet ⁴I_{11/2} energy level and the ground state ⁴I_{9/2} energy level is about 2,100 cm⁻¹ = 3,000 K which is about 10-folds of thermal energy at R. T.. Except for the ions of small value of *J* for ground multiplet, such as Eu (*J* = 0) and Sm (*J* = 5/2), the neglect of the excited multiplets does not affect the quality of the analysis of magnetic properties very much. In the following, the excited multiplets will be neglected unless otherwise mentioned.

Note 1

r_i and $|\vec{r}_i - \vec{r}_j|$ are the lengths and $\hat{L} \cdot \hat{S}$ is a scalar product. Apparently all of them are invariant under rotation-reflection operations.

Below it will be proven that $\sum_{\alpha}^{x,y,z} \partial^2 / \partial \alpha^2$ also remains unchanged under the rotation-reflection operations. Let the coordinate of a fixed in the space position be $\vec{r}(x, y, z)$ before a rotation-reflection operation. After the coordinate system is rotation-reflection operated the position vector in the new coordinate system becomes $\vec{r}'(x', y', z')$. (x', y', z') and (x, y, z) are linearly related and $|\vec{r}'| = |\vec{r}|$, that is

$$(r') = \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = (T) (r) = \begin{pmatrix} \frac{\partial x'}{\partial x} & \frac{\partial x'}{\partial y} & \frac{\partial x'}{\partial z} \\ \frac{\partial y'}{\partial x} & \frac{\partial y'}{\partial y} & \frac{\partial y'}{\partial z} \\ \frac{\partial z'}{\partial x} & \frac{\partial z'}{\partial y} & \frac{\partial z'}{\partial z} \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}, \quad (2.71)$$

$$(r')^T = (x' \ y' \ z') = (r)^T (T)^T = (x \ y \ z) \begin{pmatrix} \frac{\partial x'}{\partial x} & \frac{\partial y'}{\partial x} & \frac{\partial z'}{\partial x} \\ \frac{\partial x'}{\partial y} & \frac{\partial y'}{\partial y} & \frac{\partial z'}{\partial y} \\ \frac{\partial x'}{\partial z} & \frac{\partial y'}{\partial z} & \frac{\partial z'}{\partial z} \end{pmatrix}, \quad ((r')^T : \text{transpose of } (r)) \quad (2.72)$$

$$r'^2 = (r')^T (r') = (r)^T (T)^T (T) (r) = (r)^T (r) = r^2. \quad (2.73)$$

From above equation we get

$$(T)^T (T) = 1 = (T) (T)^T, \quad (2.74)$$

that is,

$$\sum_{\alpha}^{x,y,z} \frac{\partial \beta'}{\partial \alpha} \frac{\partial \gamma'}{\partial \alpha} = \delta(\beta', \gamma'), \quad (\beta', \gamma' = x', y', z') \quad (2.75)$$

$$\begin{aligned} \sum_{\alpha}^{x,y,z} \frac{\partial^2}{\partial \alpha^2} &= \sum_{\alpha}^{x,y,z} \sum_{\gamma}^{x',y',z'} \frac{\partial \gamma}{\partial \alpha} \frac{\partial}{\partial \gamma} \sum_{\beta}^{x',y',z'} \frac{\partial \beta}{\partial \alpha} \frac{\partial}{\partial \beta} = \sum_{\beta,\gamma}^{x',y',z'} \frac{\partial^2}{\partial \beta \partial \gamma} \sum_{\alpha}^{x,y,z} \frac{\partial \gamma}{\partial \alpha} \frac{\partial \beta}{\partial \alpha} \\ &= \sum_{\beta}^{x',y',z'} \frac{\partial^2}{\partial \beta^2}. \end{aligned} \quad (2.76)$$

Note 2

$l_1 = l_2 = l = 2$; $L = |l_1 - l_2|, |l_1 - l_2| + 1, \dots, l_1 + l_2 = 0, 1, 2, 3, 4$; $s_1 = s_2 = s = 1/2$; and $S = |s_1 - s_2|, |s_1 - s_2| + 1, \dots, s_1 + s_2 = 0, 1$. The atomic orbitals $\Phi_{LM_L}(1, 2)$ and $\Phi_{LM_L}(2, 1)$ are

$$\Phi_{LM_L}(1, 2) = \sum_{m_l, m'_l} C(l l L; m_l m'_l M_L) \varphi_{lm_l}(1) \varphi_{lm'_l}(2), \quad (\varphi_{lm_l}(i) \equiv \varphi_{3lm_l}(\vec{r}_i)) \quad (2.77)$$

$$\begin{aligned}
\Phi_{LM_L}(2, 1) &= \sum_{m_l, m'_l} C(11L; m_l m'_l M_L) \phi_{lm_l}(2) \phi_{lm'_l}(1) \\
&= (-1)^{2l-L} \sum_{m_l, m'_l} C(11L; m'_l m_l M_L) \phi_{lm'_l}(1) \phi_{lm_l}(2) \\
&= (-1)^{2l-L} \Phi_{LM_L}(1, 2), \quad (\text{a4.27})
\end{aligned} \tag{2.78}$$

where $C(11L; m_l m'_l M_L)$ is the Clebsch–Gordan coefficient (A4.8.1). In the same way

$$X_{SM_S}(2, 1) = (-1)^{1-S} X_{SM_S}(1, 2). \tag{2.79}$$

Since the wave function of the atom is antisymmetric, it holds

$$\begin{aligned}
\Phi_{LM_L}(1, 2) X_{SM_S}(1, 2) &= -\Phi_{LM_L}(2, 1) X_{SM_S}(2, 1) \\
&= (-1)^{2l-L+1-S} \Phi_{LM_L}(2, 1) X_{SM_S}(2, 1), \quad (\text{2.80})
\end{aligned}$$

thus $L + S$ should be even integer. In brief summary, the possible values of the set (L, S) are (0,0), (2,0), (4,0), (1,1), and (3,1). Therefore, the 45 degenerate configuration energy level of Ti atom splits into five energy levels of ^1S , ^1D , ^1G , ^3P , and ^3F terms.

Note 3

The Hund's rules (~ 1927) are

- ① The lowest energy term is that which has the largest S .
- ② For terms that have the same S , the term with the largest L lies lowest in energy.
- ③ If the partly filled subshell is exactly or more than half full, the level with the largest J value has the lowest energy. If the partly filled subshell is less than half full, the level with the smallest J value has the lowest energy.

Note 4

$$\begin{aligned}
&\sum_i^{1,2,\dots,n} \langle L, M'_L, S, M'_S | \hat{l}_i \cdot \hat{s}_i | L, M_L, S, M_S \rangle \\
&= n \sum_{\alpha}^{\pm 1,0} (-1)^{\alpha} \langle L, M'_L | \hat{l}_{\alpha 1} | L, M_L \rangle \langle S, M'_S | \hat{s}_{-\alpha 1} | S, M_S \rangle \quad (\text{A4.6, A4.8.3}) \\
&= n \langle l, \dots, l, L | \hat{l} | l, \dots, l, L \rangle \langle s, \dots, s, S | \hat{s} | s, \dots, s, S \rangle \\
&\quad \times \sum_{\alpha}^{\pm 1,0} (-1)^{\alpha} C(L1L; M_L \alpha M'_L) C(S1S; M_S, -\alpha, M'_S), \quad (\text{a4.35})
\end{aligned} \tag{2.81}$$

$$\begin{aligned}
& \langle L, M'_L, S, M'_S | \hat{\vec{L}} \cdot \hat{\vec{S}} | L, M_L, S, M_S \rangle \\
&= \sum_{\alpha}^{\pm 1, 0} (-1)^{\alpha} \langle L, M'_L | \hat{L}_{\alpha} | L, M_L \rangle \langle S, M'_S | \hat{S}_{-\alpha} | S, M_S \rangle \\
&= \langle L \| \hat{L} \| L \rangle \langle S \| \hat{S} \| S \rangle \sum_{\alpha}^{\pm 1, 0} (-1)^{\alpha} C(L 1 L; M_L \alpha M'_L) C(S 1 S; M_S, -\alpha, M'_S).
\end{aligned} \tag{2.82}$$

Equations (2.81) and (2.82) have the same relations with respect to M_L, M'_L, M_S and M'_S and hence (2.66) can be expressed as (2.67).

Note 5

$$\begin{aligned}
\varepsilon_{LS} &= \lambda \langle \alpha, L, S, J, M_J | \hat{\vec{L}} \cdot \hat{\vec{S}} | \alpha, L, S, J, M_J \rangle = \lambda M_L M_S \\
&= \left\langle \alpha, L, S, J, M_J \left| \sum_i^{1, 2, \dots, n} \xi(r_i) \hat{l}_{zi} \hat{s}_{zi} \right| \alpha, L, S, J, M_J \right\rangle = \langle \xi \rangle \sum_i^{1, 2, \dots, n} m_{li} m_{si},
\end{aligned} \tag{2.83}$$

$$M_L = \sum_i m_{li}, \quad M_S = \sum_i m_{si}, \tag{2.84}$$

where $\langle \xi \rangle$ is the average of $\xi(r_i)$. From (2.83) we get

$$\lambda = \langle \xi \rangle \frac{\sum_i^{1, 2, \dots, n} m_{li} m_{si}}{M_L M_S}. \quad (M_L M_S \neq 0) \tag{2.85}$$

The electron spins are strongly exchange coupled to align parallel (Sect. 2.5.2). Therefore, if the subshell is filled less than half, $m_{si} = 1/2$, $M_S = n/2 = S$, or $m_{si} = -1/2$, $M_S = -n/2 = -S$ and $M_L = \sum_i^{1, 2, \dots, n} m_{li}$, thus

$$\lambda = \langle \xi \rangle \frac{\frac{1}{2} \sum_i^{1, 2, \dots, n} m_{li}}{M_L \frac{n}{2}} = \frac{\langle \xi \rangle}{n} = \frac{\langle \xi \rangle}{2S} > 0. \tag{2.86}$$

If the subshell is filled more than half,

$$\begin{aligned}
M_S &= \frac{1}{2} \{ (2l+1) - [n - (2l+1)] \} = \frac{1}{2} [2(2l+1) - n] = S \quad (\text{or } M_S = -S), \\
\sum_i^{1, 2, \dots, n} m_{li} m_{si} &= \frac{1}{2} \left[\sum_i^{1, 2, \dots, 2l+1} m_{li} - \sum_i^{(2l+1)+1, 2l+1)+2, \dots, n} m_{li} \right]
\end{aligned}$$

$$= -\frac{1}{2} \sum_i^{(2l+1)+1, 2l+1)+2, \dots, n} m_{li} = -\frac{1}{2} M_L$$

$$\left(\text{or } \sum_i^{1, 2, \dots, n} m_{li} m_{si} = \frac{1}{2} M_L \right), \quad (2.87)$$

thus

$$\lambda = \langle \xi \rangle \frac{(-1/2)M_L}{M_L(2l+1-n/2)} = \frac{-\langle \xi \rangle}{2(2l+1)-n} = \frac{-\langle \xi \rangle}{2S} < 0. \quad (2.88)$$

2.3 Intrinsic Magnetic Moment and Gyromagnetic Ratio of Atom

2.3.1 Magnetic Moment and Gyromagnetic Ratio of an Electron Orbit

The orbital of an electron in an atom is $\varphi_{nlm_l}(\vec{r}) = |n, l, m_l\rangle$ (2.17). The z component of the orbital magnetic polarization moment is (Note 1 of this section)

$$p_J(m_l) = -m_l \mu_B = -\langle n, l, m_l | \hbar \hat{L}_z | n, l, m_l \rangle \gamma_l, \quad (2.89)$$

where

$$\mu_B = \frac{\mu_0 |e| \hbar}{2m} \quad (\text{J} \cdot \text{m/A}) \quad (2.90)$$

is the Bohr magneton (μ_B is often defined by $|e| \hbar / (2m)$ (J/T) such that all the magnetic polarization moments in this section are replaced by corresponding magnetic moments such as (2.89) by $p_M(m_l) = -m_l \mu_B$. This book adopts the μ_B of (2.90)), and

$$\gamma_l \equiv \left| \frac{p_J(m_l)}{\hbar m_l} \right| = \frac{\mu_B}{\hbar} \quad (2.91)$$

is the absolute value of the ratio of the orbital magnetic polarization moment to the orbital angular momentum, which is called the gyromagnetic ratio of the electron orbit.

2.3.2 Magnetic Moment and Gyromagnetic Ratio of an Electron Spin

The z component of an electron spin magnetic polarization moment is

$$p_J(m_s) = -g_e m_s \mu_B = -\langle s, m_s | \hbar \hat{S}_z | s, m_s \rangle \gamma_s, \quad (g_e = 2.00232 \approx 2) \quad (2.92)$$

where

$$\gamma_s \equiv \left| \frac{p_J(m_s)}{\hbar m_s} \right| = 2 \frac{\mu_B}{\hbar} = 2\gamma_l \quad (2.93)$$

is the absolute value of the ratio of the spin magnetic polarization moment to the spin angular momentum, which is called the gyromagnetic ratio of an electron spin.

2.3.3 Intrinsic Magnetic Moment, g Factor, and Effective Magnetic Moment of an Atom

The z component of the orbital magnetic polarization moment of an atom is

$$p_J(M_L) = -M_L \mu_B = -\langle L, M_L | \hbar \hat{L}_z | L, M_L \rangle \gamma_l. \quad (2.94)$$

The largest value of $p_J(M_L)$ $p_J(-L) = L \mu_B$ is called the intrinsic orbital magnetic polarization moment or tersely orbital magnetic polarization moment of an atom.

$$\sqrt{\langle L, M_L | \hbar^2 \hat{L}^2 | L, M_L \rangle} \gamma_l = \sqrt{L(L+1)} \mu_B \quad (2.95)$$

is called the effective orbital magnetic polarization moment of an atom.

The z component of the spin magnetic polarization moment of an atom is

$$p_J(M_S) = -2M_S \mu_B = -\langle S, M_S | \hbar \hat{S}_z | S, M_S \rangle \gamma_s. \quad (2.96)$$

The largest value of $p_J(M_S)$ $p_J(-S) = 2S \mu_B$ is called the intrinsic spin magnetic polarization moment or tersely spin magnetic polarization moment of an atom.

$$\sqrt{\langle S, M_S | \hbar^2 \hat{S}^2 | S, M_S \rangle} \gamma_s = 2\sqrt{S(S+1)} \mu_B \quad (2.97)$$

is called the effective spin magnetic polarization moment of an atom.

The z component of the magnetic polarization moment of an atom is

$$\begin{aligned} p_J(M_J) &= -\langle L, S, J, M_J | \hbar(\hat{L}_z + 2\hat{S}_z) | L, S, J, M_J \rangle \gamma_l \\ &= -g_J M_J \mu_B = -\langle L, S, J, M_J | \hbar \hat{J}_z | L, S, J, M_J \rangle \gamma_J, \end{aligned} \quad (2.98)$$

where

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \quad (\text{Note 2 of this section}) \quad (2.99)$$

is called the Landé g factor (or tersely g factor), and

Table 2.3 Ground electron configurations, ground multiplets, and the values of S , L , J , g_J , $g_J J$, and $g_J \sqrt{J(J+1)}$ for three-valence rare-earth ions

Ion	Configuration	Multiplet	S	L	J	g_J	$g_J J$	$g_J \sqrt{J(J+1)}$
La	4f ⁰	¹ S ₀	0	0	0	0	0	0
Ce	4f ¹	² F _{5/2}	1/2	3	5/2	6/7	2.14	2.54
Pr	4f ²	³ H ₄	1	5	4	4/5	3.20	3.58
Nd	4f ³	⁴ I _{9/2}	3/2	6	9/2	8/1	3.27	3.62
Pm	4f ⁴	⁵ I ₄	2	6	4	3/5	2.40	2.68
Sm	4f ⁵	⁶ H _{5/2}	5/2	5	5/2	2/7	0.71	0.85
Eu	4f ⁶	⁷ F ₀	3	3	0	0	0	0
Gd	4f ⁷	⁸ S _{7/2}	7/2	0	7/2	2	7	7.94
Tb	4f ⁸	⁷ F ₆	3	3	6	3/2	9	9.72
Dy	4f ⁹	⁶ H _{15/2}	5/2	5	15/2	4/3	10	10.65
Ho	4f ¹⁰	⁵ I ₈	2	6	8	5/4	10	10.61
Er	4f ¹¹	⁴ I _{15/2}	3/2	6	15/2	6/5	9	9.58
Tm	4f ¹²	³ H ₆	1	5	6	7/6	7	7.56
Yb	4f ¹³	² F _{7/2}	1/2	3	7/2	8/7	4	4.54
Lu	4f ¹⁴	¹ S ₀	0	0	0	0	0	0

$$\gamma_J = \left| \frac{p_J(M_J)}{\hbar M_J} \right| = g_J \frac{\mu_B}{\hbar} \quad (2.100)$$

is the absolute value of the ratio of the atomic magnetic polarization moment to the angular momentum, which is called the gyromagnetic ratio of an atom.

The largest value of $p_J(M_J)$ $p_J(-J) = g_J J \mu_B$ is called the intrinsic atomic magnetic polarization moment or tersely atomic magnetic polarization moment.

$$p_{J\text{eff}} \equiv g_J \sqrt{\langle J, M_J | \hat{J}^2 | J, M_J \rangle} \mu_B = g_J \sqrt{J(J+1)} \mu_B \quad (2.101)$$

is called effective magnetic polarization moment of an atom.

Table 2.3 lists the ground electron configurations, ground multiplets, and the values of S , L , J , g_J (g factor), $g_J J$ (magnetic polarization moment in μ_B unit), and $g_J \sqrt{J(J+1)}$ (effective magnetic polarization moment in μ_B unit) for three-valence rare-earth ions.

Note 1

First consider a general case in which an electron is moving in an arbitrary potential u . The orbital φ satisfies the Schrödinger equation

$$i\hbar \frac{\partial \varphi}{\partial t} = \left(-\frac{\hbar^2}{2m} \nabla^2 + u \right) \varphi. \quad (2.102)$$

The conjugate complex of the equation is

$$-i\hbar \frac{\partial \varphi^*}{\partial t} = \left(-\frac{\hbar^2}{2m} \nabla^2 + u \right) \varphi^*. \quad (2.103)$$

By subtracting the product of (2.102) and $e\varphi^*$ by the product of (2.103) and $e\varphi$, we get the law of conservation of electric charge

$$-e \frac{\partial}{\partial t} (\varphi^* \varphi) = \frac{ie\hbar}{2m} \nabla \cdot (\varphi \nabla \varphi^* - \varphi^* \nabla \varphi), \quad (2.104)$$

in which the left is the diverging rate of the electric charge density and the right the divergence of the electric current density $\vec{j} = (ie\hbar/2m)(\varphi \nabla \varphi^* - \varphi^* \nabla \varphi)$.

In this section $\varphi = \varphi_{nlm_l}(\vec{r})$ and

$$\vec{j} = \frac{ie\hbar}{2m} [\varphi_{nlm_l}(\vec{r}) \nabla \varphi_{nlm_l}^*(\vec{r}) - \varphi_{nlm_l}^*(\vec{r}) \nabla \varphi_{nlm_l}(\vec{r})]. \quad (2.105)$$

The r and θ components of $\vec{j}$ are zero. The ϕ component is

$$\begin{aligned} j_\phi &= \frac{ie\hbar}{2m} \frac{1}{r \sin \theta} \left[\varphi_{nlm_l}(\vec{r}) \frac{\partial \varphi_{nlm_l}^*(\vec{r})}{\partial \phi} - \varphi_{nlm_l}^*(\vec{r}) \frac{\partial \varphi_{nlm_l}(\vec{r})}{\partial \phi} \right] \quad (\text{a3.20}) \\ &= \frac{e\hbar m_l}{m} \frac{1}{r \sin \theta} |\varphi_{nlm_l}(\vec{r})|^2. \quad (2.17)-(2.18) \end{aligned} \quad (2.106)$$

$$p_J(m_l) = \mu_0 \int_0^\infty \int_0^\pi \pi (r \sin \theta)^2 j_\phi r d\theta dr = -m_l \mu_B. \quad ((1.21), (2.90)) \quad (2.107)$$

Note 2

$\{\hat{L}_{\pm 1}, \hat{L}_0\}$ and $\{\hat{J}_{\pm 1}, \hat{J}_0\}$ are the first-rank irreducible tensors (A4.6), thereby

$$\langle J, M_J | \hat{J}_\alpha | J, M'_J \rangle = C(J1J; M'_J \alpha M_J) \langle J || \hat{J} || J \rangle, \quad (\alpha = \pm 1, 0) \quad (2.108)$$

$$\langle L, S, J, M_J | \hat{L}_\alpha | L, S, J, M'_J \rangle = C(J1J; M'_J \alpha M_J) \langle J || \hat{L} || J \rangle, \quad (\text{a4.35}) \quad (2.109)$$

$$\begin{aligned} &\langle L, S, J, M_J | \hat{L}_\alpha + 2\hat{S}_\alpha | L, S, J, M'_J \rangle \\ &= \langle J, M_J | \hat{J}_\alpha | J, M'_J \rangle + \langle L, S, J, M_J | \hat{L}_\alpha | L, S, J, M'_J \rangle \\ &= \langle J, M_J | g_J \hat{J}_\alpha | J, M'_J \rangle, \end{aligned} \quad (2.110)$$

where the proportional coefficient g_J is irrelevant to M_J and M'_J . Equation (2.110) shows that

$$\hat{\vec{L}} + 2\hat{\vec{S}} = \hat{\vec{J}} + \hat{\vec{S}} = g_J \hat{\vec{J}}, \quad (2.111)$$

$$\hat{\vec{J}} \cdot \hat{\vec{S}} = (g_J - 1) \hat{\vec{J}}^2, \quad (2.112)$$

$$\begin{aligned} \hat{\vec{L}}^2 &= (\hat{\vec{J}} - \hat{\vec{S}})^2 = \hat{\vec{J}}^2 + \hat{\vec{S}}^2 - 2\hat{\vec{J}} \cdot \hat{\vec{S}} = \hat{\vec{J}}^2 + \hat{\vec{S}}^2 - 2(g_J - 1) \hat{\vec{J}}^2, \\ g_J \hat{\vec{J}}^2 &= \hat{\vec{J}}^2 + \frac{1}{2}(\hat{\vec{J}}^2 + \hat{\vec{S}}^2 - \hat{\vec{L}}^2), \end{aligned} \quad (2.113)$$

$$\begin{aligned} g_J &= 1 + \frac{\langle L, S, J, M_J | \hat{\vec{J}}^2 + \hat{\vec{S}}^2 - \hat{\vec{L}}^2 | L, S, J, M_J \rangle}{2\langle L, S, J, M_J | \hat{\vec{J}}^2 | L, S, J, M_J \rangle} \\ &= 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}. \end{aligned} \quad (2.114)$$

2.4 Paramagnetism and Diamagnetism of Atom

2.4.1 Magnetic Moment Operator of an Atom in a Magnetic Field

In the magnetic field $\vec{B} = B\vec{e}_z$ the Hamiltonian of an atom is

$$\begin{aligned} \hat{H} &= \sum_i^{1,\dots,Z} \left\{ \frac{1}{2m} [\hat{p}_i - e\vec{A}(\vec{r}_i)]^2 + 2\mu_B \hat{s}_{zi} H \right\} + \text{intra-atomic interactions}, \\ &\quad (\text{Sect. 1.5, (2.92), (1.75)}) \end{aligned} \quad (2.115)$$

$$\vec{A}(\vec{r}) = \frac{1}{2} \vec{B} \times \vec{r} = -\frac{1}{2} B y \vec{e}_x + \frac{1}{2} B x \vec{e}_y. \quad (\text{Note 1 of this section}) \quad (2.116)$$

The terms including the magnetic field in the Hamiltonian is

$$\sum_i^{1,\dots,Z} \left[\mu_B (\hat{l}_{zi} + 2\hat{s}_{zi}) H + \frac{(e\mu_0 H)^2}{8m} (x_i^2 + y_i^2) \right], \quad (\text{Note 2 of this section}) \quad (2.117)$$

and the projection of atomic magnetic polarization moment operator in the $\vec{H}$ direction and its eigenvalue are

$$\hat{p}_J = -\frac{\partial \hat{H}}{\partial H} = -\mu_B(\hat{L}_z + 2\hat{S}_z) - \frac{e^2\mu_0^2}{4m}H \sum_i^{1,\dots,Z} (x_i^2 + y_i^2), \quad (2.118)$$

$$\begin{aligned} & \langle \alpha, L, S, J, M_J | \hat{p}_J | \alpha, L, S, J, M_J \rangle \\ &= -g_J M_J \mu_B - \frac{e^2\mu_0^2}{4m} \frac{2Z \langle r^2 \rangle}{3} H. \quad (\langle r^2 \rangle = 3\langle x^2 \rangle = 3\langle y^2 \rangle: \text{average of } r_i^2) \end{aligned} \quad (2.119)$$

Suppose there are N atoms in a unit volume.

2.4.2 Paramagnetism of Atom

The first term in the last expression of (2.119) is the eigenvalue of the z component of the magnetic polarization moment operator of the atom. The magnetization is

$$M = \frac{N \sum_{M_J}^{-J, -J+1, \dots, J} -g_J M_J \mu_B \exp\left(-\frac{g_J M_J \mu_B H}{k_B T}\right)}{\mu_0 \sum_{M_J}^{-J, -J+1, \dots, J} \exp\left(-\frac{g_J M_J \mu_B H}{k_B T}\right)} = \frac{N g_J J \mu_B}{\mu_0} B_J(x), \quad (2.120)$$

$$x \equiv \frac{g_J J \mu_B H}{k_B T}, \quad (2.121)$$

$$B_J(x) \equiv \frac{2J+1}{2J} \text{cth}\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J} \text{cth}\frac{x}{2J}. \quad (2.122)$$

$B_J(x)$ is called Brillouin function. Such magnetic property of $M > 0$ is called paramagnetism.

If $x \ll 1$,

$$B_J(x) = \frac{x}{3} \frac{J+1}{J}, \quad (2.123)$$

$$M = \frac{N g_J^2 J(J+1) \mu_B^2}{3 \mu_0 k_B T} H, \quad (2.124)$$

and hence

$$\chi = \frac{C}{T}, \quad (2.125)$$

$$C = \frac{N g_J^2 J(J+1) \mu_B^2}{3 \mu_0 k_B}. \quad (2.126)$$

Equation (2.125) is called the Curie law and C the Curie constant. The value of C can be obtained from the slope of the straightline $1/\chi(T)$ of experiment, and the effective magnetic polarization moment of the atom $g_J\sqrt{J(J+1)}\mu_B$ can be obtained from (2.126) by using the experimental value of C .

2.4.3 Diamagnetism of Atom

The last terms in the last expressions of (2.118) and (2.119) are negative, that is, the magnetization of negative susceptibility is oriented opposite to the magnetic field direction. Such magnetic property is called diamagnetism.

The term of (2.118) can also be deduced by using the following semiclassical model. An electron circumrotating with velocity $\vec{v}$ on a circular orbit of radius r has an orbital angular momentum $\hbar\vec{l} = m\vec{r} \times \vec{v}$ and orbital magnetic polarization moment

$$\vec{p}_J = \mu_0 I \vec{S} = \mu_0 \frac{ve}{2\pi r} \pi r^2 \frac{\vec{r} \times \vec{v}}{rv} = \frac{\mu_0 e}{2m} \hbar \vec{l}. \quad (1.21) \quad (2.127)$$

The absolute value of the ratio of $\vec{p}_J$ to $\hbar\vec{l}$ is $|\mu_0 e/2m| = \gamma_l$ in coincidence with (2.91). According to the equation of motion for an angular momentum, the derivative of the angular momentum $\hbar\vec{l}$ with respect to time equals to the torque exerted on the magnetic moment by the applied magnetic field $\vec{p}_J \times \vec{H} = -\gamma_l \hbar\vec{l} \times \vec{H}$, that is,

$$\frac{d\vec{l}}{dt} = -\gamma_l \vec{l} \times \vec{H}. \quad (2.128)$$

Let $\vec{l} = \vec{l}_0 \exp(i\omega t)$. The x and y components of (2.128) are

$$i\omega l_x + \gamma_l H l_y = 0, \quad (2.129)$$

$$-\gamma_l H l_x + i\omega l_y = 0. \quad (2.130)$$

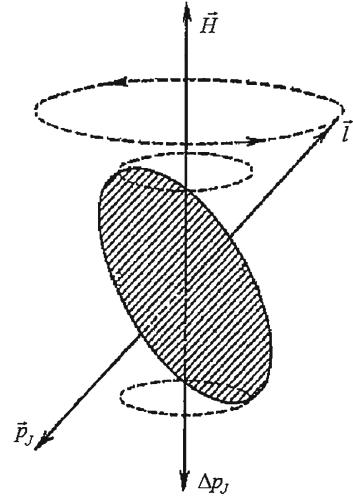
The solution of (2.129) and (2.130) are (Sect. 3.6.7.3)

$$\omega = \gamma_l H, \quad (2.131)$$

$$l_y = -il_x, \quad (2.132)$$

that is, $\vec{l}$ makes a precession about the $\vec{H}$ direction along the right-hand direction with angular speed $\gamma_l H$ (Fig. 2.4). Such precession is called Larmor precession. The precession increases the angular momentum and magnetic polarization moment in the field direction by

$$\Delta l = m\omega r_{\perp}^2 = m\gamma_l (x^2 + y^2) H, \quad (2.133)$$

Fig. 2.4 Larmor precession

and

$$\Delta p_J = -\gamma_l \Delta l = -\frac{\mu_0^2 e^2 (x^2 + y^2)}{4m} H. \quad ((2.90)-(2.91)) \quad (2.134)$$

The sum of $\Delta \vec{p}_J$ over the electrons of an atom is just the last term in the right of (2.118).

The diamagnetic susceptibility is

$$\chi = -N \frac{\mu_0 e^2}{4m} \sum_i^{1, \dots, Z} (x_i^2 + y_i^2) = -N \frac{\mu_0 Z e^2 \langle r^2 \rangle}{6m}. \quad (2.135)$$

$\langle r^2 \rangle$ being little affected by temperature, χ is essentially independent of temperature.

Note 1

A_α ($\alpha = x, y, z$) satisfying the relations of

$$\begin{aligned} B_x &= \frac{\partial A_z}{\partial y} - \frac{\partial A_y}{\partial z} = 0, & B_y &= \frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x} = 0, \\ B_z &= \frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y} = B, \end{aligned} \quad (1.11) \quad (2.136)$$

$$\nabla \cdot \vec{A} = \frac{\partial A_x}{\partial x} + \frac{\partial A_y}{\partial y} + \frac{\partial A_z}{\partial z} = 0 \quad (1.14) \quad (2.137)$$

can be expressed as

$$A_\alpha = \sum_{\beta}^{x,y,z} C_{\alpha\beta} \beta, \quad (2.138)$$

in which $C_{\alpha\beta}$ satisfies the conditions

$$C_{zy} = C_{yz}, \quad C_{xz} = C_{zx}, \quad C_{yx} - C_{xy} = B, \quad (2.136) \quad (2.139)$$

$$C_{xx} + C_{yy} + C_{zz} = 0. \quad (2.137)$$

There are many ways to select the values of $C_{\alpha\beta}$. This section takes $C_{yx} = -C_{xy} = B/2$, and the others zero.

Note 2

Let φ be an arbitrary function of $\vec{r}$.

$$\nabla \cdot (\vec{A}\varphi) = \vec{A} \cdot \nabla\varphi + (\nabla \cdot \vec{A})\varphi = \vec{A} \cdot \nabla\varphi, \quad ((a3.16), (1.14)) \quad (2.140)$$

$$\hat{\vec{p}} \cdot \vec{A}\varphi = -i\hbar \nabla \cdot (\vec{A}\varphi) = -i\hbar \vec{A} \cdot \nabla\varphi = \vec{A} \cdot \hat{\vec{p}}\varphi, \quad (2.141)$$

thus

$$\hat{\vec{p}} \cdot \vec{A} = \vec{A} \cdot \hat{\vec{p}}, \quad (2.142)$$

$$-\frac{e}{2m}(\hat{\vec{p}} \cdot \vec{A} + \vec{A} \cdot \hat{\vec{p}}) = -\frac{e}{m}\vec{A} \cdot \hat{\vec{p}} = -\frac{e\mu_0 H}{2m}(-y\hat{p}_x + x\hat{p}_y) = \mu_B \hat{l}_z H. \quad ((2.116), (2.90)) \quad (2.143)$$

2.5 Exchange Interaction in He Atom

2.5.1 Exchange Hamiltonian

By taking into account only the Coulomb interactions, the Hamiltonian of the two electron system of He atom is

$$\hat{H}(\vec{r}_1, \vec{r}_2) = \hat{h}(\vec{r}_1) + \hat{h}(\vec{r}_2) + g(\vec{r}_1, \vec{r}_2), \quad (2.144)$$

$$\hat{h}(\vec{r}) = \frac{\hat{p}^2(\vec{r})}{2m} - \frac{Ze^2}{4\pi\epsilon_0 r}, \quad (Z = 2) \quad (2.10)$$

$$g(\vec{r}_1, \vec{r}_2) = \frac{e^2}{4\pi\epsilon_0 r_{12}}. \quad (2.12)$$

Since the Hamiltonian is irrelevant to spin, the eigenstate of the system Ψ is the product of the functions of the position vectors and that of spins, which is exchange antisymmetric:

$$\Psi(\vec{r}_1, \sigma_1, \vec{r}_2, \sigma_2) = \Phi(\vec{r}_1, \vec{r}_2)X(\sigma_1, \sigma_2) = -\Psi(\vec{r}_2, \sigma_2, \vec{r}_1, \sigma_1). \quad (2.145)$$

Thereby

$$\Psi(\vec{r}_1, \sigma_1, \vec{r}_2, \sigma_2) = \begin{cases} \Phi_s(\vec{r}_1, \vec{r}_2)X_a(\sigma_1, \sigma_2), \\ \text{or} \\ \Phi_a(\vec{r}_1, \vec{r}_2)X_s(\sigma_1, \sigma_2). \end{cases} \quad (2.146)$$

The subscripts a and s denote that the function is exchange symmetric and antisymmetric, respectively. X_a and X_s are the spin eigenstates of total spin quantum number $S = 0$ and $=1$ for the two electron system, and are

$$\begin{aligned} X_a &= X_a(S = 0, M_S = 0) = \frac{1}{\sqrt{2}}[\chi_+(1)\chi_-(2) - \chi_+(2)\chi_-(1)] \\ &= |S = 0, M_S = 0\rangle, \end{aligned} \quad (2.147)$$

$$X_s(1, 1) = \chi_+(1)\chi_+(2) = |1, 1\rangle, \quad (2.148)$$

$$X_s(1, 0) = \frac{1}{\sqrt{2}}[\chi_+(1)\chi_-(2) + \chi_+(2)\chi_-(1)] = |1, 0\rangle, \quad (2.149)$$

$$X_s(1, -1) = \chi_-(1)\chi_-(2) = |1, -1\rangle. \quad (2.150)$$

Let $\varphi_\alpha(\vec{r})$ and ε_α denote the orbital eigenfunction and eigenenergy of He^{+1} ion, then

$$\begin{aligned} [\hat{h}(\vec{r}_1) + \hat{h}(\vec{r}_2)]\varphi_\alpha(\vec{r}_1)\varphi_\beta(\vec{r}_2) &= (\varepsilon_\alpha + \varepsilon_\beta)\varphi_\alpha(\vec{r}_1)\varphi_\beta(\vec{r}_2) \\ &= [\hat{h}(\vec{r}_1) + \hat{h}(\vec{r}_2)]\varphi_\alpha(\vec{r}_2)\varphi_\beta(\vec{r}_1) \\ &= (\varepsilon_\alpha + \varepsilon_\beta)\varphi_\alpha(\vec{r}_2)\varphi_\beta(\vec{r}_1). \end{aligned} \quad (2.151)$$

Take $g(\vec{r}_1, \vec{r}_2)$ perturbation. By approximating the total orbital state of He by the linear combination of $\varphi_\alpha(\vec{r}_1)\varphi_\beta(\vec{r}_2)$ and $\varphi_\alpha(\vec{r}_2)\varphi_\beta(\vec{r}_1)$ ($\alpha \neq \beta$), we get the orbital states and eigennergies

$$\Phi_s(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}[\varphi_\alpha(\vec{r}_1)\varphi_\beta(\vec{r}_2) + \varphi_\alpha(\vec{r}_2)\varphi_\beta(\vec{r}_1)], \quad (2.152)$$

$$E(S=0) = \varepsilon_\alpha + \varepsilon_\beta + K + J_A, \quad (2.153)$$

$$\Phi_a(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}[\varphi_\alpha(\vec{r}_1)\varphi_\beta(\vec{r}_2) - \varphi_\alpha(\vec{r}_2)\varphi_\beta(\vec{r}_1)], \quad (2.154)$$

$$E(S=1) = \varepsilon_\alpha + \varepsilon_\beta + K - J_A, \quad (2.155)$$

$$K \equiv \int \frac{e^2}{4\pi\epsilon_0 r_{12}} |\varphi_\alpha(\vec{r}_1)|^2 |\varphi_\beta(\vec{r}_2)|^2 d\mathbf{v}_1 d\mathbf{v}_2, \quad (2.156)$$

$$J_A \equiv \int \frac{e^2}{4\pi\epsilon_0 r_{12}} \varphi_\alpha^*(\vec{r}_1)\varphi_\beta^*(\vec{r}_2)\varphi_\alpha(\vec{r}_2)\varphi_\beta(\vec{r}_1) d\mathbf{v}_1 d\mathbf{v}_2. \quad (2.157)$$

Here K and J_A are the Coulomb interaction energy and exchange integral between the two electrons. The eigenenergy is related with S but not with M_S . Since

$$\begin{aligned} & \langle s, s, S, M_S | (\hat{s}_1 + \hat{s}_2)^2 | s, s, S, M_S \rangle \\ &= \langle s, s, S, M_S | \hat{S}^2 | s, s, S, M_S \rangle \\ &= 2s(s+1) + \langle s, s, S, M_S | 2\hat{s}_1 \cdot \hat{s}_2 | s, s, S, M_S \rangle = S(S+1), \end{aligned} \quad (2.158)$$

$$\begin{aligned} & \langle s, s, S, M_S | 2\hat{s}_1 \cdot \hat{s}_2 | s, s, S, M_S \rangle = S(S+1) - 2s(s+1) \\ &= \begin{cases} -\frac{3}{2}, & (S=1) \\ \frac{1}{2}, & (S=0) \end{cases} \end{aligned} \quad (2.159)$$

equations (2.153) and (2.155) can be expressed in a unified form of

$$E = \varepsilon_\alpha + \varepsilon_\beta + K - \frac{1}{2}J_A - \langle s, s, S, M_S | 2J_A \hat{s}_1 \cdot \hat{s}_2 | s, s, S, M_S \rangle. \quad (2.160)$$

From the above equation we get the expression of the exchange Hamiltonian (also called Heisenberg Hamiltonian) as

$$\hat{H}_{\text{ex}} = -2J_A \hat{s}_1 \cdot \hat{s}_2. \quad (2.161)$$

By extending this result to the atom in which n electrons partially fill an electron subshell, the exchange Hamiltonian in general case is expressed as

$$\hat{H}_{\text{ex}} = -\frac{1}{2} \sum_{i,j}^{1,\dots,n; i \neq j} 2J_A \hat{s}_i \cdot \hat{s}_j. \quad (2.162)$$

2.5.2 Positiveness of Exchange Integral of Form (2.157)

Assume that the electric charge of density

$$\rho^*(\vec{r}) \equiv e\varphi_\alpha^*(\vec{r})\varphi_\beta(\vec{r}) \quad (2.163)$$

is distributed in the space. $\varphi_\alpha(\vec{r})$ and $\varphi_\beta(\vec{r})$ are arbitrary functions localized within a limited space. The relations between $\rho^*(\vec{r})$ and the electric potential $V(\vec{r})$ produced by the former are

$$\frac{\rho^*(\vec{r})}{\varepsilon_0} = -\nabla^2 V(\vec{r}), \quad ((1.33), (1.35)) \quad (2.164)$$

$$V(\vec{r}) = \int \frac{\rho^*(\vec{r}')}{4\pi\varepsilon_0|\vec{r} - \vec{r}'|} dv'. \quad (1.37) \quad (2.165)$$

Inserting (2.163)–(2.165) into (2.157) we get

$$\begin{aligned} J_A &\equiv \int \frac{e^2}{4\pi\varepsilon_0|\vec{r} - \vec{r}'|} \varphi_\alpha^*(\vec{r})\varphi_\beta^*(\vec{r}')\varphi_\alpha(\vec{r}')\varphi_\beta(\vec{r}) dv dv' \\ &= \int \frac{\rho^*(\vec{r})\rho(\vec{r}')}{4\pi\varepsilon_0|\vec{r} - \vec{r}'|} dv dv' = -\varepsilon_0 \int_{\infty} V^*(\vec{r})\nabla^2 V(\vec{r}) dv \\ &= -\varepsilon_0 \oint_{\infty} V^*(\vec{r})\nabla V(\vec{r}) \cdot d\vec{S} + \varepsilon_0 \int_{\infty} |\nabla V(\vec{r})|^2 dv \quad (\text{a3.28}) \\ &= \varepsilon_0 \int_{\infty} |\nabla V(\vec{r})|^2 dv > 0, \end{aligned} \quad (2.166)$$

that is the exchange integral of the form of (2.157) is permanently positive regardless of that the electrons belong to the same atom or different atoms. J_A of (2.157) belonging to this kind of integral, the exchange interactions within an atom align the electron spins as parallel as possible. This result can explain the Hund's first rule that the ground term of an atom has the largest value of spin quantum number S . Thus, the 3d transition atom of $\text{Mn}(3d^5 4s^2)$, $\text{Fe}(3d^6 4s^2)$, $\text{Co}(3d^7 4s^2)$, and $\text{Ni}(3d^8 4s^2)$, for instance, has the spin magnetic moments of $5\mu_B$, $4\mu_B$, $3\mu_B$, and $2\mu_B$, respectively.

2.6 Exchange Interaction in H₂ Molecule

2.6.1 Eigenstates and Eigenenergies of the Two Electron System of H₂

By taking into account only the Coulomb interactions, the Hamiltonian of the two electron system is

$$\begin{aligned}\hat{H}(\vec{r}_1, \vec{r}_2) &= \frac{\hat{p}_1^2 + \hat{p}_2^2}{2m} + \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{12}} - \frac{1}{r_{1a}} - \frac{1}{r_{1b}} - \frac{1}{r_{2a}} - \frac{1}{r_{2b}} \right) \\ &= \hat{h}_a(\vec{r}_1) + \hat{h}_b(\vec{r}_2) + \hat{g}(\vec{r}_1, \vec{r}_2) = \hat{h}_a(\vec{r}_2) + \hat{h}_b(\vec{r}_1) + \hat{g}(\vec{r}_2, \vec{r}_1),\end{aligned}\quad (2.167)$$

$$\hat{h}_\alpha(\vec{r}_i) \equiv \frac{\hat{p}_i^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r_{i\alpha}}, \quad (i = 1, 2; \alpha = a, b) \quad (2.168)$$

$$\hat{g}(\vec{r}_i, \vec{r}_j) \equiv \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{ij}} - \frac{1}{r_{ib}} - \frac{1}{r_{ja}} \right), \quad ((i, j) = (1, 2), (2, 1)) \quad (2.169)$$

where the subscripts a and b denote the nuclei and $r_{i\alpha}$ the distance of the i^{th} electron from the nucleus α . Let φ_α and ε represent the ground orbital and eigenenergy of the electron in the isolated H atom of nucleus α , then

$$\hat{h}_\alpha(\vec{r})\varphi_\alpha(\vec{r}) = \varepsilon\varphi_\alpha(\vec{r}). \quad (2.170)$$

When the two H atoms are distant apart, there are two ground orbital states of the two electron system:

$$\Phi(\vec{r}_1, \vec{r}_2) \equiv \varphi_a(\vec{r}_1)\varphi_b(\vec{r}_2), \quad (2.171)$$

$$\Phi(\vec{r}_2, \vec{r}_1) \equiv \varphi_a(\vec{r}_2)\varphi_b(\vec{r}_1), \quad (2.172)$$

which satisfy the Schrödinger equations

$$[\hat{h}_a(\vec{r}_1) + \hat{h}_b(\vec{r}_2)]\Phi(\vec{r}_1, \vec{r}_2) = 2\varepsilon\Phi(\vec{r}_1, \vec{r}_2), \quad (2.173)$$

$$[\hat{h}_a(\vec{r}_2) + \hat{h}_b(\vec{r}_1)]\Phi(\vec{r}_2, \vec{r}_1) = 2\varepsilon\Phi(\vec{r}_2, \vec{r}_1). \quad (2.174)$$

Take $\hat{g}(\vec{r}_i, \vec{r}_j)$ or $\hat{g}(\vec{r}_j, \vec{r}_i)$ as perturbation when the two H atoms approach, and solve the orbital eigenfunction

$$C_1\Phi(\vec{r}_1, \vec{r}_2) + C_2\Phi(\vec{r}_2, \vec{r}_1) \quad (2.175)$$

and eigenenergy $2\varepsilon + \Delta$ from the Schrödinger equation

$$\begin{aligned}
& C_1[\hat{H} - (2\varepsilon + \Delta)]\Phi(\vec{r}_1, \vec{r}_2) + C_2[\hat{H} - (2\varepsilon + \Delta)]\Phi(\vec{r}_2, \vec{r}_1) \\
& = C_1[\hat{g}(\vec{r}_1, \vec{r}_2) - \Delta]\Phi(\vec{r}_1, \vec{r}_2) + C_2[\hat{g}(\vec{r}_2, \vec{r}_1) - \Delta]\Phi(\vec{r}_2, \vec{r}_1) = 0. \quad (2.176)
\end{aligned}$$

Let

$$\begin{aligned}
K & \equiv \langle \Phi(\vec{r}_1, \vec{r}_2) | \hat{g}(\vec{r}_1, \vec{r}_2) | \Phi(\vec{r}_1, \vec{r}_2) \rangle = \langle \Phi(\vec{r}_2, \vec{r}_1) | \hat{g}(\vec{r}_2, \vec{r}_1) | \Phi(\vec{r}_2, \vec{r}_1) \rangle \\
& = \int \frac{e^2}{4\pi\varepsilon_0} \left(\frac{1}{r_{12}} - \frac{1}{r_{2a}} - \frac{1}{r_{1b}} \right) |\varphi_a(\vec{r}_1)|^2 |\varphi_b(\vec{r}_2)|^2 dv_1 dv_2, \quad (2.177)
\end{aligned}$$

$$\begin{aligned}
J_A & \equiv \langle \Phi(\vec{r}_1, \vec{r}_2) | \hat{g}(\vec{r}_2, \vec{r}_1) | \Phi(\vec{r}_2, \vec{r}_1) \rangle = \langle \Phi(\vec{r}_2, \vec{r}_1) | \hat{g}(\vec{r}_1, \vec{r}_2) | \Phi(\vec{r}_1, \vec{r}_2) \rangle \\
& = \int \frac{e^2}{4\pi\varepsilon_0} \left(\frac{1}{r_{12}} - \frac{1}{r_{1a}} - \frac{1}{r_{2b}} \right) \varphi_a^*(\vec{r}_1) \varphi_b^*(\vec{r}_2) \varphi_a(\vec{r}_2) \varphi_b(\vec{r}_1) dv_1 dv_2, \quad (2.178)
\end{aligned}$$

$$S_{ab} \equiv \int \varphi_a^*(\vec{r}) \varphi_b(\vec{r}) dv, \quad (2.179)$$

and suppose $|S_{ab}|^2 \ll 1$.

Left multiplying $\Phi^*(\vec{r}_1, \vec{r}_2)$ and $\Phi^*(\vec{r}_2, \vec{r}_1)$, respectively, on the last relation of (2.176) and then integrating them we get

$$\begin{aligned}
& C_1[\langle \Phi(\vec{r}_1, \vec{r}_2) | \hat{g}(\vec{r}_1, \vec{r}_2) | \Phi(\vec{r}_1, \vec{r}_2) \rangle - \Delta] \\
& + C_2[\langle \Phi(\vec{r}_1, \vec{r}_2) | \hat{g}(\vec{r}_2, \vec{r}_1) | \Phi(\vec{r}_2, \vec{r}_1) \rangle - \Delta \langle \Phi(\vec{r}_1, \vec{r}_2) | \Phi(\vec{r}_2, \vec{r}_1) \rangle] \\
& = C_1(K - \Delta) + C_2(J_A - \Delta|S_{ab}|^2) = C_1(K - \Delta) + C_2J_A = 0, \quad (2.180)
\end{aligned}$$

$$\begin{aligned}
& C_1[\langle \Phi(\vec{r}_2, \vec{r}_1) | \hat{g}(\vec{r}_1, \vec{r}_2) | \Phi(\vec{r}_1, \vec{r}_2) \rangle - \Delta \langle \Phi(\vec{r}_2, \vec{r}_1) | \Phi(\vec{r}_1, \vec{r}_2) \rangle] \\
& + C_2[\langle \Phi(\vec{r}_2, \vec{r}_1) | \hat{g}(\vec{r}_2, \vec{r}_1) | \Phi(\vec{r}_2, \vec{r}_1) \rangle - \Delta] \\
& = C_1(J_A - \Delta|S_{ab}|^2) + C_2(K - \Delta) = C_1J_A + C_2(K - \Delta) = 0. \quad (2.181)
\end{aligned}$$

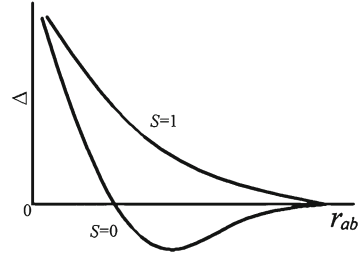
The two solutions of simultaneous (2.180) and (2.181) are

$$\Delta(S = 0) = K + J_A, \quad (2.182)$$

$$\Phi_s(\vec{r}_1, \vec{r}_2) \approx \frac{1}{\sqrt{2}}[\Phi(\vec{r}_1, \vec{r}_2) + \Phi(\vec{r}_2, \vec{r}_1)], \quad (2.183)$$

$$\Delta(S = 1) = K - J_A, \quad (2.184)$$

$$\Phi_a(\vec{r}_1, \vec{r}_2) \approx \frac{1}{\sqrt{2}}[\Phi(\vec{r}_1, \vec{r}_2) - \Phi(\vec{r}_2, \vec{r}_1)]. \quad (2.185)$$

Fig. 2.5 Δ versus r_{ab} 

Φ_s is exchange symmetric and Φ_a is antisymmetric. Since the Hamiltonian (2.167) is irrelevant to spin, the spin-orbit eigenfunctions are the products of the above orbital functions and the spin functions, and are antisymmetric, that is

$$\Psi_1 = \Phi_s(\vec{r}_1, \vec{r}_2)X_a(\sigma_1, \sigma_2), \quad (2.186)$$

$$\Psi_2 = \Phi_a(\vec{r}_1, \vec{r}_2)X_s(\sigma_1, \sigma_2). \quad ((2.147)-(2.150)) \quad (2.187)$$

2.6.2 Exchange Interaction in H₂

The relations between the perturbation energy and the total spin quantum number in (2.182) and (2.184) are completely the same with those in (2.153 and (2.155). Therefore, the perturbation energies $\Delta(S = 0)$ and $\Delta(S = 1)$ can be expressed in the unified form of

$$\Delta = K - \frac{1}{2}J_A - \langle S, M_S | 2J_A \hat{s}_1 \cdot \hat{s}_2 | S, M_S \rangle \quad (2.188)$$

as that in (2.160). The exchange Hamiltonian is

$$\hat{H}_{ex} = -2J_A \hat{s}_1 \cdot \hat{s}_2 \quad (2.189)$$

as (2.161) for He atom. The difference is that there are two extra two terms in the J_A of (2.178) for H₂ molecule then that of (2.157) for He atom. If $J_A > 0$ the energy of the $S = 1$ state is smaller than that of $S = 0$ state and hence the parallel coupled spin state is stable. If $J_A < 0$, the $S = 0$ state is stable. H₂ molecule belongs to the latter case. Figure 2.5 demonstrates Δ as a function of r_{ab} . It shows that when $S = 0$ there appears a minimum of $\Delta < 0$ at a certain value of r_{ab} , thus forming a stable H₂ molecule. Figure 2.6 demonstrates the electron density distribution on a section plane passing through the two nuclei. The electrons itinerate in the whole molecule. When $S = 1$ the two electrons of same spin repulse each other caused by the Pauli's

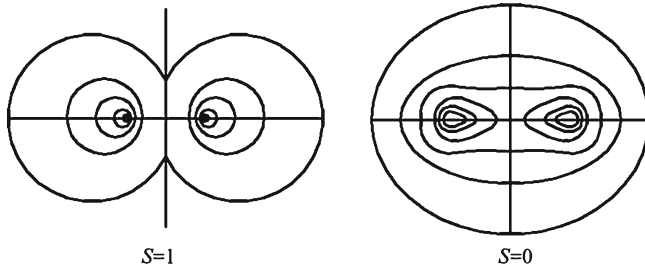


Fig. 2.6 Electron density distribution for state $S = 1$ and 0

exclusion principle and have a tendency to localize in each atom H. When $S = 0$, there is no such repulsion and the degree of itineration is higher.

2.7 Hyperfine Interactions in Atom

2.7.1 Spin, Magnetic Moment, and Quadrupole of Nucleus

A nucleus mainly constitutes of positrons and neutrons. The masses of positron and neutron are $m_p = 1836.153 m$ and $m_n = 1838.684 m$, where m is the electron rest mass. A nucleus is denoted by the nuclear symbol ${}^A_Z X$ or ${}^A X$, where Z is the atomic number which is the number of the positrons, X is the element symbol such as Fe, and A the mass number which is the sum of the number of positrons and neutrons. The spin quantum number, magnetic polarization moment, and electric charge of a positron, neutron, and nucleus are

$$I_p = \frac{1}{2}, \quad p_{Jp} = 2.79284734 \mu_N, \quad |e|, \quad (2.190)$$

$$I_n = \frac{1}{2}, \quad p_{Jn} = -1.9128 \mu_N, \quad 0, \quad (2.191)$$

$$I, \quad p_{JN} = g_N I \mu_N, \quad Z|e|, \quad (2.192)$$

respectively, where

$$\mu_N \equiv \frac{\mu_0 |e| \hbar}{2m_p} = \frac{1}{1836.153} \mu_B \quad (2.193)$$

is the nuclear magneton. I is zero if both of Z and number of the neutrons $A-Z$ are even, a half-integer if Z is even and $A-Z$ is odd, and an integer if both of Z and $A-Z$ are odd. The values of p_{JN} are three orders smaller than that of electron and can be neglected compared to the latter, but the magnetic moment plays a very important

Table 2.4 Values of I , g_N , $g_N I$, and Q_I for ^1H , ^{57}Fe , and ^{143}Nd [3]

Nucleus	I	g_N	$g_N I$	$Q_I/(10^{-28}\text{m}^2)$	State
^1H	1/2	5.585,691,2	2.792,847,34	0	Ground
^{57}Fe	1/2	0.188,8	0.090,44	0	Ground
	3/2	-0.103,3	-0.154,9	0.21	First excited
^{143}Nd	7/2	-0.304	-1.063	-0.48	Ground

role as a detector of the hyperfine magnetic field which is proportional to the magnetic moment of the atom in solids (Sect. 3.9).

If the weak interaction is neglected, the nuclear wavefunction $\psi_{\alpha I M_I}(\vec{r}) = |\alpha, I, M_I\rangle$ ($\vec{r}$: logogram of all position vectors of positrons; M_I : the magnetic quantum number; α : the quantum numbers other than I and M_I) has a definite parity:

$$\psi_{\alpha I M_I}(\vec{r}) = \pm \psi_{\alpha I M_I}(-\vec{r}), \quad (2.194)$$

and hence the dipole moment of the positrons $\langle \alpha, I, M_I | \sum_p^{1,\dots,Z} \vec{r}_p | \alpha, I, M_I \rangle$ is zero. Here $\vec{r}_p$ is the position vector of the p^{th} positron.

For most of nuclei, the space distribution of the positrons has the symmetry of rotational ellipsoid. The quadrupole Q_I characterizing the extent of deviation of the positron distribution from spherical symmetry is defined and is

$$\begin{aligned}
 Q_I &\equiv \left\langle \alpha, I, I \left| \sum_p^{1,\dots,Z} (3z_p^2 - r_p^2) \right| \alpha, I, I \right\rangle \quad (z_p: z \text{ component of } \vec{r}_p) \\
 &= \left\langle \alpha, I, I \left| 2 \sum_p^{1,\dots,Z} r_p^2 U_0^2(\vec{r}_p/r_p) \right| \alpha, I, I \right\rangle \quad (2.24, \text{Table 2.1}) \\
 &= \langle I, I | 3\hat{I}_z^2 - \hat{I}^2 | I, I \rangle \left\langle \sum_p^{1,\dots,Z} r_p^2 \right\rangle \langle I || U^2 || I \rangle \quad (\text{A4.9.2}) \\
 &= I(2I-1) \left\langle \sum_p^{1,\dots,Z} r_p^2 \right\rangle \langle I || U^2 || I \rangle, \quad (2.195)
 \end{aligned}$$

where $\langle \sum_p^{1,\dots,Z} r_p^2 \rangle$ is the average of $\sum_p^{1,\dots,Z} r_p^2$. $|e|Q_I$ is called electric-quadrupole.

Table 2.4 demonstrates the values of I , g_N , $g_N I$, and Q_I for some nuclei.

2.7.2 Hyperfine Interactions

So far a nucleus has been considered to interact with the electrons as a point electric charge (2.10). The interaction of the finite volume nucleus which has a magnetic moment is a bit different from the above interaction, but the difference is far smaller than the latter and spin-orbit interaction and is called hyperfine interaction. Some of the interaction belong to the relativity effects and the hyperfine interactions will be discussed on the basis of the Hamiltonian of Dirac equation [1]

$$\hat{H}_D = \frac{(\hat{\vec{p}} - e\vec{A})^2}{2m + (E' - eV)/c^2} + eV - \frac{e\hbar\hat{\vec{\sigma}}\cdot\vec{B}}{2m + (E' - eV)/c^2} + \frac{ie\hbar}{[2m + (E' - eV)/c^2]^2 c^2} \vec{E} \cdot [\hat{\vec{p}} - e\vec{A} + i(\hat{\vec{p}} - e\vec{A}) \times \hat{\vec{\sigma}}], \quad (2.62)$$

$$eV = u(r), \quad (2.63)$$

$$\vec{E} = \frac{E_r \vec{r}}{r} = -\frac{1}{e} \frac{du(r)}{dr} \frac{\vec{r}}{r}, \quad (2.64)$$

$$\vec{A} = \frac{\hat{\vec{p}}_{JN} \times \vec{r}}{4\pi r^3}, \quad (1.49) \quad (2.196)$$

$$\vec{H} = \frac{\vec{B}}{\mu_0} = \frac{1}{4\pi\mu_0} \left[\frac{3(\hat{\vec{p}}_{JN} \cdot \vec{r})\vec{r}}{r^5} - \frac{\hat{\vec{p}}_{JN}}{r^3} \right]. \quad (1.46) \quad (2.197)$$

2.7.3 Hyperfine Magnetic Interaction

Hyperfine magnetic interaction $\hat{H}_{hm}$ includes the terms in the right of (2.62) proportional to $\hat{\vec{p}}_{JN}$ of the nucleus and also to $\hat{\vec{p}}$ and $\hat{\vec{s}} = \hat{\vec{\sigma}}/2$ of the electron, that is

$$\hat{H}_{hm} = -\frac{e}{m} \hat{\vec{p}} \cdot \vec{A} + 2\mu_B \hat{\vec{s}} \cdot \vec{H} + \frac{2e^2 \hbar E_r}{[2m + (E' - u(r))/c^2]^2 c^2 r} \vec{r} \cdot \vec{A} \times \hat{\vec{s}}. \quad (2.198)$$

The first and second terms in the right of above equation are the same with corresponding terms of the non-relativistic Hamiltonian Equation (2.115). The third term is of relativistic effect called Fermi contact term or tersely called contact term.

$\hat{H}_{hm}$ being proportional to $\hat{\vec{p}}_{JN}$, it can be expressed as a potential energy of $\hat{\vec{p}}_{JN}$ in the hyperfine magnetic field $\hat{\vec{H}}_{hm}$ produced by the electron:

$$\hat{H}_{hm} = -\hat{\vec{p}}_{JN} \cdot \hat{\vec{H}}_{hm}. \quad (2.199)$$

First consider the hyperfine magnetic field of the first and second terms in the right of Equation (2.198). They can be reformulated as

$$-\frac{e}{m} \hat{\vec{p}} \cdot \vec{A} = -\frac{e}{m} \hat{\vec{p}} \cdot \frac{\hat{\vec{p}}_{JN} \times \vec{r}}{4\pi r^3} = -\hat{\vec{p}}_{JN} \cdot \frac{-\mu_B \hat{\vec{l}}}{2\pi \mu_0 r^3}, \quad (2.200)$$

$$2\mu_B \hat{\vec{s}} \cdot \vec{H} = -\hat{\vec{p}}_{JN} \cdot \frac{-\mu_B}{2\pi \mu_0} \left[\frac{3(\hat{\vec{s}} \cdot \vec{r})\vec{r}}{r^5} - \frac{\hat{\vec{s}}}{r^3} \right], \quad (2.201)$$

so their hyperfine magnetic fields are

$$\hat{\vec{H}}_l = \frac{-\mu_B}{2\pi \mu_0} \frac{\hat{\vec{l}}}{r^3}, \quad (2.202)$$

$$\hat{\vec{H}}_s = \frac{-\mu_B}{2\pi \mu_0} \left[\frac{3(\hat{\vec{s}} \cdot \vec{r})\vec{r}}{r^5} - \frac{\hat{\vec{s}}}{r^3} \right]. \quad (2.203)$$

These fields are produced by non-s electrons. For an s electron l is zero and hence the average of $\hat{\vec{H}}_l$ is zero. The space distribution of the s electron cloud being spherically symmetric, the average of $\hat{\vec{H}}_s$ is also zero (Note 1 of this section).

Now analyze the last term in the right of (2.198). By exploiting the relation of

$$\begin{aligned} \vec{r} \cdot \vec{A} \times \hat{\vec{s}} &= \hat{\vec{s}} \cdot \vec{r} \times \frac{\hat{\vec{p}}_{JN} \times \vec{r}}{4\pi r^3} = \hat{\vec{s}} \cdot \frac{\hat{\vec{p}}_{JN} r^2 - \vec{r}(\hat{\vec{p}}_{JN} \cdot \vec{r})}{4\pi r^3} \quad ((2.196), (a3.3)-(a3.4)) \\ &= \frac{1}{4\pi} \hat{\vec{p}}_{JN} \cdot \left[\frac{\hat{\vec{s}}}{r} - \frac{(\hat{\vec{s}} \cdot \vec{r})\vec{r}}{r^3} \right] \end{aligned} \quad (2.204)$$

we get the contact term $\hat{\vec{H}}_F$ and its hyperfine magnetic field $\hat{\vec{H}}_F$ as

$$\begin{aligned} \hat{\vec{H}}_F &= \frac{2e^2 \hbar E_r}{[2m + (E' - u(r))/c^2]^2 c^2 r} \vec{r} \cdot \vec{A} \times \hat{\vec{s}} \\ &= \frac{-e\mu_B}{4\pi m \mu_0} \frac{E_r}{[1 + (E' - eV)/2mc^2]^2 c^2} \hat{\vec{p}}_{JN} \cdot \left[\frac{\hat{\vec{s}}}{r^2} - \frac{(\hat{\vec{s}} \cdot \vec{r})\vec{r}}{r^4} \right] = -\hat{\vec{p}}_{JN} \cdot \hat{\vec{H}}_F, \end{aligned} \quad (2.205)$$

$$\hat{\vec{H}}_F = \frac{1}{4\pi} \frac{e\mu_B}{mc^2 \mu_0} \frac{E_r}{[1 + (E' - u(r))/2mc^2]^2} \left[\frac{\hat{\vec{s}}}{r^2} - \frac{(\hat{\vec{s}} \cdot \vec{r})\vec{r}}{r^4} \right]. \quad (2.206)$$

Since

$$\frac{\hat{s}}{r^2} - \frac{(\hat{s} \cdot \vec{r})\vec{r}}{r^4} = \frac{2\hat{s}}{3r^2}, \quad (\text{Note 2 of this section}) \quad (2.207)$$

and

$$\frac{-e}{2mc^2} \frac{E_r}{[1 + (E' - u(r))/2mc^2]^2} = \frac{d}{dr} \frac{1}{1 + (E' - u(r))/2mc^2} \equiv f(r) \quad (2.208)$$

has the characteristics of Dirac δ (Note 3 of this section), (2.206) simplifies to

$$\hat{H}_F = -\frac{\mu_B}{2\pi\mu_0} \delta(r) \frac{2\hat{s}}{3r^2}. \quad (2.209)$$

The hyperfine magnetic field of the contact term produced by the electron of orbital state $|n, l, m_l\rangle$ is

$$\begin{aligned} \int \hat{H}_F |\varphi_{nlm_l}(\vec{r})|^2 r^2 \sin\theta dr d\theta d\phi &= - \int \frac{\mu_B}{2\pi\mu_0} \frac{2}{3} \delta(r) R_{nl}^2(r) \hat{s} dr \\ &= -\frac{\mu_B}{2\pi\mu_0} \frac{2}{3} |\varphi_{nlm_l}(0)|^2 \hat{s}. \quad (R_{nl}^2(0) = |\varphi_{nlm_l}(0)|^2) \end{aligned} \quad (2.210)$$

Since $R_{nl}(0)$ is nonzero only for $l = 0$ (2.26), only s electrons contribute to the contact term.

The total hyperfine magnetic field is the sum of (2.202), (2.203), and (2.209):

$$\hat{H}_{\text{hm}} = -\frac{\mu_B}{2\pi\mu_0} \left[\frac{\hat{l}}{r^3} + \frac{3(\hat{s} \cdot \vec{r})\vec{r}}{r^5} - \frac{\hat{s}}{r^3} + \frac{2}{3r^2} \delta(r) \hat{s} \right]. \quad (2.211)$$

2.7.4 Electric-Quadrupole Interaction

Let $V(\vec{r}_p)$ denote the Coulomb potential produced by the electrons outside the nucleus. The Coulomb interactions of the nucleus with the electrons are

$$\begin{aligned} \hat{H}_e &= \sum_p^{1, \dots, Z} |e| V(\vec{r}_p) = |e| \sum_p^{1, \dots, Z} \left[V(0) + \sum_{\alpha}^{x, y, z} \frac{\partial V}{\partial \alpha} \Big|_0 \alpha_p \right. \\ &\quad \left. + \frac{1}{2} \sum_{\alpha, \beta}^{x, y, z} \frac{\partial^2 V}{\partial \alpha \partial \beta} \Big|_0 \alpha_p \beta_p + \dots \right]. \end{aligned} \quad (2.212)$$

The first term in the last expression is the Coulomb potential of the point charge nucleus which does not belong to the hyperfine interaction. The electric moment of the nucleus being zero, the second term is zero. The third term

$$\hat{H}_q = \frac{|e|}{2} \sum_p \sum_{\alpha, \beta}^{1, \dots, Z} V_{\alpha\beta} \alpha_p \beta_p \quad \left(V_{\alpha\beta} \equiv \frac{\partial^2 V}{\partial \alpha \partial \beta} \Big|_0 \right) \quad (2.213)$$

is called the electric-quadrupole interaction.

2.7.5 Hyperfine Coulomb Interaction of the Nucleus with an Overlapping Electron Cloud

Consider the nucleus to be approximately a sphere of radius r_N , and the orbital of the electron within the nucleus $\varphi_{nlm_l}(0)$. The Coulomb interaction energy with respect to that of the electric point charged nucleus is

$$\hat{H}_{e0} = e \int_0^{r_N} \frac{-Ze}{4\pi\epsilon_0 r} \left(\frac{r^3}{r_N^3} - 1 \right) 4\pi r^2 |\varphi_{nlm_l}(0)|^2 dr = \frac{3Ze^2}{10\epsilon_0} |\varphi_{nlm_l}(0)|^2 r_N^2. \quad (2.214)$$

$\varphi_{nlm_l}(0)$ being nonzero only for s electrons, this interaction is produced by an s electron.

2.7.6 Total Hyperfine Interaction

Total hyperfine interaction of an atom is

$$\hat{H}_{\text{hf}} = \sum_i^{1, \dots, Z} [\hat{H}_{\text{hm}}(i) + \hat{H}_q(i) + \hat{H}_{e0}(i)]. \quad (2.215)$$

Note 1

Let $\vec{e}_z$ and $\vec{e}_\perp$ denote the unit vectors in the $\hat{s}$ direction and normal to $\hat{s}$ in the plane formed by $\vec{r}$ and $\hat{s}$ and θ the angle between $\vec{r}$ and $\hat{s}$. $\vec{r} = r(\vec{e}_z \cos \theta + \vec{e}_\perp \sin \theta)$.

$$\int_0^\pi \left[\frac{3(\hat{s} \cdot \vec{r})\vec{r}}{r^5} - \frac{\hat{s}}{r^3} \right] r^2 \sin \theta d\theta$$

$$\begin{aligned}
&= \frac{\hat{s}_z}{r} \int_0^\pi [3 \cos \theta (\vec{e}_z \cos \theta + \vec{e}_\perp \sin \theta) - \vec{e}_z] \sin \theta d\theta \\
&= \frac{\hat{s}_z}{r} \left\{ [-\cos^3 \theta + \cos \theta]_0^\pi \vec{e}_z + \left[\frac{1}{3} \sin^3 \theta \right]_0^\pi \vec{e}_\perp \right\} = 0.
\end{aligned} \tag{2.216}$$

Note 2

By exploiting the relations of

$$\begin{aligned}
\hat{\sigma}_x \hat{\sigma}_y &= -\hat{\sigma}_y \hat{\sigma}_x = i\hat{\sigma}_z, & \hat{\sigma}_y \hat{\sigma}_z &= -\hat{\sigma}_z \hat{\sigma}_y = i\hat{\sigma}_x, \\
\hat{\sigma}_z \hat{\sigma}_x &= -\hat{\sigma}_x \hat{\sigma}_z = i\hat{\sigma}_y, & (2.2)
\end{aligned} \tag{2.217}$$

we get

$$(\hat{s} \cdot \vec{r})^2 = \frac{1}{4} \left[\sum_{\beta}^{x,y,z} \sigma_{\beta}^2 \beta^2 + \sum_{\beta\gamma}^{xy,yz,zx} (\sigma_{\beta} \sigma_{\gamma} + \sigma_{\gamma} \sigma_{\beta}) \beta \gamma \right] = \frac{r^2}{4}, \tag{2.27}$$

$$\tag{2.218}$$

$$\begin{aligned}
&\left\langle s, m'_s \left| \frac{\hat{s}}{r^2} - \frac{(\hat{s} \cdot \vec{r}) \vec{r}}{r^4} \right| s, m_s \right\rangle \\
&= \left\langle s, m'_s \left| \frac{\hat{s}}{r^2} - \frac{\hat{s}(\hat{s} \cdot \vec{r})^2}{s(s+1)r^4} \right| s, m_s \right\rangle \tag{a4.36} \\
&= \left\langle s, m'_s \left| \frac{2\hat{s}}{3r^2} \right| s, m_s \right\rangle \cdot \left(s = \frac{1}{2}, m'_s, m_s = \pm s \right) \tag{2.219}
\end{aligned}$$

Note 3

Dirac delta $\delta(x)$ is a function which satisfies the relations of $\delta(x \neq 0) = 0$, $\delta(0) = \infty$, and $\int \delta(x) dv = 1$.

When r is not very small ($> 10^{-3}$ nm), $(E' - u(r))/2mc^2$ in the denominator of the first expression can be neglected. eE_r in the numerator is the finite force acting on the electron and its integral is the energy of the electron of $10 \sim 10^3$ eV order which can be neglected compared with $2mc^2 \sim 10^6$ eV of the denominator,

$$\int_{r>10^{-3}\text{nm}}^{\infty} f(r) dr \approx \frac{u(r)}{2mc^2} \ll 1,$$

and hence $f(r)$ can be considered zero. When r approaches zero, $E_r \propto 1/r^2$, $u(r) \propto 1/r$, and $f(r) \rightarrow \infty$.

$$\int_0^{\infty} f(r) dr = \left[\frac{1}{1 + (E' - u(r))/2mc^2} \right]_0^{\infty} = 1. \quad (2.220)$$

Appendix 4: Selections from Group Theory

A4.1 Group

A4.1.1 Group

If a set of n elements $\{A, B, C, \dots\}$ G satisfies following four conditions, G is called group of order n .

- ① G is closed under a binary operation, that is, the combination of any two elements AB is also an element in G ;
- ② There exists an identity element E such that $EA = AE$ for all A ;
- ③

$$A(BC) = (AB)C; \quad (\text{a4.1})$$

- ④ For each element A there is an invert element A^{-1} such that $AA^{-1} = A^{-1}A = E$.

An example: A series of integer $\{n\}$ with plus-minus operations is a group of infinite order.

A4.1.2 Symmetry Group

A symmetry operation is an operation which transforms the system into a state indistinguishable from the starting state.

The group consisted of symmetry operation elements is called symmetry group.

A4.1.3 Rotation–Reflection Group

If a system is spherically symmetric, the operations of any angle rotation about any axis passing through the center of symmetry, reflection over any plane passing through the center, and combination of above operations do not change the system. The group consisting of these operations is called rotation–reflection group.

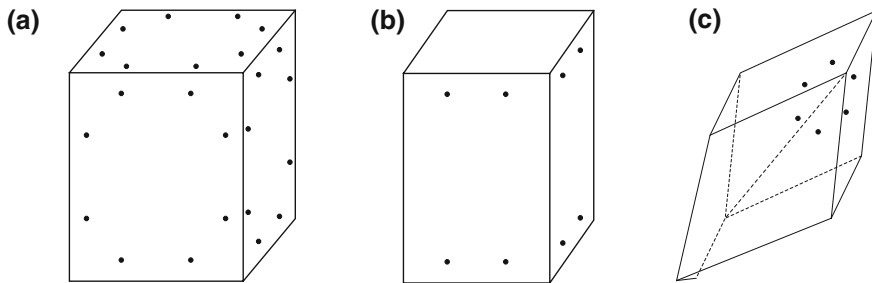


Fig. a4.1 Symmetrical points of O_h (a), D_{4h} (b) and D_{3d} (c)

A4.1.4 Point Group

If a system is a crystal, the operations of rotation about some major crystal axes by certain angles, reflections over certain crystal planes, inversion with respect to the center, and the combinations of the above operations do not change the system. The group consisting of these operations is called point group.

Examples:

- ① A crystal of cubic symmetry does not change under the operations of rotation about any fourfold rotation axis $\langle 100 \rangle$ by integral multiple of $2\pi/4$, rotation about any threefold rotation axis $\langle 111 \rangle$ by integral multiple of $2\pi/3$, inversion with respect to the center, reflection on $\{110\}$ plane, and the combinations of above operations. There are 48 such symmetry operations which constitute O_h group (sometimes tersely called O_h).
- ② If a O_h symmetrical cubic crystal is elongated or compressed along the $[001]$ axis, only 16 operations among the 48 operations of O_h satisfy the new symmetry which has only one fourfold rotation symmetry axis $[001]$ (O_h has three axes of $[100]$, $[010]$, and $[001]$). The 16 operations constitute D_{4h} group.
- ③ If an O_h symmetrical cubic crystal is elongated or contracted along the $[111]$ axis, only 12 symmetrical operations among the 48 operations of O_h satisfy the new symmetry which has only one threefold rotation symmetry axis $[111]$ (O_h has four axes of $[111]$, $[1\bar{1}1]$, $[\bar{1}11]$ and $[\bar{1}\bar{1}1]$). These 12 operations constitute D_{3d} group.

Figure a4.1 demonstrates the symmetrical points of O_h , D_{4h} , and D_{3d} obtained through symmetrical operations on a point of general position.

A4.1.5 Subgroup

If a part of the elements of group G constitute another group Q under the same binary operation, Q is called subgroup of group G .

Examples: Any point group is a subgroup of rotation-reflection group. D_{4h} and D_{3d} are subgroups of O_h .

A4.2 Vector Space and Operators (Matrices)

A4.2.1 Vector Space

A set of linearly independent n functions $\{\psi_i\}$ ($i = 1, 2, \dots, n$) constitutes n -dimensional vector (function) space L_n . Any vector $|\alpha\rangle$ in this space is a linear combination of $\{\psi_i\}$ which can be considered a column vector. The row vector $\langle\alpha|$ in the dual space is the conjugate transpose (adjoint) of $|\alpha\rangle$. Inner product $\langle\alpha|\beta\rangle$ satisfies the relation

$$\langle\alpha|\beta\rangle = \langle\beta|\alpha\rangle^*. \quad (\text{a4.2})$$

A4.2.2 Hermitian Adjoint

Hermitian adjoint $\hat{\Omega}^+$ of operator $\hat{\Omega}$ is defined by the relation

$$\langle\hat{\Omega}^+\alpha|\beta\rangle = \langle\alpha|\hat{\Omega}\beta\rangle \equiv \Omega_{\alpha\beta}. \quad (\text{a4.3})$$

It holds

$$\Omega_{\beta\alpha}^+ = \Omega_{\alpha\beta}^*, \quad \hat{\Omega}^{++} = \hat{\Omega}. \quad (\text{a4.4})$$

The matrix of operator $\hat{\Omega}$ in the vector space L_n is

$$(\Omega) \equiv \begin{pmatrix} \Omega_{11} & \Omega_{12} & \cdots & \cdots \\ \Omega_{21} & \Omega_{22} & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \Omega_{nn} \end{pmatrix},$$

$\Omega_{ij} = \langle\psi_i|\hat{\Omega}|\psi_j\rangle$. (Ω) is often represented by $\hat{\Omega}$. Equation (a4.4) shows that Hermitian adjoint matrix (Ω^+) is the conjugate transpose of (Ω) .

A4.2.3 Unitary Operator (Matrix)

The operator (matrix) which satisfies the relation

$$\hat{\Omega}^+ = \hat{\Omega}^{-1} \quad (\text{a4.5})$$

is called unitary operator (matrix). It satisfies the relation

$$\langle \hat{\Omega}\alpha | \hat{\Omega}\beta \rangle = \langle \alpha | \beta \rangle. \quad (\text{a4.6})$$

Any operator (matrix) of rotation–reflection group and point group is unitary.

A4.2.4 Hermitian Operator (Matrix)

The operator (matrix) which satisfies the relation

$$\hat{\Omega}^+ = \hat{\Omega} \quad (\text{a4.7})$$

is called Hermitian operator (matrix). It satisfies the relation

$$\Omega_{\alpha\beta} = \Omega_{\beta\alpha}^*. \quad (\text{a4.8})$$

Arbitrary operator representing physical property is Hermitian.

The operation

$$\hat{A}^{-1} \hat{B} \hat{A} = \hat{C} \quad (\text{a4.9})$$

is called similarity transformation of $\hat{B}$ by $\hat{A}$.

An Hermitian matrix $\hat{\Omega}$ can be diagonalized by an appropriate unitary matrix $\hat{U}$ through similarity transformation $\hat{U}^{-1} \hat{\Omega} \hat{U}$.

A necessary and enough condition for that two Hermitian matrices $\hat{\Omega}_1$ and $\hat{\Omega}_2$ can be diagonalized by a unitary matrix is they are commutable:

$$\hat{\Omega}_1 \hat{\Omega}_2 = \hat{\Omega}_2 \hat{\Omega}_1. \quad (\text{a4.10})$$

A4.3 Representation of Group

A4.3.1 Representation of Group

Consider a vector space L_n constituted of functions $\{\psi_i\}$ ($i = 1, 2, \dots, n$). If the function $\psi'_i(R)$ obtained through operation $\hat{P}(R)$ of arbitrary element R of group G on any ψ_i is a linear combination of $\{\psi_j\}$, that is

$$\hat{P}(R)\psi_i = \psi'_i(R) = \sum_j^{1,2,\dots,n} \psi_j D(R)_{ji}, \quad (\text{a4.11})$$

L_n is called closed under group G .

The n order matrices $\{(D(A)), (D(B)), \dots\}$, noted by (D) , are called representation of group G in the vector space L_n . In many cases $(D(R))$ is also tersely denoted by (D) . ψ_i is called a basis vector (or basis function) of representation (D) .

A4.3.2 Unitary Representation

If $\hat{P}$ in (a4.11) is a unitary operator, (D) is unitary and is called unitary representation. The transformation of (a4.11) is called unitary transformation of the basis vector.

A4.3.3 Equivalent and Inequivalent Representations

If a representation (D) of group G is similarity transformed by a non-singular matrix (determinant $\neq 0$) (S) :

$$(D') = (S)^{-1} (D) (S), \quad (\text{a4.12})$$

(D') is also a representation of G . (D') and (D) are called equivalent representations. If two representations cannot be transformed each other by a similarity transformation, the two are called inequivalent representations.

A4.4 Reduction of Representation

A4.4.1 Reduction of Representation

Suppose there are two vector spaces L_m and L_n which are closed under group G . The dimension m of L_m is smaller than the dimension n of L_n , and all vectors in L_m are included in L_n . Then L_n is called reducible under G , and L_m is called invariant subspace of L_n . The unitary representation (D) of G in L_n can be similarity transformed to a new representation consisting of the super matrices

$$(D) = \begin{pmatrix} (D_1) & 0 \\ 0 & (D_2) \end{pmatrix}, \quad (\text{a4.13})$$

where (D_1) and (D_2) are matrices of order m and $n - m$. The set of the basis vectors of (D_1) and (D_2) constitutes invariant subspace L_m and L_{n-m} , respectively. Each of (D_1) and (D_2) is a unitary representation of group G . The transformation is called the reduction of (D) into direct sum of (D_1) and (D_2) which is expressed as

$$(D) = (D_1) \oplus (D_2). \quad (\text{a4.14})$$

A4.4.2 Irreducible Representation

If after reduction we get $(D) = (D_1) \oplus (D_2) \cdots \oplus (D_k)$ where k is the largest value of possible reduction, that is, (D_i) ($i = 1, 2, \dots, k$) cannot be reduced further any

Table a4.1 Reduction of D^l for O_h , reduction of the irreducible representations of O_h for D_{3d} and D_{4h} , and basis vectors of irreducible representations of O_h produced by $\{Y_{lm_l}\}$ of D^l

D^l	Reduction of D^l for O_h , and basis vectors of irreducible representations of O_h	Reduction of irreducible representations of O_h for D_{3d}	Reduction of irreducible representations of O_h for D_{4h}
D^1	T_{1u} $Y_{11},$ $Y_{10},$ Y_{1-1}	$A_{2u} + E_u$	$A_{2u} + E_u$
D^2	E_g $Y_{20},$ $(1/2)^{1/2}(Y_{22} + Y_{2-2})$	E_g	$A_{1g} + B_{1g}$
	T_{2g} $Y_{2-1},$ $-Y_{21},$ $(1/2)^{1/2}(Y_{22} - Y_{2-2})$	$A_{1g} + E_g$	$B_{2g} + E_g$
D^3	A_{2u} $(1/2)^{1/2}(Y_{32} - Y_{3-2})$	A_{2u}	B_{1u}
	T_{1u} $-(1/8)^{1/2}(\sqrt{5}Y_{3-3} + \sqrt{3}Y_{31}),$ $Y_{30},$ $-(1/8)^{1/2}(\sqrt{5}Y_{33} + \sqrt{3}Y_{3-1})$	$A_{2u} + E_u$	$A_{2u} + E_u$
	T_{2u} $-(1/8)^{1/2}(\sqrt{3}Y_{33} + \sqrt{5}Y_{3-1}),$ $-(1/8)^{1/2}(\sqrt{5}Y_{32} + \sqrt{3}Y_{3-2}),$ $-(1/8)^{1/2}(\sqrt{3}Y_{3-3} - \sqrt{5}Y_{31})$	$A_{1u} + E_u$	$B_{2u} + E_u$

more, (D_i) is called an irreducible representation. The vector space of (D) completely reduces to k invariant subspaces.

The simultaneous eigenstate of angular momentum operators $\hat{j}^2$ and $\hat{j}_z$ $|j, m_j\rangle$ of definite j is a basis vector of $2j + 1$ -dimensional irreducible representation D^l of rotation-reflection group.

A4.4.3 Reduction of Irreducible Representation of Group for Subgroup

Among the irreducible representations $\{(D(R))\}$ of a group, the representations for a subgroup $(D(R_s))$ ($\{R_s\}$: set of elements of the subgroup) may be reducible:

$$(D(R_s)) = n_1 (D_1(R_s)) \oplus n_2 (D_2(R_s)) \oplus \dots \quad (n_i: \text{integer}) \quad (\text{a4.15})$$

Table a4.1 demonstrates reduction of the irreducible representation D^l of rotation-reflection group for its subgroup O_h , the reduction of the irreducible representations of O_h group for its subgroup D_{3d} and D_{4h} , respectively, and the basis vectors of the irreducible representation of subgroup O_h produced by the basis vectors $\{Y_{lm_l}\}$ of D^l .

Irreducible representations A , E , and T are one-, two-, and three-dimensional. The subscript g and u represent that the basis vector is symmetrical and antisymmetrical with respect to the inversion operation.

A4.5 Direct Product of Two Representations

A4.5.1 Representation of Direct Product of Two Representations

Take two-dimensional representation $(D) = \begin{pmatrix} D_{11} & D_{12} \\ D_{21} & D_{22} \end{pmatrix}$ and three-dimensional representation $(W) = \begin{pmatrix} W_{11} & W_{12} & W_{13} \\ W_{21} & W_{22} & W_{23} \\ W_{31} & W_{32} & W_{33} \end{pmatrix}$ as an example. Define the direct product of them by

$$\begin{aligned} (D) \otimes (W) &\equiv \begin{pmatrix} D_{11}(W) & D_{12}(W) \\ D_{21}(W) & D_{22}(W) \end{pmatrix} \\ &= \begin{pmatrix} D_{11}W_{11} & D_{11}W_{12} & D_{11}W_{13} & D_{12}W_{11} & D_{12}W_{12} & D_{12}W_{13} \\ D_{11}W_{21} & D_{11}W_{22} & D_{11}W_{23} & D_{12}W_{21} & D_{12}W_{22} & D_{12}W_{23} \\ D_{11}W_{31} & D_{11}W_{32} & D_{11}W_{33} & D_{12}W_{31} & D_{12}W_{32} & D_{12}W_{33} \\ D_{21}W_{11} & D_{21}W_{12} & D_{21}W_{13} & D_{22}W_{11} & D_{22}W_{12} & D_{22}W_{13} \\ D_{21}W_{21} & D_{21}W_{22} & D_{21}W_{23} & D_{22}W_{21} & D_{22}W_{22} & D_{22}W_{23} \\ D_{21}W_{31} & D_{21}W_{32} & D_{21}W_{33} & D_{22}W_{31} & D_{22}W_{32} & D_{22}W_{33} \end{pmatrix}. \end{aligned} \quad (\text{a4.16})$$

Suppose $\{\psi_i^i\}$ and $\{\psi_k^j\}$ are the set of basis vectors of irreducible representations (D^i) and (D^j) , respectively. $\psi_i^i \psi_k^j$ is a basis vector of the direct product representation $(D^i) \otimes (D^j)$ and transforms under the $(D) = (D^i) \otimes (D^j)$ representation (a4.11).

A4.5.2 Reduction of Representation of Direct Product of Irreducible Representations of Rotation–Reflect Group

The representation of direct product of irreducible representations D^L and D^S of rotation–reflect group completely reduces by

$$D^L \otimes D^S = D^{|L-S|} \oplus D^{|L-S|+1} \dots \oplus D^{L+S}. \quad (\text{a4.17})$$

A4.6 Irreducible Tensor

If a set of functions or operators $\{\hat{Q}_\kappa^\mu\}$ ($\kappa = -\mu, -\mu + 1, \dots, \mu$) transforms under the $2\mu + 1$ -dimensional irreducible representation D^μ of rotation–reflection group by

$$\hat{P}^{-1} \hat{Q}_\kappa^\mu \hat{P} = \sum_\tau \hat{Q}_\tau^\mu D_{\tau\kappa}^\mu, \quad (\hat{P}: \text{rotation-reflection operator}) \quad (\text{a4.18})$$

the set of $\{\hat{Q}_\kappa^\mu\}$ ($\kappa = -\mu, -\mu + 1, \dots, \mu$) is called irreducible tensor of rank μ , and $\hat{Q}_\kappa^\mu$ is called a component of the tensor.

The set of the spherical harmonics $\{Y_{lm_l}\}$ (and $\{U_{m_l}^l\}$ (2.24) of definite l is an irreducible tensor of rank l . The set of the three angular momentum operators

$$\hat{j}_{\pm 1} \equiv \mp \frac{1}{\sqrt{2}} \hat{j}_\pm, \quad \hat{j}_0 \equiv \hat{j}_z \quad (\text{2.33}) \quad (\text{a4.19})$$

which has the same form with the set of $\{U_{\pm 1}^1, U_0^1\}$ is a first-rank irreducible tensor.

A4.7 Orthogonal Theorem of the Basis Vectors of Irreducible Unitary Representation and Corresponding Matrix Element Theorems

Assume that (D^{l_i}) is a l_i -dimensional irreducible unitary representation of group G and ψ_m^i is an orthonormalized m^{th} row basis vectors of (D^{l_i}) . Define that (D^{l_i}) and (D^{l_j}) are inequivalent if $i \neq j$. It holds

①

$$\langle \psi_m^i | \psi_n^j \rangle = \delta(i, j) \delta(m, n) \frac{1}{l_i} \sum_{\alpha}^{1, \dots, l_i} \langle \psi_\alpha^i | \psi_\alpha^i \rangle. \quad (\text{a4.20})$$

② If operator $\hat{S}$ is invariant under the operation of group G , $\hat{S} \psi_n^i$ is also the n^{th} row basis vector of (D^{l_i}) , and hence

$$\langle \psi_m^i | \hat{S} | \psi_n^j \rangle = \delta(i, j) \delta(m, n) \frac{1}{l_i} \sum_{\alpha}^{1, \dots, l_i} \langle \psi_\alpha^i | \hat{S} | \psi_\alpha^i \rangle. \quad (\text{a4.21})$$

③ If $\hat{Q}_\kappa^\mu$ is a component of an irreducible tensor of rank μ , $\hat{Q}_\kappa^\mu \psi_m^j$ is a basis vector of representation $(D^\mu) \otimes (D^{l_j})$. If $(D^\mu) \otimes (D^{l_j})$ does not include (D^{l_i}) ,

$$\langle \psi_m^i | \hat{Q}_\kappa^\mu | \psi_n^j \rangle = 0. \quad (\text{a4.20}) \quad (\text{a4.22})$$

A4.8 Clebsch-Gordan and Racah Coefficients and Coupling of Irreducible Tensors

A4.8.1 Clebsch-Gordan Coefficient

If $\hat{j} = \hat{j}_1 + \hat{j}_2$, the simultaneous eigenfunction $|j, m\rangle$ of $\hat{j}^2$ and $\hat{j}_z$ has the following relations with the products of simultaneous eigenfunctions $|j_1, m_1\rangle$ of $\hat{j}_1^2$ and $\hat{j}_{1z}$ and $|j_2, m_2\rangle$ of $\hat{j}_2^2$ and $\hat{j}_{2z}$:

$$|j, m\rangle = |j_1, j_2, j, m\rangle = \sum_{m_1, m_2} C(j_1 j_2 j; m_1 m_2 m) |j_1, m_1\rangle |j_2, m_2\rangle, \quad (\text{a4.23})$$

$$|j_1, m_1\rangle |j_2, m_2\rangle = \sum_j C(j_1 j_2 j; m_1 m_2 m) |j_1, j_2, j, m\rangle. \quad (\text{a4.24})$$

$C(j_1 j_2 j; m_1 m_2 m)$ is called Clebsch-Gordan coefficient. It is a real function of the quantum numbers in the parenthesis. If $m_1 + m_2 \neq m$, $C(j_1 j_2 j; m_1 m_2 m) = 0$, so $C(j_1 j_2 j; m_1 m_2 m)$ in many cases are also formulated as $C(j_1 j_2 j; m_1, m - m_1)$ by omitting m . They are orthonormal:

$$\sum_{m_1, m_2} C(j_1 j_2 j; m_1 m_2 m) C(j_1 j_2 j'; m_1 m_2 m') = \delta(j, j') \delta(m, m'), \quad (\text{a4.25})$$

$$\sum_j C(j_1 j_2 j; m_1, m - m_1) C(j_1 j_2 j; m'_1, m - m'_1) = \delta(m_1, m'_1), \quad (\text{a4.26})$$

and has some symmetrical relations such as

$$C(j_1 j_2 j; m_1 m_2 m) = (-1)^{j_1 + j_2 - j} C(j_2 j_1 j; m_2 m_1 m). \quad (\text{a4.27})$$

A4.8.2 Construction of an Irreducible Tensor from Two Irreducible Tensors

A linear combination of the product $\hat{T}_{M_1}^{L_1}(A_1) \hat{T}_{M_2}^{L_2}(A_2)$ of the components of irreducible tensors $\{\hat{T}_{M_1}^{L_1}(A_1)\}$ and $\{\hat{T}_{M_2}^{L_2}(A_2)\}$ generates irreducible tensor $\{\hat{T}_M^L(A_1, A_2)\}$ (A_i represents the space of the variable (A4.8.3)) as below:

$$\begin{aligned} \hat{T}_M^L(A_1, A_2) &= \sum_{M_1, M_2} C(L_1 L_2 L; M_1, M_2, M) \hat{T}_{M_1}^{L_1}(A_1) \hat{T}_{M_2}^{L_2}(A_2) \\ &= \sum_{M_1} C(L_1 L_2 L; M_1, M - M_1) \hat{T}_{M_1}^{L_1}(A_1) \hat{T}_{M - M_1}^{L_2}(A_2). \end{aligned} \quad (\text{a4.28})$$

A4.8.3 Scalar Product of Two Irreducible Tensors

The scalar product of irreducible tensors $\hat{T}^{L_1}(A_1) (\equiv \{\hat{T}_{M_1}^{L_1}(A_1)\})$ and $\hat{T}^{L_1}(A_2)$ is defined by and equals to

$$\begin{aligned}\hat{T}^{L_1}(A_1) \cdot \hat{T}^{L_1}(A_2) &\equiv \sum_M (-1)^M \hat{T}_M^{L_1}(A_1) \hat{T}_{-M}^{L_1}(A_2) \\ &= (-1)^{L_1} \sqrt{2L_1 + 1} \hat{T}_0^{L_1}(A_1, A_2).\end{aligned}\quad (\text{a4.29})$$

If $L_1 = 1$, it equals to the scalar product of two vectors. Examples: If $\{\hat{T}_M^1(A_1)\} = (\hat{L}_0, \hat{L}_{\pm 1})$ and $\{\hat{T}_M^1(A_2)\} = (\hat{S}_0, \hat{S}_{\pm 1})$, $\hat{T}^1(A_1) \cdot \hat{T}^1(A_2) = \hat{L} \cdot \hat{S}$. If $\{\hat{T}_M^1(A_1)\} = \{\hat{T}_M^1(A_2)\} = (rU_0^1 = z, rU_{\pm 1}^1 = \mp(x \pm iy)/\sqrt{2})$, $\hat{T}^1(A_1) \cdot \hat{T}^1(A_2) = \vec{r} \cdot \vec{r} = r^2$.

A4.8.4 Racah Coefficient

Consider the addition of three angular momenta

$$\hat{j} = \hat{j}_1 + \hat{j}_2 + \hat{j}_3. \quad (\text{a4.30})$$

One kind of representation in which $\hat{j}^2$ and $\hat{j}_z$ are diagonal can be obtained by first coupling $\hat{j}_1$ and $\hat{j}_2$ into intermediate angular momentum $\hat{j}_{12} = \hat{j}_1 + \hat{j}_2$ and then coupling it with $\hat{j}_3$ into $\hat{j}$. In this case the six operators $\hat{j}_1^2, \hat{j}_2^2, \hat{j}_3^2, \hat{j}_{12}^2, \hat{j}^2$, and $\hat{j}_z$ can be diagonalized simultaneously. Another kind of representation is first couple $\hat{j}_2$ and $\hat{j}_3$ into $\hat{j}_{23} = \hat{j}_2 + \hat{j}_3$ and then couple $\hat{j}_{23}$ with $\hat{j}_1$ into $\hat{j}$. In this case $\hat{j}_1^2, \hat{j}_2^2, \hat{j}_3^2, \hat{j}_{23}^2, \hat{j}^2$, and $\hat{j}_z$ can be diagonalized simultaneously. The simultaneous eigenfunction of $\hat{j}^2$ and $\hat{j}_z$ obtained by the above two couplings are

$$|j_3, j_{12}, j, m\rangle = \sum_{m_3, m_{12}} C(j_3 j_{12} j; m_3 m_{12} m) |j_3, m_3\rangle |j_1, j_2, j_{12}, m_{12}\rangle, \quad (\text{a4.31})$$

$$|j_1, j_{23}, j, m\rangle = \sum_{m_1, m_{23}} C(j_1 j_{23} j; m_1 m_{23} m) |j_1, m_1\rangle |j_2, j_3, j_{23}, m_{23}\rangle. \quad (\text{a4.32})$$

The states $|j_3, j_{12}, j, m\rangle$ and $|j_1, j_{23}, j, m\rangle$ are related with each other through the unitary transformation

$$|j_3, j_{12}, j, m\rangle = \sum_{j_{23}} R_{j_{23} j_{12}} |j_1, j_{23}, j, m\rangle. \quad (\text{a4.33})$$

$$W(j_1 j_2 j j_3; j_{12} j_{23}) \equiv \frac{R_{j_{23} j_{12}}}{\sqrt{(2j_{12} + 1)(2j_{23} + 1)}} \quad (\text{a4.34})$$

is called Racah coefficient. It is a function of the six quantum numbers of the angular momenta in the parenthesis of the left of above equation.

A4.9 Matrix Element Theorems of Irreducible Tensor

A4.9.1 Matrix Element Theorems of Irreducible Tensor

Suppose $\hat{T}_M^L$ is a component of an irreducible tensor.

①

$$\langle j', m' | \hat{T}_M^L | j, m \rangle = C(j L j'; m M m') \langle j' | \hat{T}^L | j \rangle. \quad (\text{a4.35})$$

$\langle j' | \hat{T}^L | j \rangle$ is a function of j' , L , and j and does not depend on the magnetic quantum numbers m , M , and m' . Such kind of function characterized by the pair of symbol $\parallel$ is called reduced matrix element.

②

$$\langle j, m' | \hat{T}_M^1 | j, m \rangle = \frac{\langle j, m' | \hat{j}_M (\hat{j} \cdot \hat{T}^1) | j, m \rangle}{j(j+1)}. \quad (\text{a4.36})$$

③

$$\langle j', m' | \hat{j}_M (\hat{j} \cdot \hat{T}^1) | j, m \rangle = \langle j', m' | \hat{j}_M | j, m \rangle \langle j | \hat{j} \cdot \hat{T}^1 | j \rangle \delta(j', j). \quad (\text{a4.37})$$

④

$$\begin{aligned} & \langle j'_1, j'_2, j', m' | \hat{T}^L(1) \cdot \hat{T}^L(2) | j_1, j_2, j, m \rangle \\ &= C(j 0 j'; m 0 m') \langle j'_1 j'_2 j' | \hat{T}^L(1) \cdot \hat{T}^L(2) | j_1 j_2 j \rangle \\ &= \delta(m', m) \delta(j', j) \langle j'_1 j'_2 j' | \hat{T}^L(1) \cdot \hat{T}^L(2) | j_1 j_2 j \rangle \\ &= \delta(m', m) \delta(j', j) (-1)^{j'_1 + j_2 - j} W(j_1 j_2 j'_1 j'_2; j L) \\ &\quad \times \sqrt{(2j'_1 + 1)(2j'_2 + 1)} \langle j'_1 | \hat{T}^L(1) | j_1 \rangle \langle j'_2 | \hat{T}^L(2) | j_2 \rangle, \end{aligned} \quad (\text{a4.38})$$

where $\hat{j} = \hat{j}_1 + \hat{j}_2$, $\hat{j}' = \hat{j}'_1 + \hat{j}'_2$; $\hat{T}^L(1)$, $\hat{j}_1$, and $\hat{j}'_1$ belong to the same space (such as position space), and $\hat{T}^L(2)$, $\hat{j}_2$, and $\hat{j}'_2$ to the same space (such as spin space).

⑤

$$\begin{aligned} & \langle j'_1, j'_2, j', m' | T_M^L(1) | j_1, j_2, j, m \rangle \\ &= C(j L j'; m M m') \langle j'_1 j'_2 j' | T_M^L(1) | j_1 j_2 j \rangle \end{aligned}$$

Table a4.2 $U_{m_l}^l$ and $\tilde{O}_{lm_l}$ for $l = 1, 2, 3$ [4]

l, m_l	$U_{m_l}^l$	$\tilde{O}_{lm_l}(X = J(J+1))$
1, 0	$\cos \theta$	$\hat{J}_z$
1, ± 1	$\mp \sqrt{\frac{1}{2}} \sin \theta \exp(\pm i\phi)$	$\mp \sqrt{\frac{1}{2}} \hat{J}_{\pm}$
2, 0	$\frac{1}{2}(3 \cos^2 \theta - 1)$	$\frac{1}{2}(3\hat{J}_z^2 - X)$
2, ± 1	$\mp \sqrt{\frac{3}{2}} \cos \theta \sin \theta \exp(\pm i\phi)$	$\mp \sqrt{\frac{3}{2}} \frac{1}{2}(\hat{J}_z \hat{J}_{\pm} + \hat{J}_{\pm} \hat{J}_z)$
2, ± 2	$\sqrt{\frac{3}{8}} \sin^2 \theta \exp(\pm 2i\phi)$	$\sqrt{\frac{3}{8}} \hat{J}_{\pm}^2$
3, 0	$\frac{1}{2}(5 \cos^3 \theta - 3 \cos \theta)$	$\frac{1}{2}[5\hat{J}_z^3 - 3(X - 1)\hat{J}_z]$
3, ± 1	$\mp \sqrt{\frac{3}{16}}(5 \cos^2 \theta - 1) \sin \theta \exp(\pm i\phi)$	$\mp \sqrt{\frac{3}{16}} \frac{1}{2} \left[(5\hat{J}_z^2 - X - \frac{1}{2}) \hat{J}_{\pm} + \hat{J}_{\pm} (5\hat{J}_z^2 - X - \frac{1}{2}) \right]$
3, ± 2	$\sqrt{\frac{15}{8}} \cos \theta \sin^2 \theta \exp(\pm 2i\phi)$	$\sqrt{\frac{15}{8}} \frac{1}{2}(\hat{J}_z \hat{J}_{\pm}^2 + \hat{J}_{\pm}^2 \hat{J}_z)$
3, ± 3	$\mp \sqrt{\frac{5}{16}} \sin^3 \theta \exp(\pm i3\phi)$	$\mp \sqrt{\frac{15}{8}} \hat{J}_{\pm}^3$

$$\begin{aligned}
&= C(jLj'; m M m')(-1)^{j_2+L-j_1-j'} \\
&\quad \times \delta(j'_2, j_2) \sqrt{(2j'_1+1)(2j+1)} W(j_1 j j'_1 j'; j_2 L) \langle j'_1 \| \hat{T}^L \| j_1 \rangle. \quad (\text{a4.39})
\end{aligned}$$

A4.9.2 Racah Operator Equivalent and Stevens Coefficient

$$\langle J, M_{J'} | U_{m_l}^l(i) | J, M_J \rangle = \langle J, M'_J | \tilde{O}_{lm_l} | J, M_J \rangle \langle J \| U^l \| J \rangle, \quad (2.24) \quad (\text{a4.40})$$

where $\tilde{O}_{lm_l}$ is the operator consisting of the angular momentum operators $\hat{J}_{\alpha}$ ($\alpha = z, \pm$, (2.33)), which is called Racah operator equivalent. The relations of $\tilde{O}_{lm_l}$ with $\hat{J}_{\alpha}$ are listed in Table a4.2.

For the case of $|J, M_J\rangle$ is a state of the ground term $|3d^n, L, M_L\rangle$ for a 3d ion or the state of the ground multiplet $|4d^n, L, S, J, M_J\rangle$ for a 4f ion,

$$\theta_l = n \langle J \| U^l \| J \rangle \quad (\text{a4.41})$$

is called l^{th} order Stevens coefficient. The values of $\alpha_J \equiv \theta_2$ for trivalent 4f ions are listed in Table 5.2.

Appendix 5: Second Quantized Representation of Operators

A5.1 Occupation Number Representation and Creation, Annihilation, and Number Operators

Let $\{\psi_a = |a\rangle\}$ ($a = \alpha_1, \alpha_2, \dots, \alpha, \dots, \beta_1, \beta_2, \dots, \beta, \dots, \gamma_1, \gamma_2, \dots, \gamma, \dots$) represent a complete orthonormal set of single-electron functions. The wave function of N electrons occupying the states of $\alpha, \beta, \dots, \gamma, \dots$ is formulated by the Slater determinant

$$\Psi(1, 2, \dots, N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_\alpha(1) & \psi_\beta(1) & \dots & \psi_\gamma(1) & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \psi_\alpha(i) & \psi_\beta(i) & \dots & \psi_\gamma(i) & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \psi_\alpha(N) & \psi_\beta(N) & \dots & \psi_\gamma(N) & \dots \end{vmatrix}. \quad (\text{a5.1})$$

The state can also be formulated by the following occupation number representation

$$\begin{aligned} \Psi &= |\alpha, \beta, \dots, \gamma, \dots\rangle \\ &\equiv \begin{matrix} 0, & 0, & \bullet\bullet\bullet\bullet, & 1, & 0, & 0, & \bullet\bullet\bullet, & 1, & 0, & 0, & \bullet\bullet\bullet, & 1, & \bullet\bullet\bullet \end{matrix} \\ &\quad \begin{matrix} \uparrow & \uparrow & & \uparrow\downarrow & \uparrow\downarrow & \uparrow & & \uparrow\downarrow & \uparrow\downarrow & \uparrow & & \uparrow\downarrow & \uparrow & \end{matrix} \\ &\quad |\alpha_1, \alpha_2, \bullet\bullet\bullet\bullet, \alpha, \beta_1, \beta_2, \bullet\bullet\bullet, \beta, \gamma_1, \gamma_1, \bullet\bullet\bullet, \gamma, \bullet\bullet\bullet \rangle \end{aligned} \quad (\text{a5.2})$$

Here the ket vector $|\alpha, \beta, \dots, \gamma, \dots\rangle$ is the state that the $\alpha, \beta, \dots, \gamma, \dots$ single-electron states which appear within the $|\rangle$ are occupied while the other states that do not appear are void as shown explicitly by the arrows in the last expression. Let

$$|\alpha, \beta, \gamma, \dots\rangle \equiv \hat{a}_\alpha^+ \hat{a}_\beta^+ \hat{a}_\gamma^+ \dots |\rangle \quad (\text{a5.3})$$

where

$$| \rangle \equiv |0, 0, \dots\rangle \quad (\text{a5.4})$$

represents the state in which all $\{\psi_a = |a\rangle\}$ states are void. Equation (a5.3) shows that $\hat{a}_\alpha^+$ is the operator which creates an electron in the α state, so it is called creation operator. Ψ being antisymmetrical it holds

$$|\alpha, \beta, \dots, \gamma, \dots\rangle = -|\beta, \alpha, \dots, \gamma, \dots\rangle, \quad (\text{a5.5})$$

i.e.,

$$\hat{a}_\alpha^+ \hat{a}_\beta^+ |\dots, \gamma, \dots\rangle + \hat{a}_\beta^+ \hat{a}_\alpha^+ |\dots, \gamma, \dots\rangle = 0. \quad (\text{a5.6})$$

thus,

$$\hat{a}_\alpha^+ \hat{a}_\beta^+ + \hat{a}_\beta^+ \hat{a}_\alpha^+ = 0, \quad (\text{a5.7})$$

$$\hat{a}_\alpha^+ \hat{a}_\alpha^+ = 0. \quad (\text{a5.8})$$

$$\hat{a}_\alpha^+ \hat{a}_\alpha^+ |\gamma, \dots\rangle = |\alpha, \alpha, \gamma, \dots\rangle = 0 \quad (\text{a5.9})$$

expresses the Pauli exclusion principle.

The bra vector and counterparts of the creation operators in (a5.3) are

$$\langle \dots, \gamma, \beta, \alpha | = \langle \dots | \hat{a}_\gamma \hat{a}_\beta \hat{a}_\alpha. \quad (\text{a5.10})$$

From the analyses similar to (a5.5)–(a5.8) we get

$$\hat{a}_\alpha \hat{a}_\beta + \hat{a}_\beta \hat{a}_\alpha = 0, \quad (\text{a5.11})$$

$$\hat{a}_\alpha \hat{a}_\alpha = 0. \quad (\text{a5.12})$$

From the normal condition of

$$\langle \dots, \beta, \alpha | \alpha, \beta, \dots \rangle = \langle \dots, \beta | \hat{a}_\alpha \hat{a}_\alpha^+ | \beta, \dots \rangle = \langle \dots, \beta | \beta, \dots \rangle \quad (\text{a5.13})$$

we get

$$\hat{a}_\alpha \hat{a}_\alpha^+ | \beta, \dots \rangle = \hat{a}_\alpha | \alpha, \beta, \dots \rangle = | \beta, \dots \rangle. \quad (\text{a5.14})$$

Equation (a5.14) shows that the action of $\hat{a}_\alpha$ on a ket vector is to eliminate an electron in the α state, so it is called annihilation operator. The actions of $\hat{a}_\alpha^+$ and $\hat{a}_\alpha$ on arbitrary state are

$$\begin{aligned} & \hat{a}_\alpha^+ | 1, 2, \dots, \alpha - 1, n_\alpha, \alpha + 1, \dots \rangle \\ & (n_\alpha = 1 \text{ or } 0 \text{ represents } \alpha \text{ state is occupied or void}) \\ & = | \alpha, 1, 2, \dots, \alpha - 1, n_\alpha, \alpha + 1, \dots \rangle \\ & = (-1)^{\alpha-1} | 1, 2, \dots, \alpha - 1, \alpha, \alpha + 1, \dots \rangle \delta(n_\alpha, 0), \end{aligned} \quad (\text{a5.15})$$

$$\begin{aligned} & \hat{a}_\alpha | 1, 2, \dots, \alpha - 1, n_\alpha, \alpha + 1, \dots \rangle \\ & = (-1)^{\alpha-1} \hat{a}_\alpha | n_\alpha, 1, 2, \dots, \alpha - 1, \alpha + 1, \dots \rangle \\ & = (-1)^{\alpha-1} | 1, 2, \dots, \alpha - 1, \alpha + 1, \dots \rangle \delta(n_\alpha, 1). \end{aligned} \quad (\text{a5.16})$$

It is easily deduced from the above relations that

$$\hat{a}_\alpha^+ \hat{a}_\beta + \hat{a}_\beta \hat{a}_\alpha^+ = \delta(\alpha, \beta), \quad (\text{Sect. 2.1.1}) \quad (\text{a5.17})$$

$$\hat{a}_\alpha^+ \hat{a}_\alpha = \hat{n}_\alpha. \quad (\text{a5.18})$$

$\hat{n}_\alpha$ is the number operator of the α state eigenvalue of which is n_α .

A5.2 Second Quantized Representation of One-Particle Hamiltonian

The values of matrix elements $\langle \Psi' | \hat{H}_1 | \Psi \rangle$ of one-particle Hamiltonian

$$\hat{H}_1(1, 2, \dots, N) = \sum_i^{1, \dots, N} \hat{h}(i) \quad (\text{a5.19})$$

calculated by using ordinary representation are as follows.

① If $\Psi' = \Psi$,

$$\begin{aligned} \langle \Psi | \hat{H}_1 | \Psi \rangle &= \sum_i^{1, \dots, N} \langle \dots, \gamma, \dots, \beta, \alpha | \hat{h}(i) | \alpha, \beta, \dots, \gamma, \dots \rangle \\ &= \frac{1}{N!} N \int \begin{vmatrix} \psi_\alpha^+(1) & \psi_\beta^+(1) & \dots & \psi_\gamma^+(1) & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \psi_\alpha^+(i) & \psi_\beta^+(i) & \dots & \psi_\gamma^+(i) & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \psi_\alpha^+(N) & \psi_\beta^+(N) & \dots & \psi_\gamma^+(N) & \dots \end{vmatrix} \hat{h}(1) \\ &\quad \times \begin{vmatrix} \psi_\alpha(1) & \psi_\beta(1) & \dots & \psi_\gamma(1) & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \psi_\alpha(i) & \psi_\beta(i) & \dots & \psi_\gamma(i) & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \psi_\alpha(N) & \psi_\beta(N) & \dots & \psi_\gamma(N) & \dots \end{vmatrix} dv_1 dv_2 \dots dv_i \dots dv_N \\ &= \sum_{\mu}^{\alpha, \beta, \dots, \gamma, \dots} h_{\mu\mu}, \end{aligned} \quad (\text{a5.20})$$

$$h_{\mu\nu} \equiv \int \psi_\mu^+(i) \hat{h}(i) \psi_\nu(i) dv_i \equiv \langle \mu | \hat{h} | \nu \rangle. \quad (\text{a5.21})$$

② If one-electron state of Ψ' is different from that of Ψ ,

$$\begin{aligned} \langle \Psi' | \hat{H}_1 | \Psi \rangle &= \sum_i^{1, \dots, N} \langle \dots, \gamma', \dots, \beta, \alpha | \hat{h}(i) | \alpha, \beta, \dots, \gamma, \dots \rangle \quad (\gamma' \neq \gamma) \\ &= \frac{N}{N!} \int \begin{vmatrix} \psi_\alpha^+(1) & \psi_\beta^+(1) & \dots & \psi_{\gamma'}^+(1) & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \psi_\alpha^+(i) & \psi_\beta^+(i) & \dots & \psi_{\gamma'}^+(i) & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \psi_\alpha^+(N) & \psi_\beta^+(N) & \dots & \psi_{\gamma'}^+(N) & \dots \end{vmatrix} \hat{h}(1) \end{aligned}$$

$$\times \begin{vmatrix} \psi_\alpha(1) & \psi_\beta(1) & \cdots & \psi_\gamma(1) & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ \psi_\alpha(i) & \psi_\beta(i) & \cdots & \psi_\gamma(i) & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ \psi_\alpha(N) & \psi_\beta(N) & \cdots & \psi_\gamma(N) & \cdots \end{vmatrix} dv_1 dv_2 \cdots dv_i \cdots dv_N = h_{\gamma'\gamma}. \quad (\text{a5.22})$$

③ If two or more electron states of Ψ' are different from those of Ψ ,

$$\langle \Psi' | \hat{H}_1 | \Psi \rangle = 0. \quad (\text{a5.23})$$

The operator in second quantization form is given by

$$\hat{H}_1 = \sum_{\mu, \nu} h_{\mu\nu} \hat{a}_\mu^+ \hat{a}_\nu. \quad (\mu, \nu = \alpha_1, \alpha_2, \dots, \alpha, \dots, \beta_1, \beta_2, \dots, \beta, \dots, \gamma_1, \gamma_2, \dots, \gamma, \dots) \quad (\text{a5.24})$$

By substituting this operator for operator of (a5.19) and the occupation representations for the Slater determinants Ψ' and Ψ , the same values of the matrix elements of (a5.20), (a5.22), and (a5.23) can be obtained much easily as below.

①

$$\begin{aligned} & \left\langle \dots, \gamma, \dots, \beta, \alpha \left| \sum_{\mu, \nu} h_{\mu\nu} \hat{a}_\mu^+ \hat{a}_\nu \right| \alpha, \beta, \dots, \gamma, \dots \right\rangle \\ &= \left\langle \dots, \gamma, \dots, \beta, \alpha \left| \sum_{\mu} h_{\mu\mu} \hat{a}_\mu^+ \hat{a}_\mu \right| \alpha, \beta, \dots, \gamma, \dots \right\rangle = \sum_{\mu}^{\alpha, \beta, \dots, \gamma, \dots} h_{\mu\mu}, \end{aligned} \quad (\text{a5.25})$$

②

$$\left\langle \dots, \gamma', \dots, \beta, \alpha \left| \sum_{\mu, \nu} h_{\mu\nu} \hat{a}_\mu^+ \hat{a}_\nu \right| \alpha, \beta, \dots, \gamma, \dots \right\rangle = h_{\gamma'\gamma}, \quad (\gamma' \neq \gamma) \quad (\text{a5.26})$$

③

$$\begin{aligned} & \left\langle \dots, \delta', \dots, \gamma', \dots, \beta, \alpha \left| \sum_{\mu, \nu} h_{\mu\nu} \hat{a}_\mu^+ \hat{a}_\nu \right| \alpha, \beta, \dots, \gamma, \dots, \delta, \dots \right\rangle = 0. \\ & (\gamma' \neq \gamma \neq \delta \neq \delta') \end{aligned} \quad (\text{a5.27})$$

A5.3 Second Quantized Representation of Two-Particle Hamiltonian

The values of matrix elements $\langle \Psi' | \hat{H}_2 | \Psi \rangle$ of two-particle Hamiltonian

$$\hat{H}_2 = \frac{1}{2} \sum_{i,j}^{1,\dots,N; j \neq i} \hat{g}(i, j) \quad (\text{a5.28})$$

calculated by using ordinary representation are as follows.

① If $\Psi' = \Psi$,

$$\begin{aligned} \langle \Psi | \hat{H}_2 | \Psi \rangle &= \left\langle \dots, \delta, \dots, \gamma, \dots, \beta, \alpha \left| \frac{1}{2} \sum_{i,j}^{1,\dots,N; j \neq i} \hat{g}(i, j) \right| \alpha, \beta, \dots, \gamma, \dots, \delta, \dots \right\rangle \\ &= \frac{1}{2N!} N(N-1) \int \begin{vmatrix} \psi_\alpha^+(1) & \psi_\beta^+(1) & \dots & \psi_\gamma^+(1) & \dots & \psi_\delta^+(1) & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ \psi_\alpha^+(i) & \psi_\beta^+(i) & \dots & \psi_\gamma^+(i) & \dots & \psi_\delta^+(i) & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ \psi_\alpha^+(N) & \psi_\beta^+(N) & \dots & \psi_\gamma^+(N) & \dots & \psi_\delta^+(N) & \dots \end{vmatrix} \\ &\quad \times \hat{g}(1, 2) \begin{vmatrix} \psi_\alpha(1) & \psi_\beta(1) & \dots & \psi_\gamma(1) & \dots & \psi_\delta(1) & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ \psi_\alpha(i) & \psi_\beta(i) & \dots & \psi_\gamma(i) & \dots & \psi_\delta(i) & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ \psi_\alpha(N) & \psi_\beta(N) & \dots & \psi_\gamma(N) & \dots & \psi_\delta(N) & \dots \end{vmatrix} dv_1 dv_2 \dots dv_i \dots dv_N \\ &= \frac{1}{2} \sum_v^{>\mu} \sum_\mu^{\alpha, \beta, \dots, \gamma, \dots, \delta, \dots} \int \begin{vmatrix} \psi_\mu^+(1) & \psi_v^+(1) \\ \psi_\mu^+(2) & \psi_v^+(2) \end{vmatrix} \hat{g}(1, 2) \begin{vmatrix} \psi_\mu(1) & \psi_v(1) \\ \psi_\mu(2) & \psi_v(2) \end{vmatrix} dv_1 dv_2 \\ &= \frac{1}{2} \sum_v^{>\mu} \sum_\mu^{\alpha, \beta, \dots, \gamma, \dots, \delta, \dots} (g_{\mu\nu\nu\mu} - g_{\mu\nu\mu\nu} + g_{v\mu\mu\nu} - g_{v\mu\nu\mu}) \\ &= \frac{1}{2} \sum_{\mu, v}^{\alpha, \beta, \dots, \gamma, \dots, \delta, \dots; \mu \neq v} (g_{\mu\nu\nu\mu} - g_{\mu\nu\mu\nu}), \quad (\text{a5.29}) \end{aligned}$$

$$g_{\mu\nu\gamma\delta} \equiv \int \psi_\mu^+(1) \psi_v^+(2) \hat{g}(1, 2) \psi_\gamma(2) \psi_\delta(1) dv_1 dv_2. \quad (\text{a5.30})$$

② If one-electron state of Ψ' is different from that of Ψ ,

$$\left\langle \dots, \gamma', \dots, \beta, \alpha \left| \frac{1}{2} \sum_{i,j}^{1,\dots,N; j \neq i} \hat{g}(i, j) \right| \alpha, \beta, \dots, \gamma, \dots \right\rangle \quad (\gamma' \neq \gamma)$$

$$\begin{aligned}
&= \frac{1}{2} \sum_{\mu}^{1, \dots, N; \neq (\gamma', \gamma)} \int \left| \begin{array}{cc} \psi_{\gamma'}^+(1) & \psi_{\mu}^+(1) \\ \psi_{\gamma'}^+(2) & \psi_{\mu}^+(2) \end{array} \right| \hat{g}(1, 2) \left| \begin{array}{cc} \psi_{\gamma}(1) & \psi_{\mu}(1) \\ \psi_{\gamma}(2) & \psi_{\mu}(2) \end{array} \right| dv_1 dv_2 \\
&= \frac{1}{2} \sum_{\mu}^{\alpha, \beta, \dots, \delta, \dots; \neq (\gamma', \gamma)} (g_{\gamma' \mu \mu \gamma} - g_{\gamma' \mu \gamma \mu} + g_{\mu \gamma' \gamma \mu} - g_{\mu \gamma' \mu \gamma}). \quad (\text{a5.31})
\end{aligned}$$

③ If two electron states of Ψ' are different from those of Ψ ,

$$\begin{aligned}
&\left\langle \dots, \delta', \dots, \gamma', \dots, \beta, \alpha \left| \frac{1}{2} \sum_{i, j}^{1, \dots, N; j \neq i} \hat{g}(i, j) \right| \alpha, \beta, \dots, \gamma, \dots, \delta, \dots \right\rangle \\
&\quad (\gamma' \neq \gamma \neq \delta \neq \delta') \\
&= \frac{1}{2} \int \left| \begin{array}{cc} \psi_{\gamma'}^+(1) & \psi_{\delta'}^+(1) \\ \psi_{\gamma'}^+(2) & \psi_{\delta'}^+(2) \end{array} \right| \hat{g}(1, 2) \left| \begin{array}{cc} \psi_{\gamma}(1) & \psi_{\delta}(1) \\ \psi_{\gamma}(2) & \psi_{\delta}(2) \end{array} \right| dv_1 dv_2 \\
&= \frac{1}{2} (g_{\gamma' \delta' \delta \gamma} - g_{\gamma' \delta' \gamma \delta} + g_{\delta' \gamma' \gamma \delta} - g_{\delta' \gamma' \delta \gamma}). \quad (\text{a5.32})
\end{aligned}$$

④ If more than two electron states of Ψ' are different from those of Ψ ,

$$\langle \Psi' | \hat{H}_2 | \Psi \rangle = 0. \quad (\text{a5.33})$$

The operator in second quantization form is given by

$$\begin{aligned}
\hat{H}_2 &= \frac{1}{2} \sum_{\mu, v, \gamma, \delta} g_{\mu v \gamma \delta} \hat{a}_{\mu}^+ \hat{a}_v^+ \hat{a}_{\gamma} \hat{a}_{\delta}. \\
&(\mu, v, \gamma, \delta = \alpha_1, \alpha_2, \dots, \alpha, \beta_1, \beta_2, \dots, \beta, \dots, \gamma_1, \gamma_2, \dots, \gamma, \dots) \quad (\text{a5.34})
\end{aligned}$$

The same results of the last formulations in (a5.29), (a5.31)–(a5.33) can be obtained much easily by use of this operator as below.

①

$$\begin{aligned}
&\left\langle \dots, \delta, \dots, \gamma, \dots, \beta, \alpha \left| \frac{1}{2} \sum_{\mu, v, \gamma, \delta} g_{\mu v \gamma \delta} \hat{a}_{\mu}^+ \hat{a}_v^+ \hat{a}_{\gamma} \hat{a}_{\delta} \right| \alpha, \beta, \dots, \gamma, \dots, \delta, \dots \right\rangle \\
&= \frac{1}{2} \sum_v^{> \mu} \sum_{\mu}^{\alpha, \beta, \dots, \gamma, \dots, \delta, \dots} (g_{\mu v v \mu} - g_{\mu v \mu v} + g_{v \mu \mu v} - g_{v \mu v \mu}) \\
&= \frac{1}{2} \sum_{\mu, v}^{\alpha, \beta, \dots, \gamma, \dots, \delta, \dots; \mu \neq v} (g_{\mu v v \mu} - g_{\mu v \mu v}), \quad (\text{a5.35})
\end{aligned}$$

②

$$\begin{aligned}
& \left\langle \dots, \delta, \dots, \gamma', \dots, \beta, \alpha \left| \frac{1}{2} \sum_{\mu, \nu, \gamma, \delta} g_{\mu\nu\lambda\delta} \hat{a}_{\mu}^{+} \hat{a}_{\nu}^{+} \hat{a}_{\gamma} \hat{a}_{\delta} \right| \alpha, \beta, \dots, \gamma, \dots, \delta, \dots \right\rangle \\
& \quad (\gamma' \neq \gamma) \\
& = \frac{1}{2} \sum_{\mu}^{\alpha, \beta, \dots, \delta, \dots; \neq (\gamma', \gamma)} (g_{\gamma'\mu\mu\gamma} - g_{\gamma'\mu\gamma\mu} + g_{\mu\gamma'\gamma\mu} - g_{\mu\gamma'\mu\gamma}), \quad (\text{a5.36})
\end{aligned}$$

③

$$\begin{aligned}
& \left\langle \dots, \delta', \dots, \gamma', \dots, \beta, \alpha \left| \frac{1}{2} \sum_{\mu, \nu, \gamma, \delta} g_{\mu\nu\lambda\delta} \hat{a}_{\mu}^{+} \hat{a}_{\nu}^{+} \hat{a}_{\gamma} \hat{a}_{\delta} \right| \alpha, \beta, \dots, \gamma, \dots, \delta, \dots \right\rangle \\
& \quad (\gamma' \neq \gamma \neq \delta \neq \delta') \\
& = \frac{1}{2} (g_{\gamma'\delta'\delta\gamma} - g_{\gamma'\delta'\gamma\delta} + g_{\delta'\gamma'\gamma\delta} - g_{\delta'\gamma'\delta\gamma}), \quad (\text{a5.37})
\end{aligned}$$

④

$$\begin{aligned}
& \left\langle \dots, \delta', \dots, \gamma', \dots, \beta', \alpha \left| \frac{1}{2} \sum_{\mu, \nu, \gamma, \delta} g_{\mu\nu\lambda\delta} \hat{a}_{\mu}^{+} \hat{a}_{\nu}^{+} \hat{a}_{\gamma} \hat{a}_{\delta} \right| \alpha, \beta, \dots, \gamma, \dots, \delta, \dots \right\rangle = 0. \\
& \quad (\beta \neq \beta' \neq \gamma' \neq \gamma \neq \delta \neq \delta') \quad (\text{a5.38})
\end{aligned}$$

A5.4 Relations Between Creation and Annihilation Operators of Spin-Down and Spin-Up Electrons with Spin Operators

The following equivalent relations hold between the creation and annihilation operators of spin-up and down $\{\hat{a}_{\pm}^{+}, \hat{a}_{\pm}\}$ and the spin operators $\{\hat{s}_{\pm}, \hat{s}_z\}$.

$$\hat{a}_{+}^{+} \hat{a}_{-} = \hat{s}_{+}, \quad (\hat{s}_{\pm} \equiv \hat{s}_x \pm i\hat{s}_y) \quad (\text{2.33}) \quad (\text{a5.39})$$

$$\hat{a}_{-}^{+} \hat{a}_{+} = \hat{s}_{-}, \quad (\text{a5.40})$$

$$\hat{a}_{+}^{+} \hat{a}_{+} - \hat{a}_{-}^{+} \hat{a}_{-} = \hat{n}_{+} - \hat{n}_{-} = 2\hat{s}_z. \quad (\text{a5.41})$$

In fact, representing $\chi_{+} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$, $\chi_{-} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$ ((2.5) and (2.6)) and $\begin{pmatrix} 0 \\ 0 \end{pmatrix}$ by $|1, 0\rangle$, $|0, 1\rangle$ and $|0, 0\rangle = 0$, respectively, and by using the relations of $\hat{s}_{+} = \hat{s}_x + i\hat{s}_y =$

$\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$, $\hat{s}_- = \hat{s}_x - i\hat{s}_y = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$, and $\hat{s}_z = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$ ((2.27), (2.2)) we get

$$\hat{s}_+|1, 0\rangle = |0, 0\rangle, \quad \hat{a}_+^+ \hat{a}_-|1, 0\rangle = |0, 0\rangle; \quad (\text{a5.42})$$

$$\hat{s}_+|0, 1\rangle = |1, 0\rangle, \quad \hat{a}_+^+ \hat{a}_-|0, 1\rangle = |1, 0\rangle; \quad (\text{a5.43})$$

$$\hat{s}_-|1, 0\rangle = |0, 1\rangle, \quad \hat{a}_-^+ \hat{a}_+|1, 0\rangle = |0, 1\rangle; \quad (\text{a5.44})$$

$$\hat{s}_-|0, 1\rangle = |0, 0\rangle, \quad \hat{a}_-^+ \hat{a}_+|0, 1\rangle = |0, 0\rangle; \quad (\text{a5.45})$$

$$2\hat{s}_z|1, 0\rangle = |1, 0\rangle, \quad (\hat{a}_+^+ \hat{a}_+ - \hat{a}_-^+ \hat{a}_-)|1, 0\rangle = |1, 0\rangle; \quad (\text{a5.46})$$

$$2\hat{s}_z|0, 1\rangle = -|0, 1\rangle, \quad (\hat{a}_+^+ \hat{a}_+ - \hat{a}_-^+ \hat{a}_-)|0, 1\rangle = -|0, 1\rangle. \quad (\text{a5.47})$$

Appendix 6: Perturbation Theory

Suppose the solution of the Schrödinger equation

$$\hat{H}_0|\psi\rangle = \varepsilon|\psi\rangle \quad (\text{a6.1})$$

is known. $\{|j\rangle\}$ (j :Arabic, $= 1, 2, \dots, n$) and ε_0 are the ground eigenstates and eigenenergy, and $\{|\mu\rangle\}$, (μ : Greek) and $\{\varepsilon_\mu\}$ are the excited eigenstates and eigenenergies.

$\hat{H}'(\ll \hat{H}_0)$ is the perturbation. The Schrödinger equation

$$(\hat{H}_0 + \hat{H}')|\psi'\rangle = \varepsilon|\psi'\rangle \quad (\text{a6.2})$$

will be solved approximately as below. Inserting

$$|\psi'\rangle = \sum_j a_j |j\rangle + \sum_\mu a_\mu |\mu\rangle \quad (\text{a6.3})$$

into (a6.2) we get

$$(\hat{H}_0 - \varepsilon) \sum_j a_j |j\rangle + (\hat{H}_0 - \varepsilon) \sum_\mu a_\mu |\mu\rangle = -\hat{H}'|\psi'\rangle. \quad (\text{a6.4})$$

Left multiplying $\langle v|$ on (a6.4) we get

$$a_v = \frac{\langle v|\hat{H}'|\psi'\rangle}{\varepsilon - \varepsilon_v}$$

$$\begin{aligned}
&= \sum_j \frac{\langle v|\hat{H}'|j\rangle}{\varepsilon - \varepsilon_v} a_j + \sum_\rho \frac{\langle v|\hat{H}'|\rho\rangle}{\varepsilon - \varepsilon_v} a_\rho \\
&= \sum_j \left[\frac{\langle v|\hat{H}'|j\rangle}{\varepsilon - \varepsilon_v} + \sum_\rho \frac{\langle v|\hat{H}'|\rho\rangle \langle \rho|\hat{H}'|j\rangle}{(\varepsilon - \varepsilon_v)(\varepsilon - \varepsilon_\rho)} \right. \\
&\quad \left. + \sum_{\mu,v} \frac{\langle l|\hat{H}'|\mu\rangle \langle \mu|\hat{H}'|v\rangle \langle v|\hat{H}'|j\rangle}{(\varepsilon - \varepsilon_\mu)(\varepsilon - \varepsilon_v)} + \dots \right] a_j. \tag{a6.5}
\end{aligned}$$

Left multiplying $\langle l|$ on (a6.4) we get

$$\begin{aligned}
\sum_j (\varepsilon_0 - \varepsilon) \delta(l, j) a_j &= - \sum_j \langle l|\hat{H}'|j\rangle a_j - \sum_\mu \langle l|\hat{H}'|\mu\rangle a_\mu \\
&= - \sum_j [\langle l|\hat{H}'|j\rangle + \sum_\mu \frac{\langle l|\hat{H}'|\mu\rangle \langle \mu|\hat{H}'|j\rangle}{\varepsilon - \varepsilon_\mu} \\
&\quad + \sum_{\mu,v} \frac{\langle l|\hat{H}'|\mu\rangle \langle \mu|\hat{H}'|v\rangle \langle v|\hat{H}'|j\rangle}{(\varepsilon - \varepsilon_\mu)(\varepsilon - \varepsilon_v)} + \dots] a_j, \tag{a6.6}
\end{aligned}$$

that is

$$\sum_j [\langle l|\hat{H}_{\text{eff}}|j\rangle - \varepsilon \delta(l, j)] a_j = 0, \tag{a6.7}$$

$$\begin{aligned}
\langle l|\hat{H}_{\text{eff}}|j\rangle &\equiv \varepsilon_0 \delta(l, j) + \langle l|\hat{H}'|j\rangle + \sum_\mu \frac{\langle l|\hat{H}'|\mu\rangle \langle \mu|\hat{H}'|j\rangle}{\varepsilon - \varepsilon_\mu} \\
&\quad + \sum_{\mu,v} \frac{\langle l|\hat{H}'|\mu\rangle \langle \mu|\hat{H}'|v\rangle \langle v|\hat{H}'|j\rangle}{(\varepsilon - \varepsilon_\mu)(\varepsilon - \varepsilon_v)} + \dots. \tag{a6.8}
\end{aligned}$$

The solution of (a6.2) can be obtained by solving the perturbation secular equation

$$\begin{aligned}
&|\langle l|\hat{H}_{\text{eff}}|j\rangle - \varepsilon \delta(l, j)| \quad (l, j = 1, 2, \dots, n) \\
&\equiv \begin{vmatrix} \langle 1|\hat{H}_{\text{eff}}|1\rangle - \varepsilon & \langle 1|\hat{H}_{\text{eff}}|2\rangle & \cdots & \langle 1|\hat{H}_{\text{eff}}|n\rangle \\ \langle 2|\hat{H}_{\text{eff}}|1\rangle & \langle 2|\hat{H}_{\text{eff}}|2\rangle - \varepsilon & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ \langle n|\hat{H}_{\text{eff}}|1\rangle & \cdots & \cdots & \langle n|\hat{H}_{\text{eff}}|n\rangle - \varepsilon \end{vmatrix} = 0. \tag{a6.9}
\end{aligned}$$

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Chapter 3

Magnetism of Solids

This chapter contains the sections of Classification of magnetic properties; Magnetic moment of atom (ion) in solids; Neutron diffraction and magnetic structure; Molecular field theory; Spin wave; Crystalline electric field; Free electron gas; Essentials of band theory; and Hyperfine interactions in solid.

3.1 Classification of Magnetic Properties

Magnetism can be classified into diamagnetism, paramagnetism, antiferromagnetism, ferromagnetism, ferrimagnetism, and magnetic glass. This section introduces the main characteristics of the magnetisms.

3.1.1 Diamagnetism

3.1.1.1 Ordinary Diamagnetism

The susceptibility χ is negative and very small,

$$\chi = -10^{-6} \sim -10^{-2}. \quad (3.1)$$

Under average laboratory conditions ($\mu_0 H < 2$ T, temperature $T < 1,200$ K) χ is independent of H and T .

Examples of the materials: the inert gases of He, Ne, and Ar; the molecules of H_2 , N_2 , and H_2O ; the crystals of NaCl and diamond (C); the metals of Cu, Ge, Ag, Au, and Bi; the nonmetals of Si, P, and S; and many organic compounds. A diamagnetic material has no intrinsic magnetic moment. The negative magnetic moment is induced by applied field.

3.1.1.2 Superconductor

Inside a superconductor $\vec{B} = \mu_0(\vec{H} + \vec{M}) = 0$. This phenomenon is called the Meissner effect (1933). Therefore, a superconductor has the largest negative susceptibility of

$$\chi = -1. \quad (3.2)$$

Examples of superconductors: the metals of Hg, Ti, and Zr (10); the compounds of Nb₃Ge(23) and Cs₃RbC₆₀(33); and the oxides of Y-Ba-Cu-O(90) and Hg-Ba-Cu-O(134) all below the critical temperatures (the numerical value in parentheses). If a superconductor is placed upon a permanent magnet, a strong repulsive force makes it float in the air.

3.1.2 Paramagnetism

The susceptibility is positive and in general very small,

$$\chi = 10^{-6} \sim 10^0. \quad (3.3)$$

Under average laboratory conditions χ is independent of H .

3.1.2.1 Paramagnetism Arising From Intrinsic Magnetic Moment of the Ions

The temperature dependence of χ obeys Curie Law

$$\chi = \frac{C}{T} \quad (2.125)$$

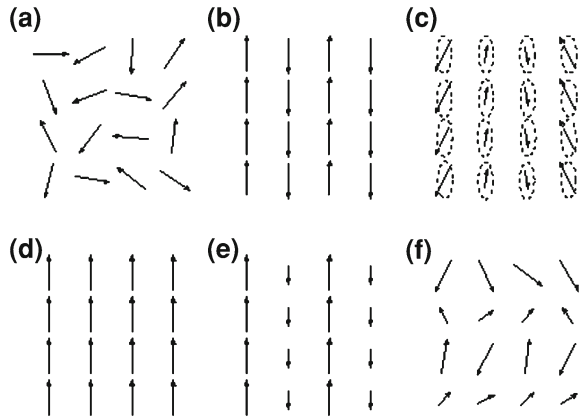
or Curie–Weiss law

$$\chi = \frac{C}{T - \theta_C}. \quad (T > \theta_C > 0) \quad (3.4)$$

θ_C is called the paramagnetic Curie temperature. At least some atoms or ions in the medium have intrinsic magnetic moments. The interactions between the magnetic moments are very weak. If magnetic field is absent, the thermal disturbance makes the magnetic moment directions of the atoms or ions distribute randomly in the space which is time-varying keeping the magnetization zero (Fig. 3.1a). In a magnetic field, the intrinsic magnetic moment is forced to tilt toward the field direction to decrease the Zeeman energy. But as the thermal energy is far larger than the Zeeman energy, the magnetization is very small.

Examples of the materials: the molecules of O₂ and NO; the 4d and 5d transition metals of Pd and Pt; the salts encompassing transition ions such as FeCl₂,

Fig. 3.1 Space distribution of atomic magnetic moments. **a** paramagnetism produced by atomic magnetic moments; **b, c** antiferromagnetism; **d** ferromagnetism; **e** ferrimagnetism; **f** canted ferrimagnetism



$\text{Gd}_2\text{SO}_4 \cdot 8\text{H}_2\text{O}$; and the 3d transition metals of Fe, Co, and Ni and 4f transition metals of Pr, Nd, and Sm all above the Curie or Néel temperature .

3.1.2.2 Pauli Paramagnetism

χ is almost independent of temperature. The paramagnetism arises from the change of the spin and orbital states of some itinerant electrons induced by the magnetic field.

Examples of the materials: the metals of Li, Na, K, Mg, Ca, etc, belonging to the IA and IIA groups of periodic table.

3.1.3 Antiferromagnetism

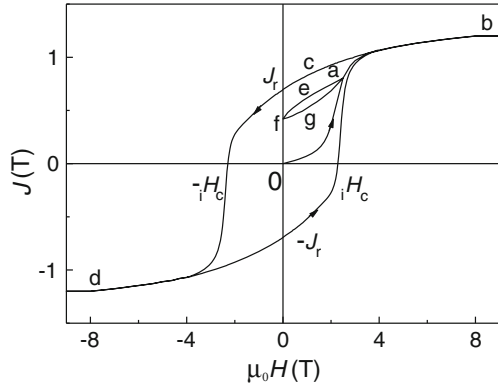
$$\chi = 10^{-4} \sim 10^{-1}. \quad (3.5)$$

χ increases with increase of temperature, reaches a maximum at the magnetic transformation temperature T_N , and becomes paramagnetism above T_N obeying Curie–Weiss law

$$\chi = \frac{C}{T + T_a}. \quad (T_a \text{ is in general positive}) \quad (3.6)$$

The transformation temperatures both from antiferromagnetism and ferrimagnetism to paramagnetism are called Néel temperature. In anti-ferromagnetic and ferrimagnetic materials at least some atoms or ions have intrinsic magnetic moments. They form two or more magnetic sublattices. Within a magnetic sublattice the environment being the same the magnetic moments, in value and direction, are the same. In an anti-ferromagnetic material the magnetic moment directions of different sublattices

Fig. 3.2 Magnetization curve, saturated magnetic hysteresis loop, and small magnetic hysteresis loop



are different, and the magnetization of the media is zero in the absence of magnetic field (Figs. 3.1b–c). In contrast to paramagnetism, the direction of the average atomic magnetic moment is fixed.

Examples of the materials: the transition metals of Cr, Mn, Pr, and Nd; and transition metal oxides MO ($M = \text{Mn, Fe, Ni, and Co}$) at low temperatures.

3.1.4 Ferromagnetism

$$\chi = 10 \sim 10^7, \quad (3.7)$$

i.e., the magnetization of this kind of material in a magnetic field is very large. χ is a complicated function of H and T , and the characteristics of the materials in a magnetic field are represented by the curves of $J(H)$ or $M(H)$ or $B(H)$. J (and M, B) is not a single-valued function of H . It depends on the history of magnetization. Figure 3.2 demonstrates the variation of J with H . Beginning from the initial demagnetized state of $J = 0$ at $H = 0$, J increases with increase of H along the curve of 0-a-b, called magnetization curve, to a saturation magnetic polarization J_s . Further increase of H only causes negligibly small increase of J_s . If H is decreased to zero after saturation, J decreases to remanence J_r along a new curve of b-c- J_r . With increase of H in the negative direction, the magnetization varies along the demagnetization curve $J_r-(-iH_c)$ in the second quadrant and becomes zero at $H = -iH_c$ and negatively saturates at large enough negative field region. iH_c is called intrinsic coercivity (sometimes tersely called coercivity). B varies along corresponding curve and becomes zero at $H = -H_c$. H_c is called coercivity, which is somewhat smaller than iH_c . If H is increased to an enough large positive value again from negative maximum field, J increases along the curve of d-(- J_r)-(iH_c)-b from negative saturation to positive saturation. This part of the curve (d-(- J_r)-(iH_c)-b) is the inversion of the upper curve of b-c- J_r -(- iH_c)-d, i.e., $J(H) = -J(-H)$. The two curves

constitute a closed-loop called saturation hysteresis loop or tersely hysteresis loop (or hysteresis curve).

If the integral $\oint H dJ$ is carried out over a cycle of hysteresis loop, it is the area of the loop and represents the magnetization energy which is dissipated in a unit volume medium and is called hysteresis loss (Note 1 of this section).

If it is magnetized to an unsaturated state of “a” along the magnetization curve (Fig. 3.2), then the field is decreased to zero, and then increased to $H(a)$ again; the magnetization follows a small hysteresis loop of a-e-f-g-a.

The derivative of the magnetization or hysteresis curve dB/dH is called differential permeability at the $B(H)$ state. If dH is applied opposite to the curve direction (Fig. 3.2) which changes B by dB' , dB'/dH is called reversible differential permeability, and the difference $dB/dH - dB'/dH$ irreversible differential permeability.

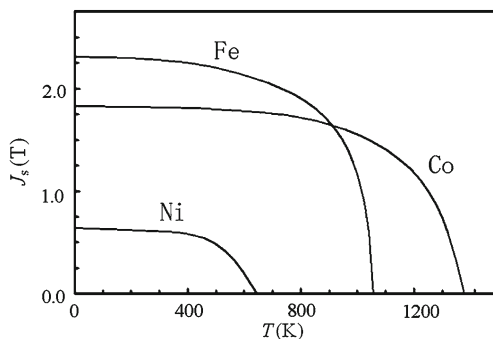
A bulk ferromagnetic body consists of many magnetic domains (tersely called domains). Each domain is spontaneously magnetized to saturation J_s even in the absence of applied magnetic field (Fig. 3.1d). The magnetization directions of different domains are different. The adjacent domains are separated by a finite thick domain wall, and the magnetization direction in the wall changes gradually with shift along the normal direction of the domain wall. The magnetization of a ferromagnetic body proceeds mainly by the variation of the volume of the domains through domain wall movement, called domain wall movement, and coherent rotation of the magnetization vector of each domain toward the field direction, called magnetic rotation process.

With increase of temperature, the thermal disturbance strengthens which causes the decrease of the parallelism of the atomic magnetic moments and hence the decrease in J_s , which becomes zero at the magnetic transformation temperature T_C . Above the temperature it becomes paramagnetism, and χ obeys the Curie–Weiss law. T_C is called Curie temperature which is a bit lower than the paramagnetic Curie temperature θ_C (3.4).

At 20°C only the metals of Fe, Co, and Ni are the single element ferromagnetic materials. Among them $J_s(20^\circ\text{C}) = 2.26$ T of Fe metal is the largest and $T_C = 1115^\circ\text{C}$ of Co metal is the highest. Figure 3.3 shows J_s as a function of temperature for Fe, Co, and Ni metals.

The overwhelming majority of ferromagnetic materials are either alloys or compounds containing $\text{Fe}(3d^6 4s^2)$, $\text{Co}(3d^7 4s^2)$, and/or $\text{Ni}(3d^8 4s^2)$. Usually the values of J_s and T_C decrease with increase of the content of non-magnetic elements. A small number of compounds containing 3d transition atoms other than Fe, Co, and Ni, such as CrO_2 ($\text{Cr}(3d^5 4s^1)$), MnBi , and MnSb ($\text{Mn}(3d^5 4s^2)$), are also ferromagnetic at R.T.. The light rare earth-3d metal compounds of SmCo_5 ($\text{Sm}(4f^5 5s^2 5p^6 5d^1 6s^2)$) and $\text{Nd}_2\text{Fe}_{14}\text{B}$ ($\text{Nd}(4f^4 5s^2 5p^6 5d^1 6s^2)$) are important ferromagnetic materials. Some compounds of 4d transition atoms, such as SrRuO_3 ($\text{Ru}(4d^7 5s^1)$), are also ferromagnetic but the T_C are much lower than R.T.. In normal ferromagnetic metals, alloys and compounds partly filled inner electric subshells of 3d, 4f, and 4d provide the atomic magnetic moments.

Fig. 3.3 J_s
versus temperature
for Fe, Co, and Ni metals



Recently, ferromagnetism of T_C higher than R.T. has been found in some nanoparticles or films not containing transition ions such as In_2O_3 ($\text{In}(5s^25p^1)$, $\text{O}(2s^22p^4)$); ZnO ($\text{Zn}(3d^{10}4s^2)$); SnO_2 ($\text{Sn}(5s^25p^2)$); GaN ($\text{Ga}(4s^24p^1)$); K, Al, Cu, Zn, or Sr doped SnO_2 ; and N doped ZnO . The first-principles calculations show that the magnetic moments arise mainly from the outermost partly filled p orbitals of the cations or anions. Such ferromagnetism is called d^0 ferromagnetism.

3.1.5 Ferrimagnetism

The medium has at least two magnetic sublattices. The magnetic moments of at least two sublattices are anti-parallel. In contrast to antiferromagnetism, the magnetization of different sublattices do not completely cancel each other and hence ferrimagnetism has a spontaneous magnetization (Fig. 3.1e). Naturally J_s of ferrimagnetic materials in general are smaller than those of ferromagnetic materials. The characteristics of domain structure and magnetization processes are the same as those of ferromagnetism. Above the Néel temperature it transforms into paramagnetism. The temperature dependence of the χ is complicated.

Examples of the materials: spinel ferrites $\text{MO} \cdot \text{Fe}_2\text{O}_3$ ($\text{M} = \text{Mn, Fe, Co, Ni, Cu, Zn et al.}$); hexagonal plumbite-type oxides $\text{MO} \cdot 6\text{Fe}_2\text{O}_3$ ($\text{M} = \text{Ba, Sr, Pb}$); rare earth iron garnets $3\text{R}_2\text{O}_3 \cdot 5\text{Fe}_2\text{O}_3$ ($\text{R} = \text{Y, rare earth}$); heavy rare earth-3d transition metal compounds TbCo_5 , $\text{Dy}_2\text{Fe}_{14}\text{B}$; and amorphous M-Gd ($\text{M} = \text{Fe, Co, Ni}$) alloys.

3.1.6 Magnetic Glass

The magnetisms belonging to this category include canted ferromagnetism, canted ferrimagnetism, canted antiferromagnetism, and spin glass. Their common characteristics are that the atomic magnetic moment directions are not colinear (i.e. parallel or antiparallel), but are noncolinear (irregular) to some extent.

3.1.6.1 Canted Ferromagnetism

The macroscopic magnetic behavior is basically the same as that of ferromagnetism. The atomic magnetic moments are aligned to some extent, and a microscopic region of two to three atoms' dimension has an apparent magnetic moment. The average value of the magnetization decreases with increase of the dimension of the region. Canted ferromagnetism approaches to ferromagnetism with increase of the preferential alignment of the atomic magnetic moments.

Example of the materials: The amorphous alloys of Fe-Y, Fe-Lu, RNi_3 ($R = Ho, Dy, Er$, etc) are canted ferromagnetic, while amorphous alloys Fe_xLa_{1-x} ($x \sim 0.7$) and Fe_xTh_{1-x} ($x \sim 0.6$) are ferromagnetic.

3.1.6.2 Canted Ferrimagnetism

There exist at least two subgrids in a canted ferrimagnetic medium in contrast to only one subgrid in a canted ferromagnetic medium. The grid corresponds to a magnetic sublattice of ferrimagnetic media. Each subgrid has canted ferromagnetism. The values of the magnetization of the microscopic regions are different for the subgrids, and the preferential directions of the regions are in the main opposite resulting in nonzero spontaneous magnetization (Fig. 3.1f).

Examples of the materials: R-Co (R: magnetic rare earth element except Gd) amorphous alloys. Each of the R and Co atoms forms a subgrid.

3.1.6.3 Canted Antiferromagnetism

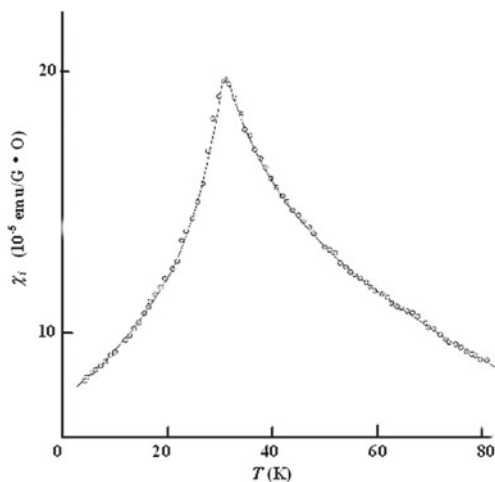
Canted antiferromagnetism is similar to canted ferrimagnetism. The difference is that the magnetization of the microscopic region for canted antiferromagnetism is zero.

3.1.7 Spin Glass

Initially, spin glass is referred to as Au-Fe or Cu-Mn alloys which contain only a small amount (about 1%) of magnetic atoms. Nowadays, there is no precise and commonly accepted definition. In the alloys, a small number of magnetic atoms are distributed in a non-magnetic matrix phase. The average atomic magnetic moment directions are fixed, randomly distributed in the space, and magnetization is zero. Therefore, it belongs to canted antiferromagnetism. An important characteristic of it is that the initial susceptibility

$$\chi_i = \lim_{H \rightarrow 0} \frac{M}{H} \quad (3.8)$$

Fig. 3.4 χ_i versus temperature for spin glass $\text{Cu}_{93.4}\text{Mn}_{6.6}$



as a function of temperature has a cusp-like sharp maximum at a critical temperature T_f (Fig. 3.4). Above T_f it transforms into paramagnetism obeying Curie–Weiss law. If it is cooled in a magnetic field from above T_f to below T_f or cooled in the absence of magnetic field, a strong enough magnetic field is applied and then removed; the medium obtains a magnetization (Sect. 5.4.8).

Examples of spin glasses: The alloys of Mn-M ($M = \text{Cu}, \text{Au}, \text{Ag}, \text{Mo}, \text{Rh}, \text{etc.}$), La-Gd and Y-Dy, and $\text{SiO}_2\text{-CaO-Fe}_2\text{O}_3$ and $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-MnO}$ in which the content of the magnetic elements are very small.

All of ferromagnetism, ferrimagnetism, canted ferromagnetism, and canted ferrimagnetism have spontaneous magnetization and are strongly magnetizable. A part of 3d and 4f magnetic elements are the basic components of such kind of media. The magnetically ordered media of small J_s or low magnetic transformation temperature along with weakly magnetizable media of diamagnetism, paramagnetism, antiferromagnetism, and canted antiferromagnetism with no spontaneous magnetization, have rarely been applied. The following sections and chapters will mainly deal with the magnetic properties of magnetic materials which have utility values.

Note 1

Some papers report that reverse hysteresis loops of $\oint H dJ < 0$ are found in some magnetic media. The results contradict the second law of thermodynamics. Faults in the experiments and analyses of the results cause the mistakes [1].

3.2 Magnetic Moment of Atom (Ion) in Solids

3.2.1 Fe-Ni Alloy

There are a number of widely applied magnetic alloys and compounds. Take Fe-Ni alloys as an example.

Figure 3.5 demonstrates the phase diagram. At high temperatures the alloy forms a single solid solution of fcc (face-centered cubic) γ phase over the full range of composition. If it is cooled to R.T., it transforms into bcc (body-centered cubic) α phase in the 0–~ 3% Ni range but remains γ phase in the ~ 50–100% Ni range. α and γ phases are mixed between the two ranges. Both the phases being substitutional solutions the mixed phase takes a long time to reach equilibrium state at R.T.. Order–disorder phase transition takes place around the compositions of FeNi₃, FeNi, and Fe₃Ni.

With decrease of Ni content, T_C of the γ phase increases from 361°C of Ni metal to 612°C around 68% Ni and then decreases to ~ 420°C around 42%Ni. With increase of Ni content T_C of the α phase decreases a bit from 770°C of pure Fe.

Figure 3.6 shows the Ni content dependence of saturation magnetic induction $B_s \equiv J_s$. With increase of Ni content from Fe to Ni B_s increases a bit, decreases, increases, and then decreases again. The values of B_s for ordered crystals are somewhat different from those of disordered. The equilibrium state being not reached under the usual thermal treatment conditions, the value depends on the treatment conditions in the mixed phase region especially around 30% Ni.

Ni₈₁Fe₁₉ known as Permalloy is a prominent soft magnetic material with large permeability. Ni₇₅Fe₂₀Cu₅ (often doped by ~ 2% Cr) known as Mumetal is easy to role to a thin plate and is an excellent magnetic shielding material. The cold rolled Ni₅₀Fe₅₀ known as Isoperm has a constant permeability in a large field range in the rolling direction. Ni₃₆Fe₆₄ called Inver is famous for its uniquely low coefficient of thermal expansion.

3.2.2 Magnetic Moment of 3d Atom in Alloys

Figure 3.7 demonstrates the experimental values of average atomic magnetic polarization moment as a function of average electron number n of the atoms at 0 K for the solid solutions of Fe, Co, and Ni with some 3d group elements. The averages of the data for pure Fe, Co, and Ni metals and Fe-V, Fe-Cr, Fe-Co, Ni-Co, and Ni-Cu alloys take the shape of a smooth curve called Slater-Pauling curve. With increase of n from ~24.6, the moment increases nearly linearly to a maximum of ~2.4 μ_B around $n \sim 26.4$ of Fe-Co alloy, and then decreases also nearly linearly to zero around $n \sim 28.6$. The slopes of the two branches are nearly $\pm 1 \mu_B/\text{electron}$, one-electron spin magnetic polarization moment per electron [3].

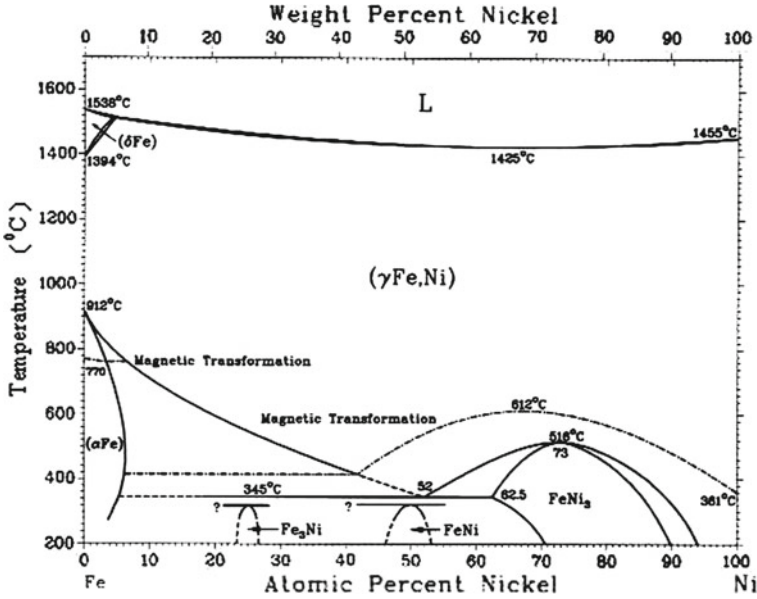
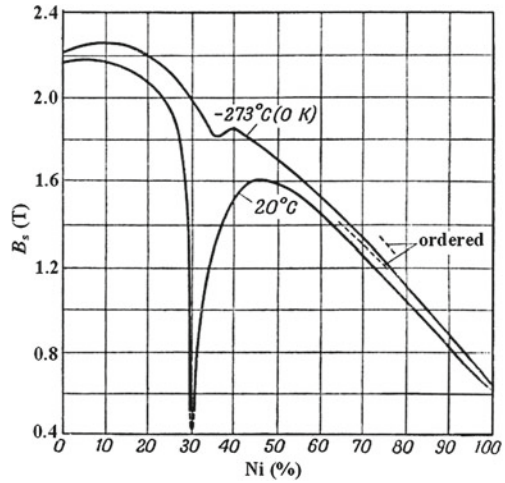


Fig. 3.5 Phase diagram of Fe-Ni alloy [2]

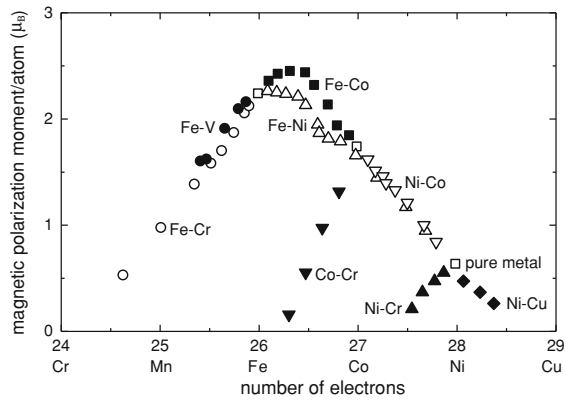
Fig. 3.6 B_s versus Ni content for Fe-Ni alloy [3]



The average atomic magnetic moment at 0 K per TM atom of TM-M (TM: Fe, Co or Ni; M: non-magnetic atom) alloy μ_{TM} decreases with increase of M content such as $\mu_{\text{Fe}}(\text{Fe}_{80}\text{Al}_{20}) \approx 2.1\mu_B$, $\mu_{\text{Fe}}(\text{Fe}_3\text{C}) \approx 2.0\mu_B$ and $\mu_{\text{Fe}}(\text{Fe}_{90}\text{Si}_{10}) \approx 1.9\mu_B$ compared to $\mu_{\text{Fe}}(\text{Fe}) \approx 2.2\mu_B$. The rate of the decrease depends on atom M and its content.

In a disordered alloy the atomic environment of the TM atom differs from atom to atom. Take Fe-rich bcc phase of Fe-Si alloy as an example. The coordination number

Fig. 3.7 Average atomic magnetic polarization moment versus average electron number per atom for Fe, Co, and Ni and their alloys



(nearest neighbor atom number) of an Fe atom is 8 among which n_{Fe} is Fe and the remaining $8-n_{Fe}$ is Si, where n_{Fe} can take any integer between 0 and 8 with different probabilities. Indeed the hyperfine magnetic field measurements show that the value of magnetic moment of the Fe atom differs for different neighboring environments in a wide range (Sect. 3.9.6.5).

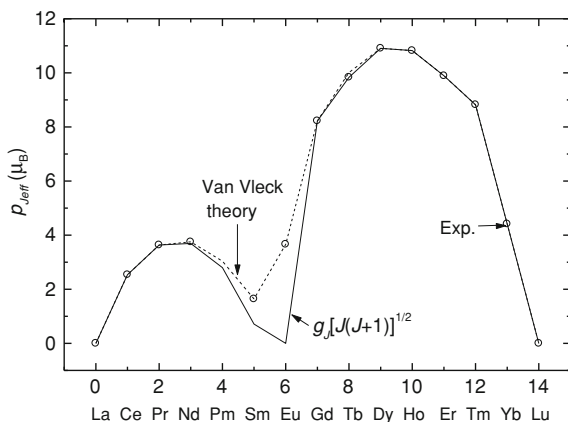
3.2.3 Magnetic Moment of 3d Ion in Oxides

In contrast to that the partly filled 3d electrons in electric conducting metals and alloys itinerate the whole medium, the electrons are essentially localized within each 3d ion in poor conducting and insulating oxides. Correspondingly, the values of the magnetic moments of 3d ions in oxides are quite different from those in metals and alloys. In many oxides such as spinel ferrites, hexagonal ferrites, and garnets, the magnetic polarization moments of most of the 3d ions at 0 K are approximately equal to $2S \mu_B$ of the spin magnetic moments of the free ions.

3.2.4 Magnetic Moment of 4f Ion in Solids

Figure 3.8 demonstrates the effective magnetic polarization of rare earth ion R^{+3} as a function of the number of 4f electrons measured for RAI_2 (R: rare earth) compound [4] and that calculated for free R^{+3} ions. The 4f electron subshell being covered by fully filled outer $5s^2 5p^6$ subshells, the state of the 4f electrons is little affected by its environment in a solid and the 4f ions preserve the value of magnetic moments of the isolated ions fairly well.

Fig. 3.8 $p_{J\text{eff}}$ of R^{+3} ion versus the number of 4f electrons. *Open circles* exp. *Curves* calculated by neglecting (—) or taking into account (---) the excited multiplets



3.3 Neutron Diffraction and Magnetic Structure

The space distribution of magnetic moment is called magnetic structure. The neutron diffraction is an extremely valuable tool to determine the magnetic structure. Magnetic and hyperfine field (Sect. 3.9) measurements can also yield some relevant information.

3.3.1 Neutron Diffraction

The neutron has no electric charge but has a magnetic moment (2.191). A neutron beam is usually emitted from a nuclear reactor. The wavelength of the neutron

$$\lambda = \frac{2\pi\hbar}{m_n v} \quad (m_n \text{ and } v : \text{mass and speed of neutron}) \quad (3.9)$$

is mostly in the range of 0.1~0.2 nm, which is nearly the same as the wavelengths of the X-ray used for crystallographic structure analyses. A high density neutron beam can be obtained from a spallation neutron source. In this installation positrons obtained high energy by successively going through a linear and circular accelerators strafe the target to knock out neutrons from the nuclei. A monochromatic beam can be obtained by reflecting the emitted beam from a single crystal surface.

By projecting the beam on the sample we can get the diffraction peaks (Bragg peaks) in the reflection directions which satisfy the Bragg condition

$$2d \sin \theta = n\lambda \quad (3.10)$$

and the structure factors are not zero (the neutrons elastic scattered by all atoms within a crystal cell do not completely cancel each other). Here, θ is the Bragg angle,

the angle between the incidence ray and the reflecting crystal plane (Bragg plane), n is the order of diffraction, and d is the spacing between the adjacent reflecting crystal planes. d is a function of the lattice constants and Millar indices of the Bragg plane (h, k, l) such as for a cubic crystal of lattice constant a

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}. \quad (3.11)$$

The Bragg condition is the same as that of X-ray diffraction. The differences are that the neutrons are diffracted by both the nuclei and magnetic moments of the electrons while the X-ray is diffracted by the electric charge of the electrons. The lattice constants for both X-ray and neutrons diffracted by nuclei are of chemical, while they are of magnetic for neutrons diffracted by the magnetic moments of electrons. The two are often different such as the magnetic lattice constant of anti-ferromagnetic MnO is twice that of chemical (Fig. 3.9). The nucleus scattering factor varies erratically while the atomic scattering factor of X-ray increases monotonically with increase in atomic number. The structure of diffraction (diffraction pattern) of the neutrons diffracted by magnetic moments depends on the magnetic structure. Therefore, the structure of the neutron diffraction is different from that of X-ray. If the magnetic lattice constants are different from those of chemical, the Bragg peaks diffracted by magnetic moments of the electrons not only appear in the same directions of X-rays of the same wavelength but also in some other directions. Figure 3.10 demonstrates the diffraction patterns of polycrystalline MnO above and below T_N . The pattern above T_N (Fig. 3.10b) is that diffracted only by the nuclei, and that below T_N (Fig. 3.10a) is the superposition of the patterns diffracted by the nuclei and magnetic moments of the electrons.

Below, the magnetic structures for some anti-ferromagnetic, ferrimagnetic, and ferromagnetic media are demonstrated. The values of magnetic polarization moment are given in μ_B unit per atom or molecular formula unit (f.u.). They are the values at 0 K except otherwise mentioned.

3.3.2 Magnetic Structure of MnO

MnO has the cubic crystal structure of NaCl. Mn^{+2} and O^{-2} ions constitute fcc lattice points, respectively, and the lattices superimpose with displacement. $O^{-2}(2p^6)$ ion has no magnetic moment. MnO is anti-ferromagnetic below $T_N = 118$ K. The magnetic moments of Mn^{+2} in each (111) layer are aligned parallel in the $\langle 112 \rangle$ axis direction, which is opposite in direction to those of adjacent layers (Fig. 3.9) [5].

3.3.3 Magnetic Structure of Ho Metal

Ho metal has an hcp (hexagonal close-packed) crystal structure. The magnetic polarization moment of the Ho^{+3} ion is $g_J J = 10$ (Table 2.3).

Fig. 3.9 Crystal and magnetic structures of anti-ferromagnetic MnO

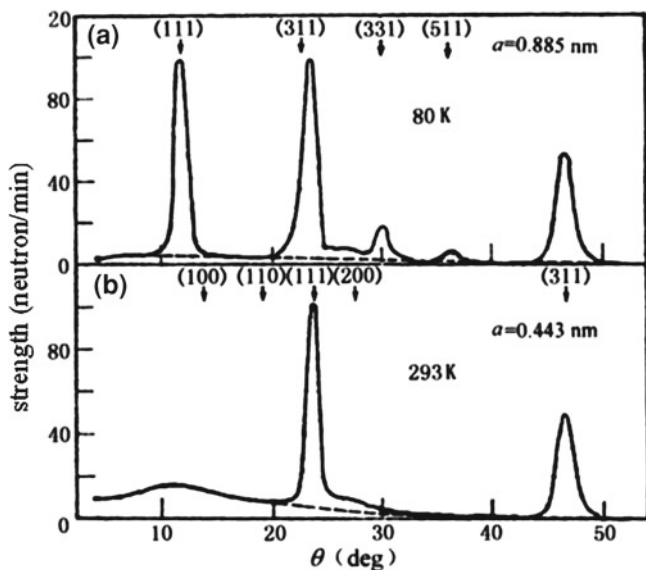
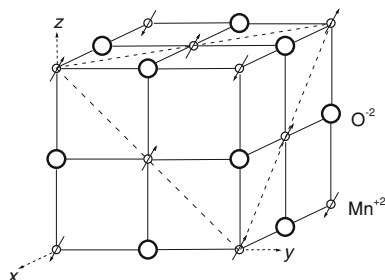


Fig. 3.10 Neutron diffraction patterns of polycrystalline MnO ($T_N = 118$ K) at 80 K and 293 K [6]

It is anti-ferromagnetic of helical magnetic structure in the temperature range of $20 \sim 132$ K. In each (001) layer the spins of the ions are aligned parallel in a direction parallel to the (001) plane. The direction rotates as the layer shifts along the c axis [4] (Fig. 3.11). Such a magnetic structure gives rise to small magnetic satellites on two sides of the diffraction peaks diffracted by nuclei.

Below 20 K Ho becomes ferromagnetism of helical magnetic structure. The ferromagnetism arises from the tilting of all magnetic moments of the helical anti-ferromagnetic structure toward the c axis direction by a certain angle. Thus the magnetic moments are aligned only partially.

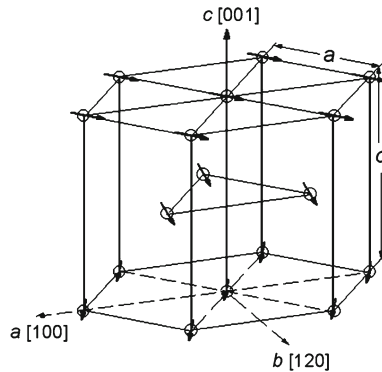


Fig. 3.11 The hcp crystal structure and helical anti-ferromagnetic magnetic structure of Ho metal

3.3.4 Magnetic Structures of Spinel Ferrites

Spinel ferrite has a cubic crystal structure. A crystal cell encompasses eight $\text{MO} \cdot \text{Fe}_2\text{O}_3$ (M: Mn, Fe, Co, Ni, Cu, Zn, etc) formula ions. The cell consists of eight cubic octants of dimension $a/2$. In an octant four O^{2-} of larger ion radius ($\sim 0.13 \text{ nm}$) occupy the same symmetrical sites of $(1/8, 1/8, 1/8)$, $(3/8, 3/8, 1/8)$, $(1/8, 3/8, 3/8)$, and $(3/8, 1/8, 3/8)$ (the three ratios in each parenthesis are approximate values of the coordinates x, y, z in lattice constant a unit) or their translations by $(0, 0, 1/2)$, $(1/2, 0, z)$, $(0, 1/2, z)$, or $(1/2, 1/2, z)$ ($z = 0$ or $1/2$). The O^{2-} ions constitute a fcc crystal lattice of lattice constant $a/2$ parallel to the spinel ferrite crystal structure. The body center of each blank octant separated by four shaded octants in Fig. 3.12b is occupied by a small ion radius ($\sim 0.08 \text{ nm}$) M or Fe metal ion. The site is the center of the tetrahedron constituted by the edges connecting the four O^{2-} ions in the octant, which is called the tetrahedral site or A site (position A in Fig. 3.12a). The eight vertexes and six face centers of a spinel cell are the occupied A sites. In each shaded octant the symmetrical sites with respect to the four O^{2-} ions such as $(1/8, 1/8, 3/8)$, $(3/8, 3/8, 3/8)$, $(1/8, 3/8, 1/8)$, and $(3/8, 1/8, 1/8)$ are occupied by four M or Fe ions, which along with the four O^{2-} ions in the same octant constitute smaller cubes of dimension $a/4$ parallel to the cell. Each of the M or Fe site is the center of the octahedron constituted by the edges connecting the six neighbor O^{2-} ions, which is called octahedral site or B site (position B in Fig. 3.12a). Eight A sites and sixteen B sites are occupied in a cell.

The molecular formula $\text{MO} \cdot \text{Fe}_2\text{O}_3$ can be written as $\text{Fe}_\alpha^{+3} \text{M}_{1-\alpha}^{+2} [\text{Fe}_{2-\alpha}^{+3} \text{M}_\alpha^{+2}] \text{O}_4$, which represents that the metal ions listed outside and inside the bracket occupy A site and B site, respectively. $\alpha = 0$ (normal spinel) for M = Cd and Zn, while $\alpha = 1$ (inversed spinel) for the other metal ions on the whole. The magnetic moments of the A and B sublattices are coupled antiparallel. The 3d ion magnetic polarization moment is in general approximately $2S$. That is, the moment of $\text{Fe}^{+3}(3d^5)$ ion is equal to 5 and that of $\text{M}^{+2}(3d^n)$ is n if $n < 5$ and $(10-n)$ if $n > 5$. Thus the magnetic

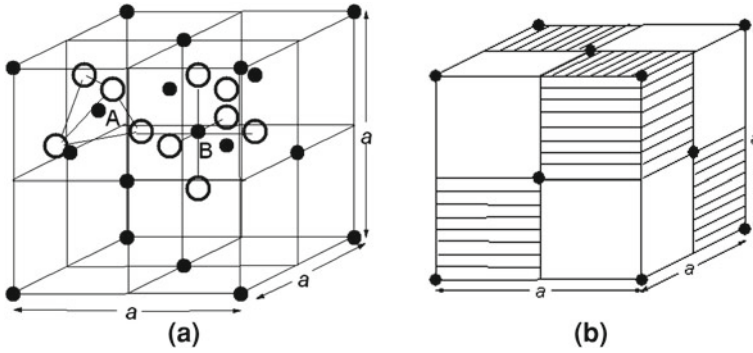


Fig. 3.12 Crystal structure of spinel ferrite. Black circle:M, Fe; white circle:O⁻²

polarization moment of $\text{Fe}_\alpha^{+3}\text{M}_{1-\alpha}^{+2} [\text{Fe}_{2-\alpha}^{+3}\text{M}_\alpha^{+2}]\text{O}_4$ is

$$\begin{aligned} p_J &= [5(2 - \alpha) + p_J(M^{+2})\alpha] - [5\alpha + p_J(M^{+2})(1 - \alpha)] \\ &= 10(1 - \alpha) + p_J(M^{+2})(2\alpha - 1). \end{aligned} \quad (3.12)$$

$\text{Fe}_3\text{O}_4 = \text{FeO} \cdot \text{Fe}_2\text{O}_3$, called magnetite, is half-metallic above Verwey transition (metal-insulator transition) temperature of $T_V = 120$ K. Upon cooling to below T_V occurs the order-disorder transformation of distribution of the Fe^{+3} and Fe^{+2} ions at the B site along with distortion of the cubic crystal structure to rhombohedral structure accompanied by sharp increase in electric resistance.

In the non-stoichiometric magnetite vacancies, denoted by N below, are normally located at the B site and the formula $\text{Fe}_{3-\delta}\text{O}_4$ can be written as $\text{Fe}^{+3}[\text{Fe}_{1+2\delta}^{+3}\text{Fe}_{1-3\delta}^{+2}\text{N}\delta]\text{O}_4$. T_V decreases with increase of δ .

$\gamma - \text{Fe}_2\text{O}_3 = 3/4\{\text{Fe}^{+3}[\text{Fe}_{5/3}^{+3}\text{N}_{1/3}]\text{O}_4\}$ has the similar to Fe_3O_4 crystal structure but without Fe^{+2} ion and is insulating. It is metastable and converts into $\alpha - \text{Fe}_2\text{O}_3$ if heated above 400°C.

Table 3.1 presents the calculated and experimental values of magnetic polarization moments of some spinels.

In $\text{CoO} \cdot \text{Fe}_2\text{O}_3$ a not very small orbital magnetic moment of the Co ion also contributes to the magnetic moment of the ion (Sect. 5.2.3.2) causing the experimental value of p_J markedly larger than that of the calculation.

3.3.5 Magnetic Structure of Ba(Sr) Ferrites

The cell encompasses two chemical formula ions of $\text{MO} \cdot 6\text{Fe}_2\text{O}_3$ ($\text{M} = \text{Ba}, \text{Sr}, \text{Pb}$). The radii 0.13~0.14 nm of the M^{+2} ions being close with ~ 0.13 nm of O^{-2} ion, they jointly construct an hcp lattice. There are 12 crystal layers along the c axis,

Table 3.1 The values of magnetic polarization moment of typical spinels

MO·Fe ₂ O ₃	2S(M ⁺²)	<i>p_J</i> cal.	exp. [7]
MnO·Fe ₂ O ₃ = Fe ⁺³ [Fe ⁺³ Mn ⁺²]O ₄	5(Mn ⁺²)	5	4.6
Fe ₃ O ₄ = Fe ⁺³ [Fe ⁺³ Fe ⁺²]O ₄	4(Fe ⁺²)	4	4.1
CoO·Fe ₂ O ₃ = Fe ⁺³ [Fe ⁺³ Co ⁺²]O ₄	3(Co ⁺²)	3	3.9
NiO·Fe ₂ O ₃ = Fe ⁺³ [Fe ⁺³ Ni ⁺²]O ₄	2(Ni ⁺²)	2	2.3
γ-Fe ₂ O ₃ = 3/4{Fe ⁺³ [Fe ⁺³ Ni ⁺²] _{5/3} }O ₄	5(Fe ⁺³)	2.5	2.3
(Mn _{1-α} Zn _α)O·Fe ₂ O ₃ = Fe ⁺³ _{1-α} Zn ⁺² _α [Fe ⁺³ _{1+α} Mn ⁺² _{1-α}]O ₄	0(Zn ⁺²)	5(1+α)	
(Ni _{1-α} Zn _α) O·Fe ₂ O ₃ = Fe ⁺³ _{1-α} Zn ⁺² _α [Fe ⁺³ _{1+α} Ni ⁺² _{1-α}]O ₄		2+8α	

Table 3.2 Distribution of Fe⁺³ ions of MO·6Fe₂O₃ on five crystallographic sites and their magnetic moment directions

Crystallographic site	Site number/f.u.	Magnetic moment direction
f ₁ Tetrahedral	2	↓
b Heptahedraltrigonal bipyramidal	1	↑
k Octahedral	6	↑
f ₂	2	↓
a	1	↑

among which 4 layers contain only O⁻² ions, 2 contain O⁻² and M⁺² ions, 4 contain O⁻² and Fe⁺² ions, and 2 contain only Fe⁺³ ions. Figure 3.13a shows the crystal structure of the lower 1 (*z* = 0) to 7 (*z* = 0.5 in lattice constant *c* unit) layers. The structure of the upper 8 to 13 layers is the reflection of the lower 1 to 6 layers upon the 7 layer followed by a rotation about the *c* axis by angle π . Between the two M⁺² ion containing layers is the spinel ferrite crystal structure of Fe₃O₄ with the [111] axis parallel to the *c* axis. Fe⁺³ ions occupy five crystal sites of a, b, f₁, f₂, and k. The f₁ and a are the tetrahedral and octahedral site neighboring environments which are the same as those of spinel ferrite.

The f₂ and k are octahedral sites, and the b trigonal bipyramidal site on the layer containing M⁺² ion. The magnetic moments of different Fe⁺³ sublattices are coupled parallel or antiparallel to the *c* axis. Table 3.2 presents the number of the Fe⁺³ ions and the magnetic moment direction on each site.

The magnetic polarization moment of the ferrite is

$$p_J = 5(1 + 6 + 1 - 2 - 2) = 20. \quad (2S(\text{Fe}^{+3}(3d^5)) = 5) \quad (3.13)$$

The experimental value for the ferrite of M = Ba, Pb, and Sr is 20, 18.6, and 20.6, respectively [7].

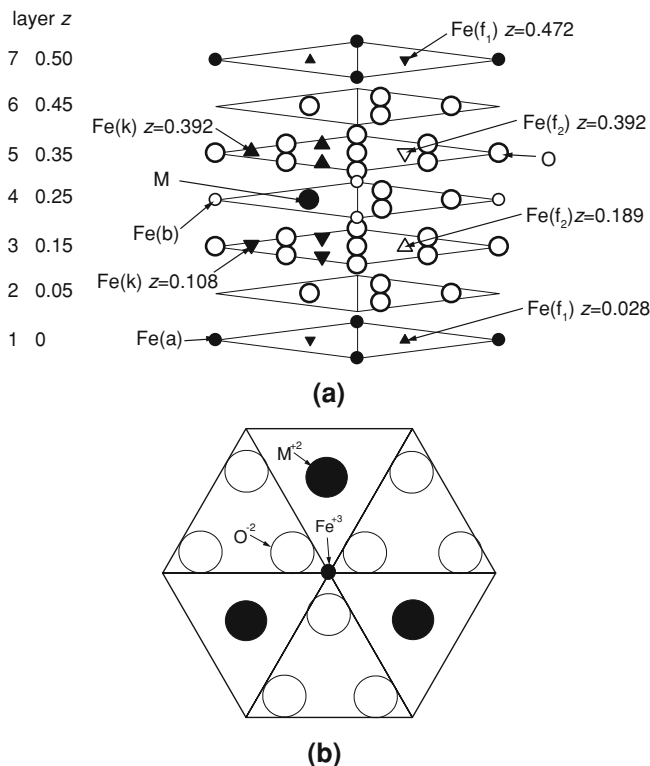


Fig. 3.13 Crystal structure of half cell of $\text{MO} \cdot 6\text{Fe}_2\text{O}_3$ (a) and neighbors of b site on the c plane (b). The nearest neighbors of b site are three O^{-2} ions on the c plane and two O^{-2} ion above and below on the c axis

3.3.6 Magnetic Structures of Rare Earth Iron Garnets

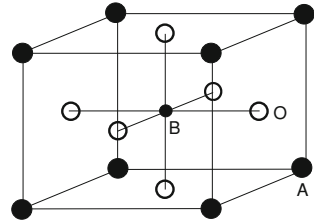
Rare earth iron garnets have a complicated cubic crystal structure encompassing four $(3\text{R}_2\text{O}_3)^c(2\text{Fe}_2\text{O}_3)^a(3\text{Fe}_2\text{O}_3)^d$ (R : rare earth or Y) formula ions in a cell. The superscripts c , a , and d in the formula refer to the lattice sites of the cations in corresponding parenthesis. The $c\text{-R}^{+3}$ ion is surrounded by eight O^{-2} ions forming a dodecahedron, $a\text{-Fe}^{+3}$ ion by six O^{-2} ions forming an octahedron, and $d\text{-Fe}^{+3}$ ion by four O^{-2} ions forming a tetrahedron. The magnetic moments of the $c\text{-R}^{+3}$ of light rare earth and $a\text{-Fe}^{+3}$ ions are parallel, which are antiparallel to those of $d\text{-Fe}^{+3}$ ions. Therefore, the magnetic polarization of the garnet is

$$p_J = [6p_J(R^{+3}) + 5 \times 4] - 5 \times 6 = 6g_J J(R^{+3}) - 10. \quad (3.14)$$

Table 3.3 Magnetic polarization moments of $3R_2O_3 \cdot 5Fe_2O_3$

R	Y	La	Pr	Nd	Sm	Eu	Gd
Cal.	10	10	9.2	9.6	5.7	10	32
Exp. [7]	10	10	9.8	8.7	5.5	5.6	32

Fig. 3.14 Perovskite structure



Spin canting appears for heavy rare earth giving rise to a significant reduction of the magnetic moments of $c\text{-}R^{+3}$ ions [8]. Table 3.3 compares the values of p_J of light rare earth iron garnets calculated by (3.14) with experiments.

3.3.7 Magnetic Structures of Perovskite Ferrites

Ideal crystal structure of Perovskite ferrite ABO_3 ($A = Y^{+3}$, rare earth, Ca^{+2} , Sr^{+2} , $Ba^{+2} \dots$; $B^{+3} = 3d$ metal ions) is cubic (Fig. 3.14). The symmetry is distorted to orthorhombic, tetragonal, or rhombohedral in many compounds. The magnetic structure depends on the composition.

Examples: $La^{+3}(4f^0)$ has no magnetic moment. $LaMO_3$ ($M = Mn, Fe, Cr$) are slightly distorted to orthorhombic and are anti-ferromagnetic. In $LaMnO_3$ ($T_N = 100$ K) the magnetic moments of $Mn^{+3}(3d^4)$ are coupled parallel within a (001) layer which are coupled antiparallel with the neighbor layers (Fig. 3.15a). In $LaFeO_3$ ($T_N = 750$ K) or $LaCrO_3$ ($T_N = 320$ K) the nearest neighbor Fe^{+3} or Cr^{+3} are coupled antiparallel (Fig. 3.15b) [7]. Strictly speaking, the magnetic moments of the magnetic sublattices of opposite magnetic moment directions are not strictly antiparallel but are inclined by a small angle giving rise to a canted ferromagnetism [9–11].

$La_{1-x}Sr_xMnO_3$ ($Sr^{+2}(4f^6)$ has no magnetic moment) is anti-ferromagnetic and insulating in the composition range of $0 \leq x \leq 0.1$, which becomes ferromagnetic and metallic if x increases above 0.17. $La_{1/3}Sr_{2/3}FeO_3$ is weakly distorted to rhombohedral structure. Below 200 K, ferromagnetically ordered layers of Fe^{3+} and Fe^{5+} are arranged in sequence of $Fe^{5+}(\uparrow) Fe^{3+}(\uparrow) Fe^{3+}(\downarrow) Fe^{5+}(\downarrow) Fe^{3+}(\downarrow) Fe^{3+}(\uparrow) \dots$ along the $\langle 111 \rangle$ direction (Fig. 3.16). Figure 3.17 demonstrates the temperature dependences of the magnetic polarization moments of the Fe^{+3} and Fe^{+5} ions. In contrast to the cases of spinel, Ba(Sr) ferrites and garnets, the values of 3 and 1.4 at 0 K are apparently smaller than 5 and 3 of the spin moments $2S$ of free Fe^{+3} and

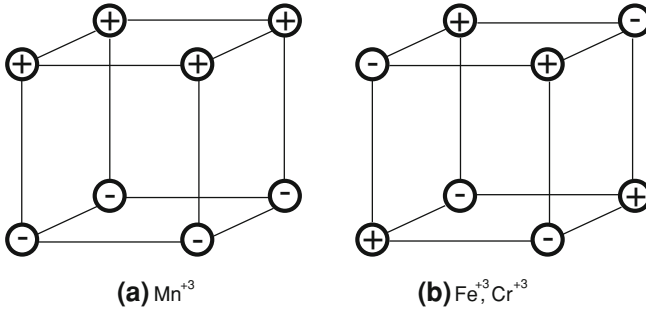
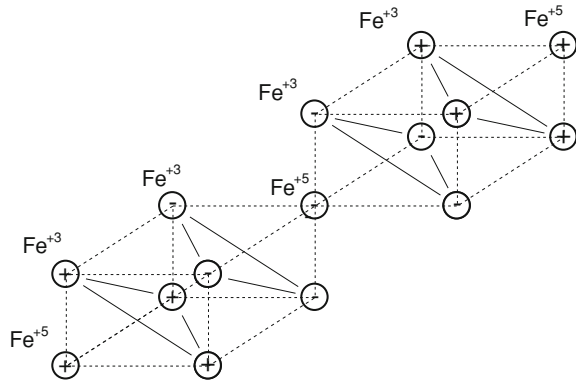


Fig. 3.15 Magnetic structures of LaMnO_3 (a) and LaFeO_3 and LaCrO_3 (b)

Fig. 3.16 Magnetic structure of $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$ [12]



Fe^{+5} ions. Strong crystalline electric field interactions give rise to the lower spin states (Sect. 3.9.6.6).

3.3.8 Magnetic Structure of Fe Metal

The magnetic polarization moment of 3d and 4s electrons of Fe measured by neutron diffraction is 2.39 and -0.21 , respectively. Figure 3.18 shows the space distribution of the magnetic moments. It can be seen that the negative magnetic moments of the 4s electrons are distributed on the ring regions distant from the 3d orbits.

Fig. 3.17 Temperature dependences of the magnetic polarization moments of Fe^{+3} and Fe^{+5} ions in $\text{La}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$ [12]

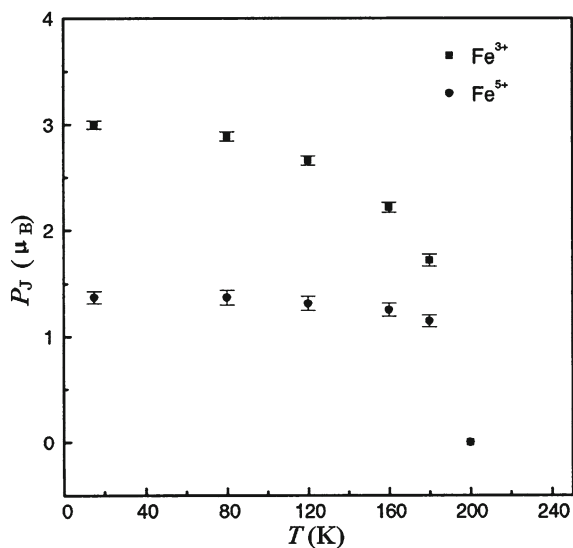
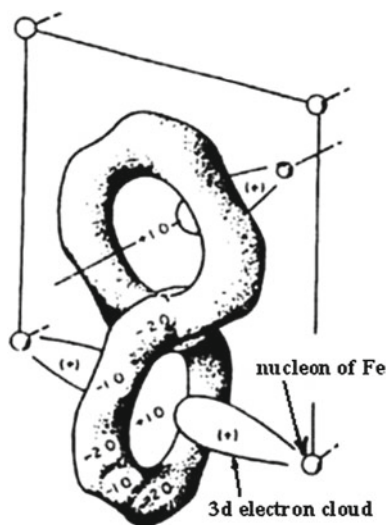


Fig. 3.18 Space distribution of 4s magnetic polarization (in 0.1 T unit) in bcc Fe metal [13]



3.4 Molecular Field Theory

3.4.1 Weiss's Molecular Field Theory

To explain the phenomena of ferromagnetism, Weiss (1907) proposed two hypotheses which were later proved correct. One is that a ferromagnetic body is constituted of

magnetic domains. Another is there exists a large internal molecular field $\vec{H}_{\text{ml}}$ in each domain which magnetizes the domain to saturation. The theory successfully explains the spontaneous magnetization, its temperature dependence, the magnetic transformation between ferromagnetism and paramagnetism, and the Curie–Weiss law of the paramagnetism. The theory is widely applied nowadays as before.

3.4.1.1 Magnetization as a Function of Magnetic Field Strength and Temperature

The theory is applicable to the single sublattice ferromagnetism. It assumes that

$$\vec{H}_{\text{ml}} = w\vec{M}. \quad (3.15)$$

$w(> 0)$ is called molecular field coefficient. The larger the magnetization M , smaller the potential energy $-w\mu_0 M^2$ of $\vec{M}$ in $\vec{H}_{\text{ml}}$, and hence the state of spontaneous saturation magnetization becomes stable. Assume that there are N magnetic atoms in a unit volume. In an applied magnetic field $\vec{H}$, $\vec{H}_{\text{ml}}$ is parallel to $\vec{H}$, and the magnetization in a combined field of $\vec{H}$ and $\vec{H}_{\text{ml}}$ is

$$M(T) = M_s(0)B_J(x), \quad (2.120) \quad (3.16)$$

$$x = \frac{gJ\mu_B(H + H_{\text{ml}})}{k_B T}. \quad (2.121) \quad (3.17)$$

Here,

$$M_s(0) = N \frac{gJ\mu_B}{\mu_0} \quad (3.18)$$

is the saturation magnetization of completely parallel aligned atomic magnetic moments at 0 K (2.98). Inserting (3.15) into (3.17) and rearranging the latter we get

$$\frac{M(T)}{M_s(0)} = \frac{\mu_0 k_B T}{Nw g^2 J^2 \mu_B^2} x - \frac{H}{w M_s(0)}. \quad (3.19)$$

3.4.1.2 Temperature Dependence of Spontaneous Magnetization

Consider the case of $H = 0$. The solution $M(T) = M_s(T)$ of simultaneous equations (3.16) and (3.19) is the spontaneous magnetization, which can be solved by graphic treatment as below. Figure 3.19 shows $M_s(T)/M_s(0)$ as a function of x . The curve is that of (3.16) and the straight lines those of (3.19) at three temperatures of $T < T_C$, $T = T_C$, and $T > T_C$.

Below a critical temperature T_C the line and curve intersect at the origin and point P. The origin is a non-magnetized state while P is a spontaneously magnetized state, and according to the preceding analysis the latter is the stable solution. When

Fig. 3.19 $M_s(T)/M_s(0)$ versus x

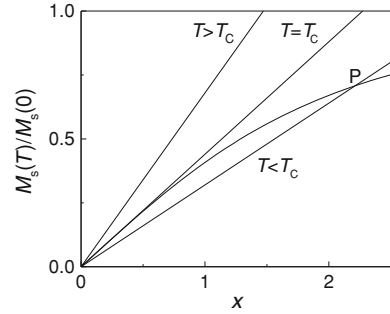
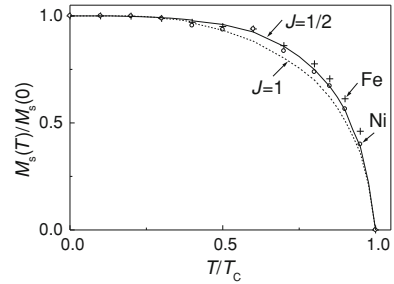


Fig. 3.20 $M_s(T)/M_s(0)$ versus T/T_C . Circles and criss-crosses exp. curves theory



T approaches zero, the slope of the straight line becomes very small and hence the abscissa $x(P)$ becoming infinite the ordinate $M_s(T)/M_s(0)$ approaches 1, that is, the atomic magnetic moments align completely parallel. With increase of T the slope of the straight line increases and hence $x(P)$ decreases causing decrease in $M_s(T)/M_s(0)$, that is, under increasingly large thermal disturbance the value of spontaneous magnetization decreases. When T increases to T_C , the slope of the straight line becomes that of the curve at the origin:

$$\frac{\mu_0 k_B T_C}{N w g_J^2 J^2 \mu_B^2} = \frac{J+1}{3J}, \quad (2.123) \quad (3.20)$$

and both $x(P)$ and $M_s(T)/M_s(0)$ become zero, that is, the spontaneous magnetization disappears. At a higher temperature, the slope of the straight line is larger than that of the curve at the origin the spontaneous magnetization remaining zero. Apparently T_C is the Curie temperature. From (3.20) we get

$$T_C = \frac{N w g_J^2 J(J+1) \mu_B^2}{3 \mu_0 k_B}. \quad (3.21)$$

Figure 3.20 compares the theoretical T/T_C dependences of $M_s(T)/M_s(0)$ for $J = 1/2$ and 1 with experimental data of Fe and Ni metals. The curve of $J = 1/2$ coincides with the experiments fairly well.

Table 3.4 The values of $M_s(0)$, T_C , θ_C , C [14], and $wM_s(0) = T_C M_s(0)/C$ for metals of Fe, Co, and Ni

Metal	$M_s(0)/(10^6 \text{ A/m})$	T_C/K	θ_C/K	C/K	$wM_s(0)/(10^9 \text{ A/m})$
Fe	1.74	1043	1101	0.1784	10.2
Co	1.43	1398	1428	0.1830	10.9
Ni	0.51	631	650	0.0485	6.6

3.4.1.3 Curie–Weiss Law

The maximum magnetic field available at usual laboratories is around $2 \times 10^6 \text{ A/m}$ which is three orders smaller than the molecular fields of metals of Fe, Co, and Ni at low temperatures (Table 3.4). Therefore, the effect of magnetic field on the saturation magnetization is very small except near T_C .

Above Curie temperature, (3.16) can be simplified to

$$\frac{M(T)}{N \frac{g_J J \mu_B}{\mu_0}} = \frac{g_J J \mu_B [H + wM(T)]}{k_B T} \frac{J+1}{3J}, \quad ((2.123), (3.17)–(3.18)) \quad (3.22)$$

from which we get the Curie–Weiss law

$$\chi = \frac{M}{H} = \frac{C}{T - T_C}, \quad (3.23)$$

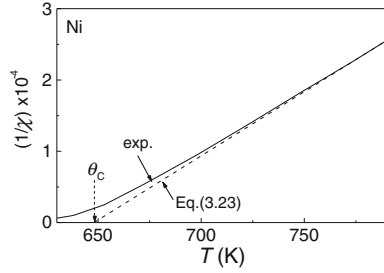
$$C = \frac{T_C}{w} = \frac{N g_J^2 J(J+1) \mu_B^2}{3 \mu_0 k_B}. \quad (3.24)$$

The Curie constant C is independent of w and is the same as that of non-interacting atoms (2.126). The $1/\chi$ versus T linear relation of (3.23) is verified by experiments (Fig. 3.21), but deviation is apparent near T_C . By prolonging the linear section down to the abscissa we get paramagnetic Curie temperature θ_C . θ_C does not coincide with T_C expected by (3.23) but is slightly higher. This result reveals that the molecular field model is not very precise. Table 3.4 shows the experimental values of $M_s(0)$, T_C , θ_C , C , and $wM_s(0) = T_C M_s(0)/C$ (3.24) for metals of Fe, Co, and Ni.

3.4.2 Néel's Molecular Field Theory

Different from metals of single magnetic sublattice, ferrites, rare earth 3d metal compounds, etc encompass two or more magnetic sublattices.

Fig. 3.21 $1/\chi$ versus temperature for Ni metal. Dashed line theory; full curve exp



3.4.2.1 Magnetization as a Function of Magnetic Field Strength and Temperature

Consider a magnetic medium encompassing two magnetic sublattices T and R. Let M_T and M_R denote the magnetization of T and R sublattices, $\alpha_T w$ and w the molecular field coefficient of the molecular field produced by the T sublattice and acting on a T and R ions, respectively, and w and $\alpha_R w$ the molecular field coefficient of the molecular field produced by the R sublattice acting on the T and R ion, respectively. Since the exchange interaction between T and R sublattices can be formulated as the potential energy of the magnetic moment of T sublattice in the molecular field produced by the R sublattice as well as the potential energy of the magnetic moment of R sublattice in the molecular field produced by the T sublattice, the molecular field coefficient of the molecular field produced by the R sublattice and acting on a T ion w is the same as the molecular field coefficient of the molecular field produced by the R sublattice and acting on the T ion. The total molecular fields acting on a T and R ion H_T and H_R are

$$H_T = w(\alpha_T M_T + M_R), \quad (3.25)$$

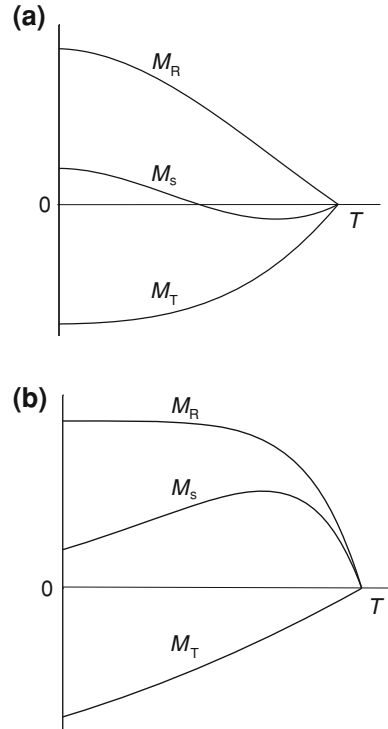
$$H_R = w(M_T + \alpha_R M_R), \quad (3.26)$$

and the magnetization of the sublattices M_T and M_R in an applied magnetic field H are

$$M_T = N_T \frac{g J_T J_T \mu_B}{\mu_0} B_{J_T} \left[\frac{g J_T J_T \mu_B (H + H_T)}{k_B T} \right], \quad ((2.120), (2.121)) \quad (3.27)$$

$$M_R = N_R \frac{g J_R J_R \mu_B}{\mu_0} B_{J_R} \left[\frac{g J_R J_R \mu_B (H + H_R)}{k_B T} \right]. \quad (N_R: \text{number of R ions in a unit volume}) \quad (3.28)$$

Fig. 3.22 The $M_s(T)$, $M_T(T)$ and $M_R(T)$ curves



3.4.2.2 Temperature Dependence of Spontaneous Magnetization

Consider the case of $H = 0$. The temperature dependences of the spontaneous magnetizations M_T , M_R , and $M_s = M_R + M_T$ can be obtained by numerically solving (3.25)–(3.28). Depending on the values of N_T , N_R , g_{J_T} , g_{J_R} , J_T , J_R , w , α_T , and α_R , we can get different shape $M_s(T)$ curves. Such curves can be classified to the following three types: With increase of temperature from 0 K

- ① M_s decreases monotonically to zero at T_C or T_N ;
- ② M_s decreases to a negative minimum crossing the abscissa (the temperature of the intersection is called compensation temperature), and then increases to zero at T_N (Fig. 3.22(a)). Apparently the sign of M_T is opposite to that of M_R , and the medium is ferrimagnetic;
- ③ M_s increases to a maximum, and then decreases to zero at T_N (Fig. 3.22b). The signs of M_T and M_R are opposite, and the medium is also ferrimagnetic.

3.4.2.3 Temperature Dependence of Paramagnetic Susceptibility

At high temperature range above the magnetic transformation temperature (3.27) and (3.28) simplify to

$$M_T = \frac{C_T}{T} [H + w(\alpha M_T + M_R)], \quad C_T = \frac{N_T g J_T J_T (J_T + 1) \mu_B^2}{3 \mu_0 k_B},$$

((2.125)–(2.126)) (3.29)

$$M_R = \frac{C_R}{T} [H + w(M_T + \beta M_R)], \quad C_R = \frac{N_R g J_R J_R (J_R + 1) \mu_B^2}{3 \mu_0 k_B}. \quad (3.30)$$

From the above equations we get

$$\frac{1}{\chi} = \frac{H}{M_T + M_R} = \frac{T^2 - T w (C_T \alpha_T + C_R \alpha_R) - C_T C_R w^2 (1 - \alpha_T \alpha_R)}{T (C_T + C_R) + C_T C_R w (2 - \alpha_T - \alpha_R)}. \quad (3.31)$$

The numerator of (3.31) becomes zero at the magnetic transformation temperature $T_N(\chi \rightarrow \infty)$:

$$T_N^2 - T_N w (C_T \alpha_T + C_R \alpha_R) - C_T C_R w^2 (1 - \alpha_T \alpha_R) = 0. \quad (3.32)$$

If R is nonmagnetic, $C_R = 0$ and the magnetic transformation temperature T_T is

$$T_T = w \alpha_T C_T. \quad (3.33)$$

If T is nonmagnetic, $C_T = 0$ and the magnetic transformation temperature T_R is

$$T_R = w \alpha_R C_R. \quad (3.34)$$

If $\alpha_T = \alpha_R = 0$ and $w \neq 0$, the magnetic transformation temperature T_{TR} is

$$T_{TR}^2 = C_T C_R w^2. \quad (3.35)$$

Inserting (3.33)–(3.35) into (3.32) we get

$$T_N^2 - T_N (T_T + T_R) - (T_{TR}^2 - T_T T_R) = 0, \quad (3.36)$$

$$T_N = \frac{1}{2} [T_T + T_R + \sqrt{(T_T - T_R)^2 + 4 T_{TR}^2}]. \quad (3.37)$$

3.4.3 Origin of Molecular Field

The largest value of magnetic field produced by magnetic moments is three orders smaller than molecular field (Table 3.4) and cannot explain the molecular field.

The orbital angular momentum of 3d transition metal atom is quenched (Sect. 3.6.5). Thereby the orbital magnetic moment is very small and the atomic magnetic moment is mostly from the electron spins and $\vec{p}_J \approx -2\vec{S}\mu_B$. Consider the simple case of the single sublattice magnetic medium. If the exchange integral of nearest neighbor atoms J_A is positive, the spins are put in ferromagnetic order. Consider the exchange interaction of an atom with z nearest neighbor atoms apart a from the atom as the potential energy of the atomic magnetic moment in a molecular field H_{ml} . The order of magnitude of J_A being that of $e^2/4\pi\epsilon_0 a$ (2.178) it holds

$$-2\vec{S} \cdot \langle \vec{S} \rangle z J_A \approx -2\vec{S} \cdot \langle \vec{S} \rangle z \frac{e^2}{4\pi\epsilon_0 a} = 2\vec{S} \mu_B \cdot \vec{H}_{ml},$$

(Equation(2.189), $\langle \vec{S} \rangle$: average spin of z nearest neighbor atoms) (3.38)

$$\vec{H}_{ml} \approx \frac{-e^2 z \langle \vec{S} \rangle}{4\pi\epsilon_0 a \mu_B}. \quad (3.39)$$

Inserting typical experimental values of the parameters into the right-hand side of the above equation we get

$$H_{ml} \sim 10^9\text{--}10^{10} (\text{A/m}). \quad (3.40)$$

The order of the H_{ml} coincides with those of the experimental $wM_s(0)$ values (Table 3.4). Moreover, (3.39) coincides with the fundamental hypothesis of molecular field theory (3.15) that the molecular field is in the direction of the magnetization vector $\vec{M} (\propto -\vec{S})$ and the value is proportional to the value of $\vec{M}$. From above it can be concluded that the molecular field originates from the exchange interactions arising from electrical Coulomb interaction.

J_A being proportional to w (3.38) it is proportional to T_C (3.24).

3.5 Spin Wave

Although Weiss's molecular field theory achieved great success and its fundamental relation of (3.15) is deduced through the average treatment of exchange interaction, apparent deviation of the theory from experiments is obvious. One is the susceptibility versus temperature near T_C (Fig. 3.21). Another is spontaneous magnetization versus temperature near 0 K.

According to the theory it is

$$\frac{M_s(T)}{M_s(0)} = 1 - \frac{1}{J} \exp\left(-\frac{3}{J+1} \frac{T_C}{T}\right), \quad (\text{Note 1 of this section}) \quad (3.41)$$

which is not in accordance with the experimental $T^{3/2}$ law

$$\frac{M_s(T)}{M_s(0)} = 1 - bT^{\frac{3}{2}}. \quad (b = \text{const.}) \quad (3.42)$$

The deviation arises from its average approximation of the fundamental relation of (3.15). Bloch (1930) deduced the $T^{3/2}$ law by rigorously solving the Schrödinger equation of exchange Hamiltonian.

3.5.1 Spin Wave

Consider a unit volume cube of the edges parallel to the $\langle 100 \rangle$ axes of the cubic crystal which contains N magnetic atoms. Each atom has a magnetic electron on the same orbit and exchange interacts with the z nearest neighbor atoms with positive exchange integral J_A . The exchange Hamiltonian of the spin system is

$$\hat{H}_{\text{ex}} = -\frac{1}{2} \sum_{\vec{i}}^{\vec{1}, \vec{2}, \dots, \vec{N}} \sum_{\vec{\rho}}^{z(\vec{i})} 2J_A \hat{s}_{\vec{i}} \cdot \hat{s}_{\vec{\rho}} = -J_A \sum_{\vec{i}}^{\vec{1}, \vec{2}, \dots, \vec{N}} \sum_{\vec{\rho}}^{z(\vec{i})} \left[\hat{s}_{z\vec{i}} \hat{s}_{z\vec{\rho}} + \frac{1}{2} (\hat{s}_{+\vec{i}} \hat{s}_{-\vec{\rho}} + \hat{s}_{-\vec{i}} \hat{s}_{+\vec{\rho}}) \right], \quad (2.189) \quad (3.43)$$

where the sum $\frac{1}{2} \sum_{\vec{i}}^{\vec{1}, \vec{2}, \dots, \vec{N}} \sum_{\vec{\rho}}^{z(\vec{i})}$ is over all pairs of nearest neighbors in which $\sum_{\vec{\rho}}^{z(\vec{i})}$ is the sum over the z nearest neighbors of lattice point $\vec{i}$. Assume that the periodical boundary conditions hold on the surface of the cube. Let

$$\alpha \equiv \chi_+, \quad \beta \equiv \chi_-, \quad (3.44)$$

then

$$\hat{s}_z \alpha = \frac{1}{2} \alpha, \quad \hat{s}_z \beta = -\frac{1}{2} \beta, \quad \hat{s}_- \alpha = \beta, \quad \hat{s}_+ \beta = \alpha, \quad \hat{s}_+ \alpha = \hat{s}_- \beta = 0. \quad (\text{Sect. 2.1.1}) \quad (3.45)$$

At the ground state all spins are parallel, and the eigenstate and eigenenergy are

$$|g\rangle \equiv \alpha_{\vec{1}} \alpha_{\vec{2}} \cdots \alpha_{\vec{N}}, \quad (3.46)$$

$$E_g = \langle g | \hat{H}_{\text{ex}} | g \rangle = -J_A \left\langle g \left| \sum_{\vec{i}}^{\vec{1}, \vec{2}, \dots, \vec{N}} \sum_{\vec{\rho}}^{z(\vec{i})} \hat{s}_{z\vec{i}} \hat{s}_{z\vec{\rho}} \right| g \right\rangle = -\frac{1}{4} N z J_A. \quad (3.47)$$

At a first excited state a spin is reversed. Let

$$|\vec{l}\rangle \equiv \alpha_1 \alpha_2 \cdots \alpha_{\vec{l}} \beta_{\vec{l}} \alpha_{\vec{l}'} \cdots \alpha_{\vec{N}} \quad (3.48)$$

denote the state in which the spin at $\vec{l}$ is reversed. The spin reversed state spreads out to the surroundings through exchange interactions keeping the energy of the system unchanged, thus $|\vec{l}\rangle$ is not an eigenstate. In fact exploiting the relations of

$$\sum_{\vec{i}} \sum_{\vec{\rho}}^{\vec{1}, \vec{2}, \dots, \vec{N}} \hat{s}_{z\vec{i}} \hat{s}_{z\vec{\rho}} |\vec{l}\rangle = \left[(Nz - 2z) \frac{1}{4} - 2z \frac{1}{4} \right] |\vec{l}\rangle = \frac{1}{4} (N - 4) z |\vec{l}\rangle, \quad (3.49)$$

$$\sum_{\vec{i}}^{\vec{1}, \vec{2}, \dots, \vec{N}} \sum_{\vec{\rho}} \hat{s}_{-\vec{i}} \hat{s}_{+\vec{\rho}} |\vec{l}\rangle = \sum_{\vec{\rho}} \hat{s}_{-\vec{\rho}} |g\rangle = \sum_{\vec{\rho}} |\vec{\rho}\rangle, \quad (3.50)$$

$$\sum_{\vec{i}}^{\vec{1}, \vec{2}, \dots, \vec{N}} \sum_{\vec{\rho}} \hat{s}_{+\vec{i}} \hat{s}_{-\vec{\rho}} |\vec{l}\rangle = \sum_{\vec{\rho}} \hat{s}_{-\vec{\rho}} |g\rangle = \sum_{\vec{\rho}} |\vec{\rho}\rangle, \quad (3.51)$$

we get

$$\hat{H}_{\text{ex}} |\vec{l}\rangle = -J_A \left(\frac{1}{4} N - 1 \right) z |\vec{l}\rangle - J_A \sum_{\vec{\rho}} |\vec{\rho}\rangle. \quad (3.52)$$

Consider the Fourier expansion of $|\vec{l}\rangle$

$$|\vec{l}\rangle = \frac{1}{\sqrt{N}} \sum_{\vec{k}} \exp(-i\vec{k} \cdot \vec{l}) |\vec{k}\rangle. \quad (3.53)$$

Under the periodical boundary conditions of

$$\begin{aligned} |\vec{l}\rangle &= |\vec{l} + \vec{e}_\alpha\rangle \quad (\vec{e}_\alpha: \text{unit vector in the } \alpha \text{ direction, } \alpha = x, y, z) \\ &= \frac{1}{\sqrt{N}} \sum_{\vec{k}} \exp(-i\vec{k} \cdot \vec{l}) |\vec{k}\rangle = \frac{1}{\sqrt{N}} \sum_{\vec{k}} \exp[-i\vec{k} \cdot (\vec{l} + \vec{e}_\alpha)] |\vec{k}\rangle, \end{aligned} \quad (3.54)$$

$\vec{k}$ takes the values of

$$\vec{k} = 2\pi \sum_{\alpha}^{x, y, z} \nu_\alpha \vec{e}_\alpha. \quad (\nu_\alpha: \text{integer; } \vec{e}_\alpha: \text{unit vector in the } \alpha \text{ direction}) \quad (3.55)$$

By inserting (3.53) into (3.52) we get

$$\begin{aligned}
\hat{H}_{\text{ex}}|\vec{l}\rangle &= \hat{H}_{\text{ex}} \frac{1}{\sqrt{N}} \sum_{\vec{k}} \exp(-i\vec{k}\cdot\vec{l})|\vec{k}\rangle = -J_A \left(\frac{1}{4}N - 1\right) z|\vec{l}\rangle - J_A \sum_{\vec{\rho}}^{z(\vec{l})} |\vec{\rho}\rangle \\
&= -J_A \left(\frac{1}{4}N - 1\right) z \frac{1}{\sqrt{N}} \sum_{\vec{k}} \exp(-i\vec{k}\cdot\vec{l})|\vec{k}\rangle \\
&\quad - J_A \sum_{\vec{\rho}}^{z(\vec{l})} \frac{1}{\sqrt{N}} \sum_{\vec{k}} \exp[-i\vec{k}\cdot(\vec{l} + \vec{\rho} - \vec{l})]|\vec{k}\rangle.
\end{aligned} \tag{3.56}$$

The above equation shows that

$$\hat{H}_{\text{ex}}|\vec{k}\rangle = J_A \left[-\frac{1}{4}Nz + z(1 - \tau_{\vec{k}}) \right] |\vec{k}\rangle, \tag{3.57}$$

$$\tau_{\vec{k}} \equiv \frac{1}{z} \sum_{\vec{\rho}}^{z(\vec{l})} \exp[-i\vec{k}\cdot(\vec{\rho} - \vec{l})], \tag{3.58}$$

that is, the first excited eigenstate and its eigenenergy are

$$|\vec{k}\rangle = \frac{1}{\sqrt{N}} \sum_{\vec{l}} \exp(i\vec{k}\cdot\vec{l})|\vec{l}\rangle, \tag{3.59}$$

$$E_1 = E_g + zJ_A(1 - \tau_{\vec{k}}). \tag{3.60}$$

Equation (3.59) shows that the probability of spin turnover is the same for every lattice point and the phase of neighbor point varies in order showing the characteristic of a wave. The state is called spin wave or magnon, and $\vec{k}$ is called the wave vector. The energy of a spin wave is the energy with respect to the energy of ground state

$$\varepsilon(k) = E_1 - E_g = zJ_A(1 - \tau_{\vec{k}}). \tag{3.61}$$

For simple cubic crystal $z=6$ and $\vec{\rho} - \vec{l} = \pm a\vec{e}_\alpha$ (a : lattice constant, $\alpha = x, y, z$),

$$\tau_{\vec{k}} = \frac{1}{3} [\cos(k_x a) + \cos(k_y a) + \cos(k_z a)], \tag{3.62}$$

and if $k_\alpha a \ll 1$,

$$\begin{aligned}
\varepsilon(k) &= 2J_A \{ [1 - \cos(k_x a)] + [1 - \cos(k_y a)] + [1 - \cos(k_z a)] \} \\
&\approx 2J_A \sum_{\alpha}^{x,y,z} \frac{1}{2} (k_\alpha a)^2 = J_A a^2 k^2.
\end{aligned} \tag{3.63}$$

In the same way the energies of a spin wave for fcc and bcc crystals are

$$\varepsilon(\vec{k}) = 4J_A \sum_{(\alpha,\beta)}^{(x,y),(y,z),(z,x)} \left[1 - \cos\left(k_\alpha \frac{a}{2}\right) \cos\left(k_\beta \frac{a}{2}\right) \right] \approx J_A k^2 a^2, \quad (3.64)$$

$$\varepsilon(\vec{k}) = 8J_A \left[1 - \cos\left(k_x \frac{a}{2}\right) \cos\left(k_y \frac{a}{2}\right) \cos\left(k_z \frac{a}{2}\right) \right] \approx J_A k^2 a^2. \quad (3.65)$$

3.5.2 Quasiclassical Picture of Spin Wave

Consider a one-dimensional spin lattice of lattice constant a and $N = 1/a$ spins in a unit length. The periodical boundary conditions hold. The exchange interaction of the n^{th} spin with the two neighbor spins is

$$\hat{H}_{\text{ex}} = -2J_A \hat{S}_n \cdot (\hat{S}_{n-1} + \hat{S}_{n+1}). \quad (n = 1, 2, \dots, N) \quad (3.66)$$

The energy can be considered as the potential energy of the classic spin magnetic polarization moment $-2\mu_B \vec{S}_n$ in the effective magnetic field of

$$\vec{H}_{\text{ef}} = -\frac{J_A}{\mu_B} (\vec{S}_{n-1} + \vec{S}_{n+1}). \quad (3.67)$$

$\vec{S}_n$ makes precession about $\vec{H}_{\text{ef}}$ according to the equation of motion of the angular momentum

$$\hbar \frac{d\vec{S}_n}{dt} = 2J_A \vec{S}_n \times (\vec{S}_{n-1} + \vec{S}_{n+1}). \quad (3.68)$$

Suppose $\vec{S}_n = S^z \vec{e}_z + \sum_{\alpha}^{x,y} S_n^\alpha \vec{e}_{n\alpha}$, where S^z is the component of $\vec{S}_n$ in the spin lattice axis direction for all n and $S_n^x, S_n^y \ll S^z$. The relations of the components of (3.68) by neglecting square order terms of small quantities $\{S_n^x, S_n^y\}$ are

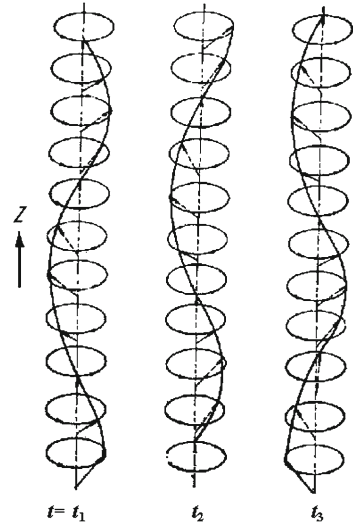
$$\begin{aligned} \hbar \frac{dS_n^x}{dt} &= -2J_A S^z (S_{n-1}^y - 2S_n^y + S_{n+1}^y), \\ \hbar \frac{dS_n^y}{dt} &= 2J_A S^z (S_{n-1}^x - 2S_n^x + S_{n+1}^x), \end{aligned} \quad (3.69)$$

which can be expressed by a single equation of

$$\hbar \frac{dS_n^+}{dt} = i2J_A S^z (S_{n-1}^+ - 2S_n^+ + S_{n+1}^+). \quad (S_n^+ \equiv S_n^x + iS_n^y) \quad (3.70)$$

The solution of the above equation has the form of

Fig. 3.23 Quasiclassical picture of spin wave [15]



$$S_n^+ = S_0^+ \exp[i(nka - \omega t)]. \quad (3.71)$$

Inserting (3.71) into (3.70) we get

$$\begin{aligned} \hbar\omega &= -2J_A S^z [\exp(-ika) - 2 + \exp(ika)] \\ &= 4J_A S^z [1 - \cos(ka)] = 8J_A S^z \sin^2\left(\frac{ka}{2}\right). \end{aligned} \quad (3.72)$$

Under the periodical boundary condition of

$$S_{n+N}^+ = S_n^+ \quad (3.73)$$

k takes the values of

$$k = 2\pi \times \text{integer}. \quad (3.74)$$

Figure 3.23 demonstrates a spin wave and its variation with time.

3.5.3 Bloch $T^{3/2}$ Law

At finite temperatures several spin waves are excited. If temperature is low, the number of spin waves N_s is much smaller than N , the possibility of contiguity of

reversed spins of different waves is very small, and each spin wave can be considered independent. In this case the energy of the waves is the sum of the energy of each wave,

$$E = \sum_{\vec{k}} n_{\vec{k}} \varepsilon(\vec{k}) \quad (3.75)$$

where $n_{\vec{k}}$ is the number of spin waves of wave vector $\vec{k}$.

The average number $\langle n_{\vec{k}} \rangle$ of spin wave of wave vector $\vec{k}$ and N_s are

$$\begin{aligned} \langle n_{\vec{k}} \rangle &= \frac{\sum_{n_{\vec{k}}=0,1,2,\dots} n_{\vec{k}} \exp(n_{\vec{k}} \xi)}{\sum_{n_{\vec{k}}=0,1,2,\dots} \exp(n_{\vec{k}} \xi)} \quad (\xi \equiv -\frac{\varepsilon(\vec{k})}{k_B T}) \\ &= \frac{d}{d\xi} \ln \left[\sum_{n_{\vec{k}}=0,1,2,\dots} \exp(n_{\vec{k}} \xi) \right] = \frac{d}{d\xi} \ln \frac{1}{1 - \exp \xi} = \frac{\exp \xi}{1 - \exp \xi} \\ &= \frac{1}{\exp \frac{J_A k^2 a^2}{k_B T} - 1}, \quad ((3.63)-(3.65)) \end{aligned} \quad (3.76)$$

$$\begin{aligned} N_s &= \sum_{\vec{k}} \langle n_{\vec{k}} \rangle = \frac{1}{(2\pi)^3} \int_0^\infty \frac{4\pi k^2 dk}{\exp \frac{J_A k^2 a^2}{k_B T} - 1} \\ &= \frac{1}{2\pi^2} \left(\frac{k_B T}{J_A a^2} \right)^{\frac{3}{2}} \int_0^\infty \frac{z^2 dz}{\exp z^2 - 1} \quad \left(z^2 \equiv \frac{J_A k^2 a^2}{k_B T} \right) \\ &= \frac{1}{2\pi^2} \left(\frac{k_B T}{J_A a^2} \right)^{\frac{3}{2}} \int_0^\infty z^2 \sum_{n=1,2,3,\dots} \exp(-nz^2) dz = \frac{1}{a^3} \left(\frac{k_B T}{4\pi J_A} \right)^{\frac{3}{2}} \sum_{n=1,2,3,\dots} n^{-\frac{3}{2}}, \end{aligned} \quad (3.77)$$

where $1/a^3 = cN$ in which $c=1$, $1/2$ and $1/4$ for simple cubic, bcc, and fcc crystal, respectively. The magnetization as a function of temperature is

$$\frac{M_s(T)}{M_s(0)} = \frac{N - 2N_s}{N} = 1 - 2 \left(\frac{k_B T}{4\pi J_A} \right)^{\frac{3}{2}} c \sum_{n=1,2,3,\dots} n^{-\frac{3}{2}}. \quad (3.78)$$

Thus it is deduced that $M_s(T)$ is proportional to $T^{3/2}$ at low temperatures in agreement with experiment. The coefficient of $T^{3/2}$, however, does not coincide with experi-

ment. Other factors such as spin–lattice interactions should be taken into account to explain the experimental $T^{3/2}$ law quantitatively.

Note 1

At low temperatures

$$\begin{aligned}
 \frac{M_s(T, x)}{M_s(0)} &= \frac{J+1}{3J} \frac{T}{T_C} x \approx 1 \quad ((3.19), (3.21)) \\
 &= \frac{2J+1}{2J} \frac{\exp(y) + \exp(-y)}{\exp(y) - \exp(-y)} - \frac{1}{2J} \frac{\exp(y') + \exp(-y')}{\exp(y') - \exp(-y')} \\
 &\quad \left((3.16), (2.122), y \equiv \frac{2J+1}{2J} x, y' \equiv \frac{1}{2J} x \right) \\
 &= \frac{2J+1}{2J} [1 + 2 \exp(-2y)] - \frac{1}{2J} [1 + 2 \exp(-2y')] \\
 &= 1 + \frac{2J+1}{J} \exp\left(-\frac{2J+1}{J} x\right) - \frac{1}{J} \exp\left(-\frac{x}{J}\right) \\
 &= 1 + \frac{1}{J} [(2J+1) \exp(-2x) - 1] \exp\left(\frac{-x}{J}\right) \approx 1 - \frac{1}{J} \exp\left(\frac{-x}{J}\right) \\
 &= 1 - \frac{1}{J} \exp\left(-\frac{3}{J+1} \frac{T_C}{T}\right). \quad (3.79)
 \end{aligned}$$

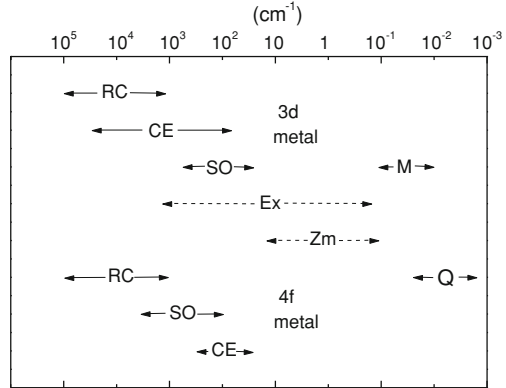
3.6 Crystalline Electric Field

In solids the magnetic electrons of an atom are under the actions of the electric field produced by the environmental electric charges called crystalline electric field (CEF) (or crystal electric field or tersely crystal field) in addition to the intra-atomic interactions.

3.6.1 CEF Interactions of 3d and 4f Electrons

For a 3d atom the outermost 4s electrons move away and the 3d subshell electrons are exposed to the environment and directly interact with the CEF. The CEF interaction in most cases is much smaller than the residual Coulomb interaction of the free ion but much larger than the spin–orbit interaction (Fig. 3.24). Therefore, in usual CEF interaction can be treated as perturbation to the ground term energy level by neglecting the spin–orbit interaction.

Fig. 3.24 Magnitude of the energies of residual Coulomb interaction (noted by RC in the figure), spin-orbit interaction (SO), CEF interaction (CE), exchange interaction (Ex), hyperfine magnetic interaction (M), electric-quadrupole interaction (Q), and that of Zeeman energy in the field of 1 T (Zm) [16]



For a 4f atom the outermost 5d and 6s electrons move away but the 4f subshell still remains enclosed by the full outer $5s^2$ and $5p^6$ subshells of the atom which are distorted by the CEF interaction thus screening the CEF. Contrary to the case of 3d atoms, the CEF interaction in most cases is smaller than the spin-orbit interaction (Fig. 3.24). Thus in general the CEF interaction can be treated as perturbation to the ground multiplet energy level.

3.6.2 CEF Hamiltonian

Consider a magnetic ion (hereafter called central ion) with n magnetic electrons. Let $\vec{r}_i \equiv \vec{r}(r_i, \theta_i, \phi_i)$ denote the position vector of the i^{th} magnetic electron and $\rho(\vec{R})$ the environmental electric charge density at position $\vec{R}(R, \Theta, \Phi)$ with respect to the nucleus of the central ion. The charge also includes that part of the central ion arising from the distortion of the outer electron cloud affected by the CEF. By neglecting the constant term, the CEF Hamiltonian is

$$\begin{aligned}
 \hat{H}_{\text{CF}} &= \sum_i^{1,2,\dots,n} \hat{H}_{\text{CF}}(i) = \sum_i^{1,2,\dots,n} \int \frac{e\rho(\vec{R})}{4\pi\epsilon_0|\vec{R}-\vec{r}_i|} dv_{\vec{R}} \\
 &= \frac{e}{4\pi\epsilon_0} \sum_i^{1,2,\dots,n} \sum_{\lambda}^{1,2,\dots,\infty} \sum_{\kappa}^{-\lambda,-\lambda+1,2,\dots,\lambda} \int \left[\frac{4\pi}{2\lambda+1} \frac{\rho(\vec{R})}{R^{\lambda+1}} Y_{\lambda\kappa}^*(\Theta, \Phi) dv_{\vec{R}} \right] r_i^{\lambda} Y_{\lambda\kappa}(i). \\
 &\quad (Y_{\lambda\kappa}(i) \equiv Y_{\lambda\kappa}(\theta_i, \phi_i)) \tag{3.80}
 \end{aligned}$$

The last relation holds when $R > r_i$. The perturbation equations for 3d and 4f ions under the representations of $|3d^n, L, M_L\rangle$ and $|4f^n, L, S, J, M_J\rangle$ is

$$\left| \langle 3d^n, L, M'_L | \sum_i^{1,2,\dots,n} \hat{H}_{CF}(i) | 3d^n, L, M_L \rangle - \varepsilon \delta(M'_L, M_L) \right| = 0$$

$$(M_L, M'_L = -L, -L+1, \dots, L) \quad (3.81)$$

and

$$\left| \langle 4f^n, L, S, J, M'_J | \sum_i^{1,2,\dots,n} \hat{H}_{CF}(i) | 4f^n, L, S, J, M_J \rangle - \varepsilon \delta(M'_J, M_J) \right| = 0,$$

$$(M_J, M'_J = -J, -J+1, \dots, J) \quad (3.82)$$

respectively. $|3d^n, L, M_L\rangle$ and $|4f^n, L, S, J, M_J\rangle$ being linear combinations of product of the orbitals $R_{nl}(1)R_{nl}(2)\cdots R_{nl}(n) Y_{lm_l}(1)Y_{lm'_l}(2)\cdots Y_{lm''_l}(n)$ ($m_l, m'_l, \dots, m''_l = -l, -l+1, \dots, l$) the calculation of a matrix element in the equations ends up to the calculations of a series of matrix elements $\langle Y_{lm_l}(i) | Y_{\lambda\kappa}(i) | Y_{lm_l}(i) \rangle$. Y_{lm_l} is both of a basis vector of irreducible representation of rotation-reflect group (A1.4.2) and a component of the irreducible tensor $\{Y_{lm_l}\}$ (A1.6). Thus $Y_{\lambda\kappa} | Y_{lm_l} \rangle$ transforms according to the representation of direct product of rotation-reflect group $D^\lambda \otimes D^l$ (A1.5.1), which completely reduces to $D^{\lambda+l} \oplus D^{\lambda+l-1} \oplus \dots \oplus D^{|\lambda-l|}$ (A4.5.2). Only if $D^{\lambda+l} \oplus D^{\lambda+l-1} \oplus \dots \oplus D^{|\lambda-l|}$ includes the irreducible representation D^l , that is only if $\lambda \leq 2l < Y_{lm_l} | Y_{\lambda\kappa} | Y_{lm_l} \rangle$ can be nonzero (A1.7). Furthermore, since

$$Y_{lm_l}(\pi - \theta, \pi + \phi) = (-1)^l Y_{lm_l}(\theta, \phi), \quad (3.83)$$

$\langle Y_{lm_l} | Y_{\lambda\kappa} | Y_{lm_l} \rangle$ may be nonzero only if λ is even. Thus $\hat{H}_{CF}$ of infinite linear sum (3.80) simplifies to the finite linear sum of

$$\hat{H}_{CF} = \sum_{\lambda}^{2 \times (1,2,\dots,l)} \langle r^\lambda \rangle \sum_k^{-\lambda, -\lambda+1, \dots, \lambda} A_{\lambda\kappa} \sum_i^{1,2,\dots,n} Y_{\lambda\kappa}(i). \quad (3.84)$$

$A_{\lambda\kappa} = \int \{e\rho(\vec{R}) Y_{\lambda\kappa}^*(\Theta, \Phi) / [(2\lambda+1)\varepsilon_0 R^{\lambda+1}] \} dv_{\vec{R}}$ is related to the electric charge distribution of the environment and is called CEF constant.

The symmetry of CEF reduces the number of the terms on the right-hand side of (3.84) further. Take a crystal site of D_{4h} symmetry (A1.1.4) as an example. Take the 4-fold rotation symmetry axis z axis. The rotation by the angle $\pm \pi/2$ about the z axis does not change $\hat{H}_{CF}$, so it should hold

$$Y_{\lambda\kappa} \left(\theta, \phi \pm \frac{\pi}{2} \right) = Y_{\lambda\kappa}(\theta, \phi), \quad (3.85)$$

that is $\kappa\pi/2 = 2\pi \times \text{integer}$, from which the value of κ is reduced to

$$\kappa = 0, \pm 4. \quad (3.86)$$

The reflection on the (100) plane also does not change $\hat{H}_{\text{CF}}$, so it should hold

$$A_{2\lambda,-4} \exp[-i4(-\phi)] + A_{2\lambda,4} \exp[i4(-\phi)] = A_{2\lambda,-4} \exp(-i4\phi) + A_{2\lambda,4} \exp(i4\phi), \quad (3.87)$$

that is

$$A_{2\lambda,-4} = A_{2\lambda,4}. \quad (3.88)$$

In this way, (3.84) for 3d ion at the site of D_{4h} symmetry and for 4f ion at the site of hexagonal symmetry, for example, simplifies to

$$\begin{aligned} \hat{H}_{\text{CF}} &= \sum_i^{1,2,\dots,n} \left\{ \sum_{\lambda}^{2,4} \langle r^{\lambda} \rangle A_{\lambda 0} Y_{\lambda 0}(i) + \langle r^4 \rangle A_{44} [Y_{44}(i) + Y_{4-4}(i)] \right\} \\ &= \sum_i^{1,2,\dots,n} \left\{ \sum_{\lambda}^{2,4} \langle r^{\lambda} \rangle A_{\lambda}^0 U_0^{\lambda}(i) + \langle r^4 \rangle A_4^4 [U_4^4(i) + U_{-4}^4(i)] \right\}, \end{aligned} \quad (2.24)$$

$$(3.89)$$

and

$$\begin{aligned} \hat{H}_{\text{CF}} &= \sum_i^{1,2,\dots,n} \left\{ \sum_{\lambda}^{2,4,6} \langle r^{\lambda} \rangle A_{\lambda}^0 U_0^{\lambda}(i) + \langle r^6 \rangle A_6^6 [U_6^6(i) + U_{-6}^6(i)] \right\}, \\ &\quad \left(A_{\lambda}^{\kappa} \equiv \sqrt{\frac{2\lambda+1}{4\pi}} A_{\lambda\kappa} \right), \end{aligned} \quad (3.90)$$

respectively.

3.6.3 CEF Effects for 3d Ion at the B Site of Spinel Ferrite

Take $3d^1(\text{Ti}^{+3})$ ion as an example. The ground term of the free ion is ^2D . First consider the effects of the O_h symmetric (A4.1.4) CEF produced by the six nearest O^{2-} ions (Fig.3.25). Under the interaction the energy level of ^2D splits into two energy levels of E_g of orbital degeneracy 2 and T_{2g} of orbital degeneracy 3 (Fig.3.26, A4.4.3, A4.7).

The orbital eigenstates can be represented by the real functions of

$$\begin{aligned} E_g : d(z^2) &\equiv |n=3, l=2, m_l=0\rangle = \frac{C}{\sqrt{3}} \frac{3z^2 - r^2}{r^2}, \quad \left(C \equiv \sqrt{\frac{15}{16\pi}} \right) \\ d(x^2 - y^2) &\equiv \frac{1}{\sqrt{2}} (|3, 2, 2\rangle + |3, 2, -2\rangle) = C \frac{x^2 - y^2}{r^2}, \end{aligned} \quad (3.91)$$

Fig. 3.25 Ion distribution around a B site of spinel ferrite. ●: metal ion; ○: O^{2-} ion

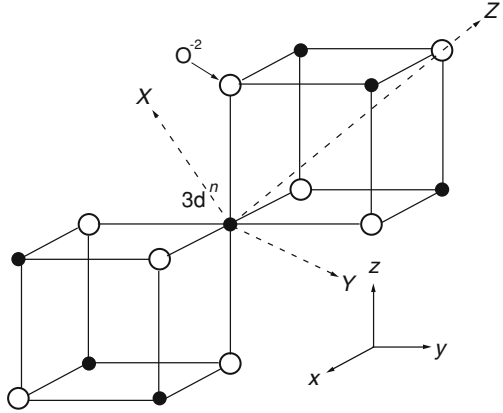
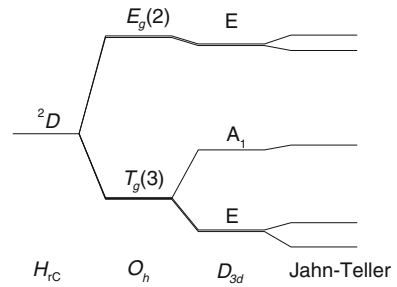


Fig. 3.26 The splitting of energy levels of $Ti^{+3}(3d^1)$ at the B site of spinel ferrite under the CEF interactions and the Jahn-Teller effect



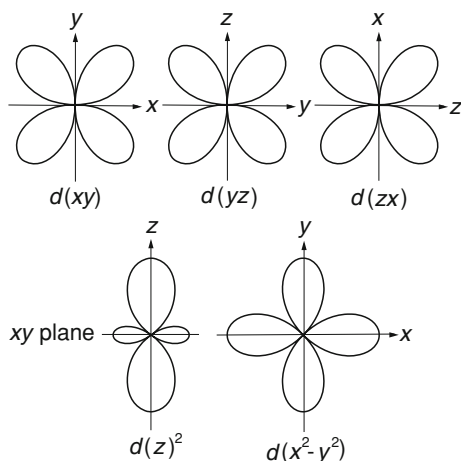
$$\begin{aligned}
 T_{2g} : d(xy) &\equiv \frac{1}{i\sqrt{2}}(|3, 2, 2\rangle - |3, 2, -2\rangle) = 2C \frac{xy}{r^2}, \\
 d(yz) &\equiv -\frac{1}{i\sqrt{2}}(|3, 2, 1\rangle - |3, 2, -1\rangle) = 2C \frac{yz}{r^2}, \\
 d(zx) &\equiv -\frac{1}{\sqrt{2}}(|3, 2, 1\rangle + |3, 2, -1\rangle) = 2C \frac{zx}{r^2}. \quad (3.92)
 \end{aligned}$$

Figure 3.27 shows the angular distribution of the electron density for the above functions.

The electron clouds of $d(xy)$, $d(yz)$, and $d(zx)$ states of T_{2g} energy level avoid the O^{2-} ions, while the clouds of $d(z^2)$ and $d(x^2 - y^2)$ states of E_g level stretch toward the O^{2-} ion directions. The electrons of 3d and O^{2-} ions repulsing each other T_{2g} energy level is lower than E_g and the states of T_{2g} become ground states.

The CEF splitting of $3d^6(Fe^{+2})$ ion is the same as that of $3d^1$ ion. This is because five 3d electrons of same spins fill all five $l = 2$ orbits making their total angular momentum zero. Therefore, only the remaining $3d^1$ electron of different spin interacts with the CEF.

Fig. 3.27 Angular distribution of electron density of $d(xy)$, $d(yz)$, $d(zx)$, $d(z^2)$, and $d(x^2-y^2)$ states



$3d^4(\text{Mn}^{+3})$ in respect to the CEF interaction is equivalent to the ion in which an electron of positive electric charge is added into the 3d subshell of $3d^5$ ion. Therefore, the CEF behavior is the same as that of $3d^1$ ion but with the opposite sign of the interaction, that is E_g is the ground state and T_{2g} is the excited state with the energy gap between them remaining the same as that of $3d^1$ ion.

The behavior of $3d^9(\text{Cu}^{+2})$ ion is the same as that of $3d^4(\text{Mn}^{+3})$ ion.

The $3d^1$ ion at the B site also interacts with the smaller CEF produced by the next nearest six metal ions (Fig.3.25). If all the metal ions are the same, they produce a D_{3d} symmetric (A4.1.4) CEF. Under the CEF interaction the ground T_{2g} energy level splits into 2-fold orbit degenerate ground E energy level and non-degenerate A_1 energy level, while the E_g energy level shifts a bit without splitting (Fig.3.26, A4.4.3, A4.7).

3.6.4 Jahn–Teller Effect

Consider a $3d^1$ ion in the cubic symmetric CEF at the B site of spinel ferrite as an example. The electron cloud of $d(x^2 - y^2)$ or $d(z^2)$ state of E_g energy level stretches along the x and y axes or z axis (Fig.3.27) pressuring the nearest neighbor O^{2-} ions outward. The former expands the crystal in the x and y axes directions while the latter elongates the crystal along the z axis. The crystal being distorted in different ways the sum of the CEF and elastic energies for the two states become different leading to the splitting of the E_g energy level into two.

The phenomenon can also be explained in the language of group theory as below. The O_h symmetric CEF distorts to the D_{4h} symmetric CEF. Thus, the 2-fold irreducible representation E_g of O_h group reduces to two 1-fold irreducible representations $A_{1g} + B_{1g}$ of D_{4h} group, that is, the 2-fold orbital degenerate E_g

energy level splits into two levels (A4.4.3, A4.7). Such kind of crystal distortion and the splitting of the energy level are called Jahn-Teller effect. The Jahn-Teller effect can be observed in many cases.

3.6.5 Quenching of Orbital Angular Momentum

The spin-orbit interactions being neglected, the Hamiltonian of the $3d^n$ electrons in a CEF is a real function. In such a case of real Hamiltonian, if the orbital state of the system is non-degenerate, any component of the orbital angular momentum of the system is zero. This phenomenon is called quenching of orbital angular momentum. The theorem is proved as below.

Let $\hat{H}$ the Hamiltonian and $\Phi(1, 2, \dots, n)$ the orbital state of the system. The Schrödinger equation and its conjugate complex are

$$\hat{H}\Phi = E\Phi, \quad \hat{H}\Phi^* = E\Phi^*, \quad (3.93)$$

thereby

$$\Phi^* = c\Phi, \quad cc^* = 1. \quad (3.94)$$

The angular momentum operator

$$\hat{L} = \sum_i \vec{r}_i \times (-i\nabla_i) \quad (\vec{r}_i : \text{position vector of } i^{\text{th}} \text{ electron, (2.30)}) \quad (3.95)$$

is imaginary Hermitian (A4.2), so its average over Φ is zero:

$$\int \Phi^* \hat{L} \Phi dv = \int \Phi \hat{L}^* \Phi^* dv = \int c^* \Phi^* (-\hat{L}) c \Phi dv = - \int \Phi^* \hat{L} \Phi dv = 0. \quad (3.96)$$

The eigenfunction of perturbation equation (3.81) being a linear function of $\{|3d^n, L, M_L\rangle\}$ ($M_L = -L, -L+1, \dots, L$) which have a definite value of L , L remains a good quantum number for the $3d^n$ ion in a CEF, i.e., the average of $\hat{L}^2$ is still $L(L+1)$ in contrast to the average of $\hat{L}_\alpha$ ($\alpha=x, y, z$) is zero.

3.6.6 Gyromagnetic Effect

An isolate atom has a definite value of gyromagnetic ratio:

$$\gamma_J = \left| \frac{p_J(M_J)}{\hbar M_J} \right| = g_J \frac{\mu_B}{\hbar}, \quad (2.100)$$

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}. \quad (2.99)$$

If an atomic magnetic moment totally comes from orbits ($S = 0$) or from spins ($L = 0$), g_J equals to 1 or 2.

In solids, the magnetic moment and angular momentum of an atom have similar intrinsic relations. Experiments show that rotation of a magnetic body accompanies magnetization, and magnetization induces rotation of the magnet. This phenomenon is called the gyromagnetic effect. The gyromagnetic ratio γ and g factor of the atom, however, are different from those of isolate atom, which can be measured exploring gyromagnetic effect. Take the experiment of Einstein-de Haas (1916) as an example. A magnetic rod is overhung by a thin string in a vertically installed solenoid. First, the rod is magnetized and set static. Quickly change the field direction, and measure the change of the magnetic polarization moment Δp_J . At this point the rod begins to rotate. The change of the angular momentum of the lattice of the rod Δp_{lat} could be measured from the maximum deflection angle of the rod. Since the rod is not exerted by torque, the sum of Δp_{lat} and the spin and orbital angular momenta of the electrons Δp_S and Δp_L should be zero:

$$\Delta(p_S + p_L) = -\Delta p_{\text{lat}}. \quad (3.97)$$

The gyromagnetic ratio of the rod is the absolute value of the ratio of the change in the magnetic polarization moment to the change in the angular momentum of the electrons:

$$\gamma = \left| \frac{\Delta p_{JS} + \Delta p_{JL}}{\Delta p_S + \Delta p_L} \right| = \left| \frac{\Delta p_J}{\Delta p_{\text{lat}}} \right|. \quad (3.98)$$

The g factor is the absolute value of the ratio of the change in magnetic polarization moment in μ_B unit to the change in the angular momentum in $\hbar$ unit (2.100):

$$g = \left| \frac{\Delta p_J / \mu_B}{(\Delta p_S + \Delta p_L) / \hbar} \right| = \gamma \frac{\hbar}{\mu_B}. \quad (3.99)$$

The ratio of the change in the orbital angular momentum to the change in the spin angular momentum

$$\varepsilon \equiv \frac{\Delta p_L}{\Delta p_S} \quad (3.100)$$

can be deduced from the g factor as below. Since

$$\frac{\Delta p_{JS}}{\Delta p_S} = -2 \frac{\mu_B}{\hbar}, \quad \frac{\Delta p_{JL}}{\Delta p_L} = -\frac{\mu_B}{\hbar}, \quad (3.101)$$

$$g = \left| \frac{\Delta p_{JS} + \Delta p_{JL}}{\Delta p_S + \Delta p_L} \frac{\hbar}{\mu_B} \right| = \frac{\Delta p_S(2 + \varepsilon)}{\Delta p_S(1 + \varepsilon)} = 2 - \varepsilon. \quad (\varepsilon \ll 1) \quad (3.102)$$

Table 3.5 Values of g factor and ε of some 3d magnetic materials [17]

Material	g	ε
Fe metal	1.92	0.04
Co metal	1.85	0.07
Ni metal	1.84	0.08
Fe ₃ O ₄	1.85	0.07
Fe ₂₂ Ni ₇₈	1.90	0.05

Table 3.5 shows the values of g and ε for the 3d atoms or ions in some 3d magnetic materials measured by gyromagnetic experiments.

The values are close to 2, that is the magnetic moments originate mainly from the spins while the orbital magnetic moments are very small. The results can be explained by the quenching of orbital angular momentum. The value of g , however, is a bit smaller than 2 showing that orbital angular momentum is not completely quenched. In the case of non-degenerate orbital state this is caused by the spin–orbit interaction $\hat{H}_{LS} = \lambda \hat{\vec{L}} \cdot \hat{\vec{S}}$ which includes complex operator terms. If $\hat{H}_{LS}$ is taken into account in the total Hamiltonian $\hat{H}$ in (3.93), the second relations in (3.93) and (3.94) hold only approximately leading to that the average of $\hat{\vec{L}}$ is not rigorously zero. Since the spin–orbit interaction is small, the residual orbital angular momentum is very small. If the orbital state is degenerate, the quenching of orbital angular momentum may not be complete (Sect. (5.2.3.2)).

The situation of 4f transition ion in solid is quite different. The spin–orbit interaction being larger than the CEF interaction no quenching of orbital angular momentum occurs.

3.6.7 Precession Motion of Magnetization Vector in a Magnetic Field

The proportionality between a magnetic polarization vector $\vec{J}$ and the angular momentum gives rise to a common characteristic of precession motion of $\vec{J}$ in a magnetic field $\vec{H}$ ($\parallel z$ axis).

3.6.7.1 Equation of Precession Motion of Magnetization Vector

The equation of precession motion for the system of atoms is (2.128)

$$-\frac{1}{\gamma} \frac{d\vec{J}}{dt} = \vec{J} \times \vec{H} \left(-\frac{1}{\gamma} \frac{d\vec{M}}{dt} = \vec{M} \times \vec{H} \right) + \text{damping term.} \quad (3.103)$$

Here, the torque $\vec{J} \times \vec{H}$ (1.44) which is perpendicular to $\vec{J}$ rotates $\vec{J}$ about the z axis in the right-hand direction. The damping term arises from the interactions of $\vec{J}$ with the medium, and the phenomenological expressions of $-(\alpha\gamma/M)\vec{M} \times (\vec{M} \times \vec{H})$ (Landau-Lifshitz, 1935) and $(\alpha/M)\vec{M} \times d\vec{M}/dt$ (Gilbert, 1955) are in common use.

Different from the atomic system, the sign of the ratio of $\vec{J}$ to the angular momentum differs for different nuclei (Table 2.4). For the system, the equations of precession motion proposed by Bloch (1946) are in common use. The equations read as

$$\left(\frac{d\vec{M}}{dt}\right)_z = -\frac{M_z - M_0}{T_1}, \quad (3.104)$$

$$\left(\frac{d\vec{M}}{dt}\right)_\alpha = \begin{cases} -\gamma(\vec{M} \times \vec{H})_\alpha - \frac{M_\alpha}{T_2}, & (-\gamma = g_N\mu_N < 0) \\ \gamma(\vec{M} \times \vec{H})_\alpha - \frac{M_\alpha}{T_2}, & (\gamma = g_N\mu_N > 0) \end{cases} \quad (3.105)$$

where M_0 is the steady magnetization and T_1 and T_2 are constants,

Equations (3.103)–(3.105) describe the motion of magnetization vector but not of individual magnetic moment.

3.6.7.2 Forced Precession of Magnetization Vector

Assume that an isotropic ferri- and ferromagnetic medium is in a static magnetic field $\vec{H}$ superposed by a small alternating linear magnetic field of angular frequency $\omega = 2\pi f$ (f : frequency)

$$\vec{h} = \vec{h}_0 \exp(i\omega t) = \sum_{\alpha}^{x,y,z} h_\alpha \vec{e}_\alpha. \quad (3.106)$$

$\vec{M}$ is forced to make a synchronized motion

$$\vec{M} = \vec{M}_0 \vec{e}_z + \vec{m}, \quad (m \ll M_0) \quad (3.107)$$

$$\vec{m} = \vec{m}_0 \exp(i\omega t) = \sum_{\alpha}^{x,y,z} m_\alpha \vec{e}_\alpha. \quad (3.108)$$

Inserting (3.106)–(3.108) into (3.103) in which $\vec{H}$ is replaced by $\vec{H} + \vec{h}$, and the damping term is neglected we get

$$\frac{d\vec{M}_s}{dt} = i\omega \sum_{\beta}^{x,y,z} m_\beta \vec{e}_\beta = -\gamma \begin{vmatrix} \vec{e}_x & \vec{e}_y & \vec{e}_z \\ m_x & m_y & M_0 + m_z \\ h_x & h_y & H + h_z \end{vmatrix}, \quad (3.109)$$

i.e.

$$\mathrm{i}\omega \begin{pmatrix} m_x \\ m_y \\ m_z \end{pmatrix} = -\gamma \begin{pmatrix} m_y(H + h_z) - (M_0 + m_z)h_y \\ (M_0 + m_z)h_x - m_x(H + h_z) \\ m_x h_y - m_y h_x \end{pmatrix}. \quad (3.110)$$

let

$$\omega_M \equiv \gamma M_s, \quad (3.111)$$

$$\omega_H \equiv \gamma H. \quad (3.112)$$

By neglecting the square order terms of small quantities $\{h_\alpha, m_\alpha\}(\alpha = x, y, z)$, (3.110) becomes

$$\mathrm{i}\omega m_x + \omega_H m_y = \omega_M h_y, \quad (3.113)$$

$$-\omega_H m_x + \mathrm{i}\omega m_y = -\omega_M h_x, \quad (3.114)$$

$$m_z = 0. \quad (3.115)$$

The solution of (3.113)–(3.114) is

$$m_x = \frac{\begin{vmatrix} \omega_M h_y & \omega_H \\ -\omega_M h_x & \mathrm{i}\omega \end{vmatrix}}{\begin{vmatrix} \mathrm{i}\omega & \omega_H \\ -\omega_H & \mathrm{i}\omega \end{vmatrix}} = \chi h_x - \mathrm{i}\chi_a h_y, \quad (3.116)$$

$$m_y = \frac{\begin{vmatrix} \mathrm{i}\omega & \omega_M h_y \\ -\omega_H & -\omega_M h_x \end{vmatrix}}{\begin{vmatrix} \mathrm{i}\omega & \omega_H \\ -\omega_H & \mathrm{i}\omega \end{vmatrix}} = \mathrm{i}\chi_a h_x + \chi h_y, \quad (3.117)$$

$$\chi = \frac{\omega_M \omega_H}{\omega_H^2 - \omega^2}, \quad (3.118)$$

$$\chi_a = -\frac{\omega_M \omega}{\omega_H^2 - \omega^2}, \quad (3.119)$$

and (3.110) can be reformulated as

$$\begin{pmatrix} m_x \\ m_y \\ m_z \end{pmatrix} = \begin{pmatrix} \chi & -\mathrm{i}\chi_a & 0 \\ \mathrm{i}\chi_a & \chi & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} h_x \\ h_y \\ h_z \end{pmatrix} \equiv (m) = (\chi) (h) = \vec{m} = (\chi) \vec{h}. \quad (3.120)$$

The susceptibility with respect to $\vec{h}$ is a tensor of complex elements. Thus $\vec{m}$ is not parallel to $\vec{h}$ and its time phase is different from that of $\vec{h}$. The susceptibility becoming infinite, the magnetic resonance occurs at the frequency of

$$\omega = \omega_H. \quad (3.121)$$

The first relation of (3.105) in the case of $-\gamma = g_N \mu_N < 0$ results in the same results for m_x, m_y ((3.113)–(3.119)) and resonance frequency (3.121).

3.6.7.3 Free Precession of Magnetization Vector

If the alternating field is cut off after forced precession, (3.113)–(3.114) become

$$i\omega m_x + \omega_H m_y = 0, \quad (3.122)$$

$$-\omega_H m_x + i\omega m_y = 0, \quad (3.123)$$

from which we get

$$\begin{vmatrix} i\omega & \omega_H \\ -\omega_H & i\omega \end{vmatrix} = 0, \quad \text{i.e. } \omega = \omega_H, \quad (3.124)$$

$$m_y = -im_x = \exp\left(-i\frac{\pi}{2}\right) m_x. \quad (3.125)$$

The magnetic moment makes Larmor precession in the right-hand direction around $\vec{H}$ direction with the resonance angular frequency $\omega = \omega_H$ (3.124). If $\gamma = g_N \mu_N > 0$, the second relation of (3.105) makes the precession in the opposite direction with the same frequency. The damping term being neglected, the precession maintains for an infinitely long time keeping the magnetization M_0 unchanged.

3.6.7.4 Relaxation

Now take into account the damping terms. Consider the Bloch equations as an example. Suppose the alternating field is cut off at time $t = 0$. Equation (3.104)–(3.105) become

$$i\omega m_z = -\frac{m_z}{T_1}, \quad (3.126)$$

$$\left(i\omega + \frac{1}{T_2}\right) m_x + \omega_H m_y = 0, \quad (3.127)$$

$$-\omega_H m_x + \left(i\omega + \frac{1}{T_2}\right) m_y = 0. \quad (3.128)$$

Solution of (3.126) is

$$m_z(t) = m_z(0) \exp\left(-\frac{t}{T_1}\right). \quad (3.129)$$

m_z decays with relaxation time T_1 . It is known that the relaxation proceeds through spin–lattice interaction and T_1 is called spin-lattice relaxation time. From (3.127)–(3.128) we get

$$\begin{vmatrix} i\omega + \frac{1}{T_2} & \omega_H \\ -\omega_H & i\omega + \frac{1}{T_2} \end{vmatrix} = 0, \quad (3.130)$$

$$\omega = \omega_H + i\frac{1}{T_2}, \quad (3.131)$$

$$m_\alpha(t) = m_\alpha(0) \exp(i\omega_H t) \exp\left(-\frac{t}{T_2}\right). \quad (3.132)$$

T_2 represents the relaxation time for the breakdown of the coherent Larmor precession into spin waves (Fig.3.23) through spin–spin interactions, and is called spin–spin relaxation time.

The decaying characteristics of (3.129), (3.132) are irrelevant to the sign of the ratio of the magnetic polarization moment to the angular momentum and hold for any nucleus system.

3.7 Free Electron Gas

Free electron model (Sommerfeld, 1928) approximates ion cores in a solid as a uniformly distributed positive electric charge and valence electrons as free electrons moving around in the positive charge background without any interactions between themselves.

3.7.1 Eigenstate and Eigenenergy of Free Electron

Consider N free electrons contained in a unit volume cube. The Hamiltonian of an electron is the kinetic energy. By solving the Schrödinger equation

$$\frac{\hat{p}^2}{2m} \varphi(\vec{r}) = -\frac{\hbar^2}{2m} \nabla^2 \varphi(\vec{r}) = \varepsilon \varphi(\vec{r}) \quad (3.133)$$

we get the eigenstate and eigenenergy of

$$\varphi(\vec{r}) = \exp(i\vec{k} \cdot \vec{r}) = |\vec{k} \rangle, \quad (3.134)$$

$$\varepsilon = \frac{k^2 \hbar^2}{2m}. \quad (3.135)$$

$\varphi(\vec{r})$ is the plane wave of wave vector $\vec{k}$, which is also the eigenfunction of the momentum operator, i.e.,

$$-i\hbar \nabla \varphi(\vec{r}) = \hbar \vec{k} \varphi(\vec{r}), \quad (3.136)$$

and has a momentum of

$$\vec{p} = \hbar \vec{k}. \quad (3.137)$$

The spin-orbital is $\psi_{\vec{k}, \pm} = \exp(i\vec{k} \cdot \vec{r}) \chi_{\pm} = |\vec{k}, \pm \rangle$. Under the periodical boundary conditions

$$\exp[ik_{\alpha}(\alpha + 1)] = \exp(ik_{\alpha}\alpha), \quad (\alpha = x, y, z) \quad (3.138)$$

$\vec{k}$ takes the values of

$$\vec{k} = 2\pi \sum_{\alpha}^{x, y, z} v_{\alpha} \vec{e}_{\alpha}. \quad (v_{\alpha} : \text{integer}; \vec{e}_{\alpha} : \text{unit vector in the } \alpha \text{ direction}) \quad (3.55)$$

3.7.2 Energy Band of Free Electron Gas

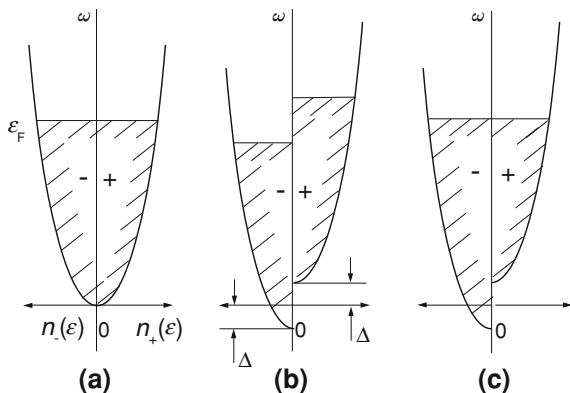
At 0 K, N electrons fully fill all spin-up and spin-down states up to Fermi energy level (Fig. 3.28a). The Fermi radius k_F , Fermi energy ε_F , spin-resolved density of states (DOS) $n(\varepsilon)$ (DOS for spin-up (+) spin and spin-down (-) spin. In case the two are different they are differentiated by e.g. $n_+(\varepsilon)$ and $n_-(\varepsilon)$ (Fig. 3.33)) and that at the Fermi level $n(\varepsilon_F)$ are

$$\frac{N}{2} = \frac{1}{(2\pi)^3} \frac{4\pi k_F^3}{3}, \quad (3.139)$$

$$\varepsilon_F = \frac{k_F^2 \hbar^2}{2m}, \quad (3.140)$$

$$n(\varepsilon) = \frac{d}{d\varepsilon} \left[\frac{1}{(2\pi)^3} \frac{4\pi}{3} k^3 \right] = \frac{d}{d\varepsilon} \left[\frac{1}{(2\pi)^3} \frac{4\pi}{3} \frac{(2m\varepsilon)^{\frac{3}{2}}}{\hbar^3} \right] = \frac{m^{\frac{3}{2}}}{\sqrt{2}\pi^2 \hbar^3} \sqrt{\varepsilon}, \quad (3.141)$$

$$n(\varepsilon_F) = \frac{mk_F}{2\pi^2 \hbar^2} = \frac{3N}{4\varepsilon_F}. \quad (3.142)$$

Fig. 3.28 Spin-up and spin-down energy bands

3.7.3 Magnetic Properties of Free Electrons

In a static magnetic field $H\vec{e}_z$, the Hamiltonian of an electron is

$$\hat{H} = \frac{1}{2m}(\hat{\vec{p}} - e\vec{A})^2 + 2\mu_B\hat{s}_zH. \quad (2.115) \quad (3.143)$$

The term of $2\mu_B\hat{s}_zH$ on the right-hand side of the above equation produces paramagnetism: The Zeeman energies of the magnetic moments of spin-up and spin-down spin electrons being $\langle \chi_{\pm} | 2\mu_B\hat{s}_zH | \chi_{\pm} \rangle = \pm\mu_B H$, the spin energy band of spin-up and spin-down shifts upward and downward by $\Delta = \mu_B H$ ($\ll \varepsilon_F$, Fig. 3.28b), respectively. To decrease the system energy, $n(\varepsilon_F)\mu_B H$ electrons of spin-up band above the Fermi level transfer into the vacant states of the spin-down band below the Fermi level by changing the spin and $\vec{k}$ simultaneously (Fig. 3.28c). The electron system is magnetized, and the susceptibility is

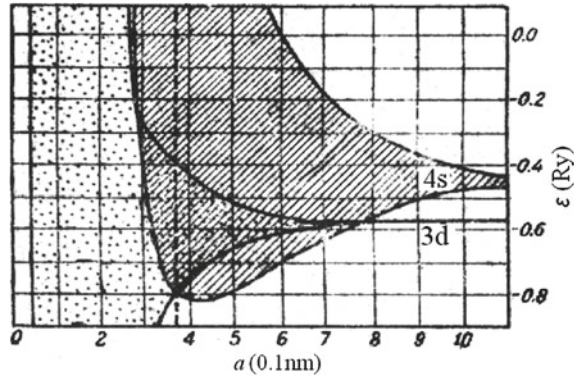
$$\chi_P\mu_0 = \frac{J}{H} = \frac{2n(\varepsilon_F)\mu_B H\mu_B}{H} = 2n(\varepsilon_F)\mu_B^2. \quad (3.144)$$

In the temperature range of average experimental conditions, the distribution of spin states in the energy band being affected little by temperature, the susceptibility is essentially temperature independent.

The free electron model successfully explains Pauli paramagnetism of the metals of the elements belonging to the group IA and IIA of periodical table. The values of susceptibility of the metals are in the range of $(10-30) \times 10^{-6}$ per gram molecule.

The first term on the right-hand side of (3.143) produces diamagnetism. It has little impact on the magnetic properties of magnetic materials in use and will not be analyzed here.

Fig. 3.29 Bandwidth as a function of lattice constant for the 3d and 4s bands of Cu metal [18]



3.8 Essentials of Band Theory

3.8.1 Introduction

In Sect. 2.6 it was seen that when two H atoms approach each other, the two sets of the 1s energy levels of the two atoms, which can accommodate 4 electrons altogether, split into a nondegenerate $S = 0$ energy level and 3-fold degenerate $S = 1$ energy level. With decrease of the distance between the atoms, the electrons superpose more and more, the energy level of $S=1$ increases monotonically, and the energy level of $S=0$ decreases down to a minimum thereby forming a stable molecule H_2 (Fig. 2.5). The electrons in the molecule H_2 no longer localize in each atom but itinerate the whole molecule (Fig. 2.6).

A similar situation occurs when a large number of atoms are brought together to form a solid. The outer electrons of the atoms superpose each other making them possible to migrate and become itinerant. The energy levels of isolated atoms transform into the energy band of the whole solid. The number of the atoms being enormously large, the band can accommodate extremely large number of electrons making the most of the energy levels almost continuous. The smaller the lattice constant, the larger the extent of overlap of electrons, and the broader the bandwidth. Some intervals of energy, however, contain no orbitals forming band gaps. For a 3d metal, 3d electrons reside inside the 4s electrons, so the extent of superposition with the electrons of neighbor atoms is smaller than that of the 4s electrons resulting in thinner bandwidth and correspondingly larger DOS (Fig. 3.29). Such is the primary physical picture of itinerant model and electronic band structure.

The energy band theory is a theory of itinerant model exploiting the one-electron method (Sect. 2.1.2). It sorts the electrons of each atom to two kinds. One is core electrons fully residing in the inner electron subshells, which superpose little with the electrons of the neighbor atoms and hence the states are affected little by the environment. Another is valence electrons residing on the outer subshells which superpose with the electrons of the neighbor atoms more appreciably and are easily

affected by the environment. The 4s and 3d electrons for 3d atoms and the 4f, 5s, 5p, 5d, and 6s electrons for 4f atoms are usually treated as valence electrons.

The eigenstates and energies of the electron system can be obtained by solving the Shrödinger equations. Approximate wave functions are often used for the core electrons, most simple of which are those of the free atoms. In this case the core electrons of n^{th} atom at position $\vec{R}_n$ along with the nucleus produce the core potential $u(\vec{r}, \vec{R}_n)$, and the states of the valence electrons can be obtained by solving the Shrödinger equations

$$\hat{H}\varphi_\alpha(\vec{r}) = \left[\frac{\hat{p}^2}{2m} + U(\vec{r}) \right] \varphi_\alpha(\vec{r}) = \varepsilon_\alpha \varphi_\alpha(\vec{r}), \quad (3.145)$$

where U is the sum of the external crystal potential (tersely called external potential) $\sum_n u(\vec{r}, \vec{R}_n)$ and that produced by the other valence electrons.

3.8.2 Bloch Wave

The points in a crystal which have completely the same environment constitute the Bravais lattice of the crystal. Let $\vec{a}_j$ denote a primitive vector of the Bravais lattice.

$$U(\vec{r} + \vec{R}_n) = U(\vec{r}), \quad (3.146)$$

where

$$\vec{R}_n \equiv \sum_j^{1,2,3} n_j \vec{a}_j \quad (n_j : \text{integer}) \quad (3.147)$$

is a lattice vector. Let N_j denote the number of primitive cells per unit length in the $\vec{a}_j$ axis direction, then

$$N_j a_j = 1. \quad (j = 1, 2, 3) \quad (3.148)$$

Suppose the eigenfunction of (3.145) satisfies the periodical boundary conditions

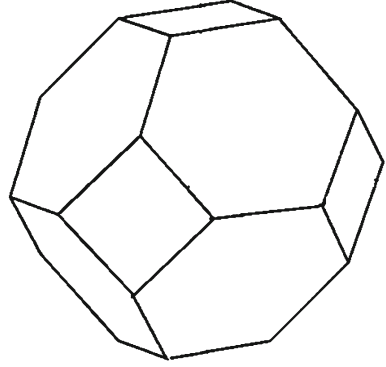
$$\varphi_\alpha(\vec{r} + N_j \vec{a}_j) = \varphi_\alpha(\vec{r}). \quad (3.149)$$

$\varphi_\alpha(\vec{r})$ has the form of

$$\varphi_\alpha(\vec{r}) = \varphi_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r}) \exp(i\vec{k} \cdot \vec{r}) \quad (3.150)$$

and is called Bloch wave. Here, $u_{\vec{k}}(\vec{r})$ is a periodical function of lattice (Note 1 of this section),

Fig. 3.30 First Brillouin zone of fcc lattice



$$\vec{k} = \sum_j^{1,2,3} k_j \vec{b}_j, \quad k_j = 2\pi \times \text{integer}/N_j, \quad (3.151)$$

in which

$$\vec{b}_1 \equiv \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}, \quad \vec{b}_2 \equiv \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_2 \cdot (\vec{a}_3 \times \vec{a}_1)}, \quad \vec{b}_3 \equiv \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_3 \cdot (\vec{a}_1 \times \vec{a}_2)} \quad (3.152)$$

are the reciprocal primitive vectors which satisfy the relations of

$$\vec{a}_j \cdot \vec{b}_l = \delta(j, l). \quad (j, l = 1, 2, 3) \quad (3.153)$$

$\{\varphi_k^-(\vec{r})\}$ are orthogonal (Note 2 of this section). The head points of the reciprocal vectors

$$\vec{K}_{\vec{m}} = \sum_j^{1,2,3} m_j \vec{b}_j \quad (m_j: 2\pi \times \text{integer}) \quad (3.154)$$

constitute reciprocal lattice. The first Brillouin zone is a uniquely defined primitive cell in the reciprocal space enclosed by the polyhedral surfaces. Each of the surfaces bisects the line section connecting the origin ($\vec{K} = 0$) and a neighbor reciprocal lattice point. Figure 3.30 demonstrates the first Brillouin zone for fcc crystal.

The wave vector $\vec{k}$ takes the values within the first Brillouin zone, and the wave vectors out of the zone are denoted by $\vec{k} + \vec{K}_{\vec{m}}$.

3.8.3 Band Theory Based on the Mean Field Approximation

Before the 1970s, band theory was largely been based on the Hartree-Fock approximation. In this approximation $U(\vec{r})$ in (3.145) can be expressed as

$$U(\vec{r}) = \sum_n u(\vec{r}, \vec{R}_n) + \int \frac{[\rho(\vec{r}') + \rho_\alpha^{\text{HF}}(\vec{r}, \vec{r}')]e^2}{4\pi\epsilon_0|\vec{r} - \vec{r}'|} d\vec{v}', \quad (3.155)$$

$$\rho(\vec{r}) = \sum_\beta |\varphi_\beta(\vec{r})|^2, \quad (3.156)$$

$$\rho_\alpha^{\text{HF}}(\vec{r}, \vec{r}') = - \sum_{\beta, //} \frac{\varphi_\beta^*(\vec{r}')\varphi_\alpha(\vec{r}')\varphi_\alpha^*(\vec{r})\varphi_\beta(\vec{r})}{\varphi_\alpha^*(\vec{r})\varphi_\alpha(\vec{r})} \cdot \left(\sum_{\beta, //} : \text{sum over } \beta \text{ of same spin with } \alpha \right) \quad (3.157)$$

$\rho_\alpha^{\text{HF}}(\vec{r}, \vec{r}')$ is the density produced by the exchange interaction which is short range around $\vec{r}$ and forms the exchange hole there,

$$\int \rho_\alpha^{\text{HF}}(\vec{r}, \vec{r}') d\vec{v}' = -1. \quad (3.158)$$

The electron of $\varphi_\alpha(\vec{r})$ itinerates in the potential consisted of the external potential $V(\vec{r}) = \sum_n u(\vec{r}, \vec{R}_n)$ and the average potential $\int \frac{[\rho(\vec{r}') + \rho_\alpha^{\text{HF}}(\vec{r}, \vec{r}')]e^2}{4\pi\epsilon_0|\vec{r} - \vec{r}'|} d\vec{v}'$ produced by the other valance electrons of density distribution $\rho(\vec{r}') + \rho_\alpha^{\text{HF}}(\vec{r}, \vec{r}')$. $\rho(\vec{r}')$ being irrelevant to $\vec{r}$ the electron correlation, that is, when an electron moves to position $\vec{r}$ the valance electrons originally positioned there should be squeezed out by the repulsive Coulomb force and changes in its state, is neglected. The electron correlation is taken into account to some extent only between the electrons of same spins as displayed by the exchange hole (3.158). This is an accidental correlation caused by the Pauli exclusion principle but not electric Coulomb repulsion. According to the physical pattern of hole, every electron should have a correlation hole around itself. As a result of the neglect of correlation the superposition of electrons is exaggerated and the Coulomb interaction energy is overestimated. The fault of neglect of electron correlation originates from the mean field approximation.

The exchange potential $\int \frac{\rho_\alpha^{\text{HF}}(\vec{r}, \vec{r}')e^2}{4\pi\epsilon_0|\vec{r} - \vec{r}'|} d\vec{v}'$ is commonly simplified by some kind of average $V_{\text{ex}}(\vec{r})$. A widely used one is to approximate it by the exchange potential of free electron gas of same density $\rho(\vec{r})$ (Slater 1951)

$$V_{\text{ex}}(\vec{r}) = -6b \left[\frac{3\rho(\vec{r})}{4\pi} \right]^{1/3}, \quad (3.159)$$

in which b is 1 (Slater 1951) or $2/3$ (Gasper 1954; Kohn and Sham 1965; Rajagopal and Callaway 1973). Thus (3.155) simplifies to

$$U(\vec{r}) = V(\vec{r}) + \int \frac{\rho(\vec{r}')e^2}{4\pi\epsilon_0|\vec{r}-\vec{r}'|}d\vec{r}' + V_{\text{ex}}[\rho(\vec{r})]. \quad (3.160)$$

The correlation is very important for 3d electrons. Very strong correlation in ferrites forces the 3d electrons to essentially localize in each ion. The band theory based on the mean field approximation cannot explain the magnetic properties of 3d metals and alloys satisfactorily.

3.8.4 Stoner Model of Ferromagnetism

3.8.4.1 Stoner Model

The Stoner theory of ferromagnetism for metal is based on the mean field approximation.

Let $\varepsilon_{\vec{k}}$ denotes the eigenenergy of Bloch wave $\varphi_{\vec{k}}(\vec{r})$ in the effective potential field not including exchange potential V_{ex} (3.160) and $N_{\pm}$ the number of spin-up and -down electrons in a unit volume. The total number of valence electrons N and magnetic polarization J in the μ_B unit are

$$N = N_- + N_+, \quad J = N_- - N_+ = Nm. \quad (3.161)$$

Consider the exchange energy. Suppose the exchange integral J_A is positive and define

$$U \equiv J_A N. \quad (3.162)$$

By taking the exchange energy between a pair of the same spin electrons zero, the exchange energy between a pair of opposite spin electrons is $2J_A$. Therefore, the exchange energy of the electron system is $2J_A N_+ N_- = (1/2)[N_+(2J_A N_-) + N_-(2J_A N_+)]$ in which $2J_A N_- = 2J_A(N+J)/2 = 2U(1/2+m/2)$ is the exchange energy of a spin-up electron with all spin-down electrons, and $2J_A N_+ = 2J_A(N-J)/2 = 2U(1/2-m/2)$ is that of a spin-down electron with all spin-up electrons. By neglecting the irrelevant to spin terms of $U/2$, the total energy of the system in a magnetic field H is

$$\begin{aligned} E &= \sum_{\vec{k},-} \left(\varepsilon_{\vec{k}} - \frac{U}{2}m - \mu_B H \right) + \sum_{\vec{k},+} \left(\varepsilon_{\vec{k}} + \frac{U}{2}m + \mu_B H \right) \\ &= \int_0^\infty n(\varepsilon) \left[\varepsilon - \frac{U}{2}m - \mu_B H \right] f \left[\varepsilon - \frac{U}{2}m - \mu_B H \right] d\varepsilon \\ &\quad + \int_0^\infty n(\varepsilon) \left[\varepsilon + \frac{U}{2}m + \mu_B H \right] f \left[\varepsilon + \frac{U}{2}m + \mu_B H \right] d\varepsilon, \end{aligned} \quad (3.163)$$

and (3.161) can be expressed as

$$N = \int_0^{\infty} n(\varepsilon) f \left[\varepsilon - \frac{U}{2}m - \mu_B H \right] d\varepsilon + \int_0^{\infty} n(\varepsilon) f \left[\varepsilon + \frac{U}{2}m + \mu_B H \right] d\varepsilon, \quad (3.164)$$

$$J = \int_0^{\infty} n(\varepsilon) f \left[\varepsilon - \frac{U}{2}m - \mu_B H \right] d\varepsilon - \int_0^{\infty} n(\varepsilon) f \left[\varepsilon + \frac{U}{2}m + \mu_B H \right] d\varepsilon. \quad (3.165)$$

Here $n(\varepsilon)$ is the spin-resolved DOS for $U=H=0$, and

$$f(\varepsilon) = \frac{1}{\exp \left(\frac{\varepsilon - \zeta}{k_B T} \right) + 1} \quad (\zeta : \text{chemical potential}) \quad (3.166)$$

is the Fermi-Dirac distribution. If $T=0$,

$$f(\varepsilon \leq \zeta) = 1, f(\varepsilon > \zeta) = 0, -\frac{df(\varepsilon)}{d\varepsilon} = \delta(\varepsilon - \zeta), \quad (3.167)$$

and if $T=U=H=0$, $\zeta = \varepsilon_F$.

By the by, $-(U/2)m$ can be seen as the potential energy of the spin-down electron magnetic moment in the molecular field and $(U/2)m$ that of the spin-up electron magnetic moment. The value of ζ and m can be obtained from (3.164) and minimum condition of E (3.163), respectively. The following are some results.

3.8.4.2 Stoner Criterion for Ferromagnetism

Consider the case of $H = T = 0$.

If $U = 0$, $\varepsilon_{\vec{k}}$ being irrelevant to spin, the same spin-resolved band structure (Fig.3.28a) of $J_s = 0$ is the stable state with the smallest energy of

$$\sum_{\vec{k}, -} \varepsilon_{\vec{k}} + \sum_{\vec{k}, +} \varepsilon_{\vec{k}}.$$

If $U \neq 0$, the up- and down-spin band may shift upward and downward by $\Delta = Um/2 (\ll \varepsilon_F)$, respectively, (3.163) and the spin-up electrons above the Fermi energy level transfer into the vacant states of the spin-down band below the Fermi energy level by changing the spin and $\vec{k}$ bringing the Fermi energy levels of the spin bands to the same level (Fig.3.28b–c). Thus, with respect to the same spin-resolved band structure the exchange energy decreases by

$$2J_A \left\{ \left[\frac{N}{2} + \frac{n(\varepsilon_F)Um}{2} \right] \left[\frac{N}{2} - \frac{n(\varepsilon_F)Um}{2} \right] - \left(\frac{N}{2} \right)^2 \right\} = -2J_A \left(\frac{n(\varepsilon_F)J_A J}{2} \right)^2, \quad (3.168)$$

but other energies $\sum_{\vec{k},-} \varepsilon_{\vec{k}} + \sum_{\vec{k},+} \varepsilon_{\vec{k}}$ increase by

$$n(\varepsilon_F) \left(\frac{Um}{2} \right)^2 = n(\varepsilon_F) \left(\frac{J_A J}{2} \right)^2. \quad (3.169)$$

The change in total energy is the sum of them:

$$\Delta E = \frac{J_A^2 J^2 n(\varepsilon_F)}{4} [-2J_A n(\varepsilon_F) + 1]. \quad (3.170)$$

If $\Delta E > 0$, the state of same spin-resolved band structure of $J_s=0$ (Fig.3.28a) remains stable. If $\Delta E < 0$, i.e.

$$2J_A n(\varepsilon_F) > 1, \quad (3.171)$$

the state of spontaneous magnetization becomes stable. The above equation is called Stoner criterion for ferromagnetism. The $n(\varepsilon)$ of 4s electrons being small the electrons are difficult to produce spontaneous magnetization. In contrast to the 4s electrons the $n(\varepsilon_F)$ of 3d electrons is large and hence they are easier to produce spontaneous magnetization.

The following results are deduced for the $n(\varepsilon)$ of free electrons (3.141):

Equation (3.171) becomes

$$\frac{U}{2\varepsilon_F} > \frac{2}{3}. \quad (3.172)$$

If

$$\frac{2}{3} < \frac{U}{2\varepsilon_F} < 2^{-1/3}, \quad (3.173)$$

$$0 < m < 1, \quad (3.174)$$

that is both of spin-up and -down bands are filled but by different number of electrons (Fig.3.28c), and the atomic magnetic polarization moment in general is not an integer multiple of μ_B .

If

$$\frac{U}{2\varepsilon_F} \geq 2^{-1/3}, \quad (3.175)$$

$$m = 1, \quad (3.176)$$

that is, only one spin-resolved band is filled and the other spin-resolved band is void, and the atomic magnetic polarization moment is an integral multiple of μ_B .

3.8.4.3 Pauli Paramagnetism

Consider the case of $2J_A n(\varepsilon_F) < 1$ and $H \neq 0$.

$J_s = 0$ and

$$f\left(\varepsilon_{\vec{k}} \pm \frac{U}{2}m \pm \mu_B H\right) \approx f(\varepsilon_{\vec{k}}) \pm \frac{df(\varepsilon_{\vec{k}})}{d\varepsilon_{\vec{k}}} \left(\frac{U}{2}m + \mu_B H\right),$$

$$\left(\frac{U}{2}m + \mu_B H \ll \varepsilon\right) \quad (3.177)$$

and (3.164)–(3.165) become

$$N = 2 \int_0^{\infty} n(\varepsilon) f(\varepsilon) d\varepsilon, \quad (3.178)$$

$$J = -2 \left(\frac{J_A J}{2} + \mu_B H \right) \int_0^{\infty} n(\varepsilon) \frac{df(\varepsilon)}{d\varepsilon} d\varepsilon. \quad (3.179)$$

If $U = 0$, the susceptibility is

$$\chi_p \mu_0 = \frac{\mu_B J}{H} = -2\mu_B^2 \int_0^{\infty} n(\varepsilon) \frac{df(\varepsilon)}{d\varepsilon} d\varepsilon, \quad (3.180)$$

which is

$$\chi_p \mu_0 = 2n(\varepsilon_F) \mu_B^2 \quad (3.181)$$

at 0 K. The relation is the same as (3.144) of the free electron gas.

If $U \neq 0$ and $T = 0$,

$$\chi \mu_0 = \frac{\mu_B J}{H} = \frac{\chi_p \mu_0}{1 - J_A n(\varepsilon_F)} > \chi_p \mu_0. \quad (3.182)$$

3.8.4.4 Comparison of the Theory with Experiments

Equation (3.182) explains the Pauli paramagnetism of transition metals such as Nb($4d^4 5s^1$), Tc($4d^5 5s^2$), U($5f^3 6s^2 6p^6 6d^1 7s^2$), Pu($5f^5 6s^2 6p^6 6d^1 7s^2$), etc. The values of susceptibility for them are in the range of $200 \times 10^{-6} \sim 600 \times 10^{-6}$ per gram molecule, one order larger than those of nontransition metals (Sect. 3.7.3).

Figure 3.31 shows $M_s(T)/M_s(0)$ ($T/T_C \leq 1$) and $[M_s(0)\mu_B/k_B T_C]/\chi$ ($T/T_C \geq 1$) as a function of T/T_C for different values of $U/2\varepsilon_F$. The theoretical

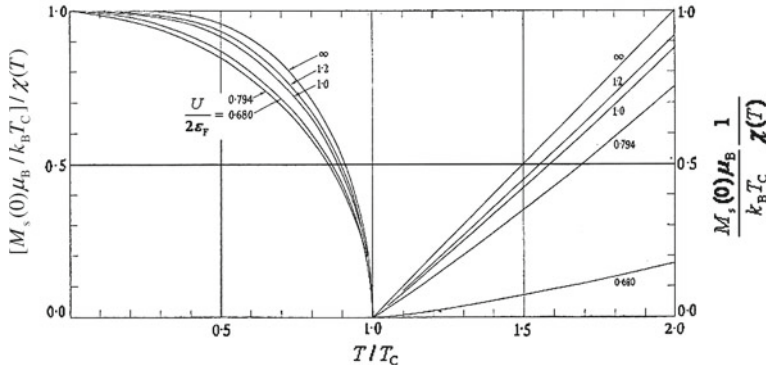


Fig. 3.31 $M_s(T)/M_s(0)(T/T_C \leq 1)$ and $[M_s(0)\mu_B/k_B T_C]/\chi(T)(T/T_C \geq 1)$ versus T/T_C for different values of $U/2\varepsilon_F$ [19]

results coincide with experiments qualitatively. But they are not satisfactory quantitatively.

According to the theory temperature dependence of $J_s(T)/J_s(0)$ at low temperatures is

$$\frac{J_s(T)}{J_s(0)} = 1 - \frac{\pi^2}{12} \left(\frac{k_B T}{\varepsilon_F} \right)^2, \quad (3.183)$$

which does not coincide with the $T^{3/2}$ law. The T_C of theory

$$T_C = \frac{\varepsilon_F}{k_B} \sqrt{\frac{12}{\pi^2} \frac{n(\varepsilon_F) - 1}{J_A n(\varepsilon_F)}} \quad (3.184)$$

is far larger than the experimental values. The theoretical paramagnetic susceptibility

$$\chi \sim \frac{(\varepsilon_F/k_B)^2}{T^2 - T_C^2} \quad (3.185)$$

does not coincide with Curie-Weiss law.

The above results show that the Stoner model (1938-1939) is not satisfactory. The limited success of the theory roots on the mean field approximation which neglects the electron correlation.

3.8.5 Density Functional Theory

The density functional theory (DFT) founded in the mid-1960s provides a rigorous basis of one-electron method and became the foundation of the modern band theory since then. The essentials of the DFT are as follows:

3.8.5.1 Corollary to the Hohenberg–Kohn Theorem

There is an invertible one-to-one relationship between the external potential $V(\vec{r})$ and the density of electrons $\rho(\vec{r})$ for the ground state of electron system.

3.8.5.2 Basic Variable $\rho(\vec{r})$

If $V(\vec{r})$ is given, the eigenstate Ψ , eigenenergy E , kinetic energy T , and the interaction energy between the electrons V_{ee} for the ground state are determined. According to the above HK corollary, the physical quantities can be expressed as the functional of $\rho(\vec{r})$: $\Psi[\rho]$, $E[\rho]$, $T[\rho]$, and $V_{ee}[\rho]$, i.e. $\rho(\vec{r})$ is the basic variable for all physical properties.

3.8.5.3 HK Theorem

The energy functional is

$$E[\rho, V] = T[\rho] + V_{ee}[\rho] + \int V(\vec{r})\rho(\vec{r})d\mathbf{v}. \quad (3.186)$$

When $\rho(\vec{r})$ becomes rigorously the ground state density, $E[\rho, V]$ takes the minimum value, which is just the ground state energy.

3.8.5.4 Exchange-Correlation Functional

Suppose $\{\varphi_\alpha(\vec{r})\}$ ($\alpha = 1, 2, \dots, N$) is a set of independent orthonormal one-electron orbitals which can produce rigorous ground state density

$$\rho(\vec{r}) = \sum_{\alpha}^{1,2,\dots,N} |\varphi_\alpha(\vec{r})|^2. \quad (3.187)$$

Then (3.186) can be reformulated as

$$E[\rho, V] = T_0[\rho] + V_H[\rho] + E_{xc}[\rho] + \int V(\vec{r})\rho(\vec{r})d\mathbf{v}, \quad (3.188)$$

where

$$T_0[\rho] = \sum_{\alpha}^{1,2,\dots,N} \int \varphi_\alpha^*(\vec{r}) \left(-\frac{\hbar^2}{2m} \nabla^2 \right) \varphi_\alpha(\vec{r}) d\mathbf{v}, \quad (3.189)$$

$$V_H[\rho] = \frac{1}{2} \int \frac{e^2 \rho(\vec{r}) \rho(\vec{r}')}{4\pi \epsilon_0 |\vec{r} - \vec{r}'|} d\mathbf{v} d\mathbf{v}', \quad (3.190)$$

$$E_{xc}[\rho] = T[\rho] - T_0[\rho] + V_{ee}[\rho] - V_H[\rho]. \quad (3.191)$$

The difference of the right of (3.188) from that of Hartree-Fock approximation is the term of $E_{xc}[\rho]$. It contains the exchange and correlation energies $V_{ee}[\rho] - V_H[\rho]$, and all of many-body effects $T[\rho] - T_0[\rho]$ caused by the replacement of kinetic energy functional $T[\rho]$ by the kinetic energy of the noninteracting electron system $T_0[\rho]$. $E_{xc}[\rho]$ is called exchange-correlation functional.

3.8.5.5 Kohn–Sham Self Consistent Equations

According to the HK theorem, the ground state energy and density can be obtained from variation (minimum condition) of energy functional with respect to density $\rho(\vec{r})$, which can be transformed into the variation with respect to $\{\varphi_\alpha(\vec{r})\}$ and $\{\varphi_\alpha^*(\vec{r})\}$. The orthonormality of $\{\varphi_\alpha(\vec{r})\}$ is the restriction condition. Let $\{\lambda_\alpha\}$ a set of Lagrange multipliers. By solving the variation equation of $E[\rho, V] - \sum_{\alpha=1,2,\dots,N} \lambda_\alpha \int \varphi_\alpha^*(\vec{r}) \varphi_\alpha(\vec{r}) d\mathbf{v}$, we get the effective independent electron equation (3.145) in which

$$U(\vec{r}) \equiv V(\vec{r}) + \int \frac{e^2 \rho(\vec{r}')}{4\pi \epsilon_0 |\vec{r} - \vec{r}'|} d\mathbf{v}' + \frac{\delta E_{xc}[\rho]}{\delta \rho(\vec{r})}. \quad (3.192)$$

Equations (3.145) and (3.192) are called KS self-consistent equations.

3.8.6 Local Density Approximation and Generalized Gradient Approximation

To solve the KS self-consistent equations, the specific expression of $E_{xc}[\rho]$ should be known. $E_{xc}[\rho]$ can be written in the form of

$$E_{xc}[\rho] = \int g_{\vec{r}}[\rho] d\mathbf{v}, \quad (3.193)$$

where $g_{\vec{r}}[\rho]$ is an energy functional at position $\vec{r}$ which is affected by variation of density at any position $\vec{r}'$. If the variation of $\rho(\vec{r})$ with position is sufficiently slow, $g_{\vec{r}}[\rho]$ can be expanded as

$$g_{\vec{r}}[\rho] = g_0[\rho(\vec{r})] + g_1[\rho(\vec{r})] \nabla \rho(\vec{r}) + \dots \quad (3.194)$$

The local density approximation (LDA) takes into account only the first term on the right-hand side of the above equation. Under this approximation (3.193) simplifies to a localized integration

$$E_{\text{xc}}^{\text{LDA}}[\rho] = \int \varepsilon_{\text{xc}}[\rho(\vec{r})]\rho(\vec{r})d\mathbf{v}, \quad (3.195)$$

where $\varepsilon_{\text{xc}}[\rho(\vec{r})]$ is the exchange-correlation energy per electron for a uniform electron system, and the last term of exchange-correlation on the right-hand side of (3.192) simplifies to

$$\frac{\delta E_{\text{xc}}^{\text{LDA}}}{\delta \rho(\vec{r})} = V_{\text{xc}}^{\text{LDA}}(\vec{r}) = \varepsilon_{\text{xc}}(\rho(\vec{r})) + \rho(\vec{r}) \frac{d\varepsilon_{\text{xc}}(\rho(\vec{r}))}{d\rho(\vec{r})}. \quad (3.196)$$

A corresponding approximation for a spin polarized system is the local spin-density approximation (LSDA). The exchange-correlation energy functional for LSDA is

$$E_{\text{xc}}^{\text{LSDA}}[\rho_+, \rho_-] = \int \varepsilon_{\text{xc}}[\rho_+(\vec{r}), \rho_-(\vec{r})]\rho(\vec{r})d\mathbf{v}. \quad (3.197)$$

ε_{xc} is the sum of exchange energy ε_{x} and correlation energy ε_{c} per electron,

$$\varepsilon_{\text{xc}} = \varepsilon_{\text{x}} + \varepsilon_{\text{c}}. \quad (3.198)$$

The generalized gradient approximation (GGA) takes into account also the second term of the expansion in (3.194), and the exchange-correlation energy functional is

$$E_{\text{xc}}^{\text{GGA}}[\rho_+, \rho_-] = \int f_{\text{xc}}[\rho_+(\vec{r}), \rho_-(\vec{r}), \nabla\rho_+, \nabla\rho_-]d\mathbf{v}. \quad (3.199)$$

The GGA calculation gets substantially better agreement with experiment than LSDA. The expressions of $\varepsilon_{\text{xc}}[\rho_+(\vec{r}), \rho_-(\vec{r})]$ of a uniform electron gas is well established, but the best choice of $f_{\text{xc}}[\rho_+(\vec{r}), \rho_-(\vec{r}), \nabla\rho_+, \nabla\rho_-]$ is still a matter of debate.

Other methods, such as the GGA+ U scheme, are also in use.

3.8.7 Methods of Energy Band Calculations

Regardless of whether the basis of the band theory is mean field approximation or DFT, (3.145) should be solved.

Many approaches of calculation have been used. The main differences between different approaches are in two aspects. One is a different set of functions by which the wave function φ_{α} is expanded. Another is different approximation made on $U(\vec{r})$. Each method introduces several approximations further to carry out the calcu-

lations. Typical methods include tight-binding (TB) method, orthogonalized plane wave (OPW) method, pseudopotential method, cellular method, linear muffin-tin orbital (LMTO) method, augmented plane wave (APW) method, linear augmented plane wave (LAPW) method, full-potential LAPW method, Korringa Kohn Rostoker (KKR) method (also called Green's function method), etc.

Take the LAPW method based on DFT as an example. It is one of the most precise methods. A crystal cell is divided into non-overlapping atomic spheres and remaining interstitial region. In many cases the potential in each atomic sphere is approximated to be spherically symmetrical which is called Muffin-tin potential. In a more accurate method non-spherical full-potential is adopted. In the remaining interstitial region, the potential is approximated as a constant.

Each radial function of the atom $R_{nl}(r)$ in the atomic sphere is Taylor expanded at an energy E_{nl} around the eigenenergy E of the orbit (n, l) . The linear augmented plane wave of wave vector $\vec{k}$ is

$$\varphi_{\vec{k}}(\vec{r}) = \begin{cases} \sum_{n,l,m_l} [A_{nlm_l,\vec{k}} R_{nl}(r, E_{nl}) + B_{nlm_l,\vec{k}} \frac{\partial R_{nl}(r, E_{nl})}{\partial E}] Y_{lm_l}(\vec{r}), & \text{(in each atomic sphere)} \\ \Omega^{-1/2} \exp(i\vec{k} \cdot \vec{r}), & \text{(in interval space)} \end{cases} \quad (3.200)$$

The values of $A_{nlm_l,\vec{k}}$ and $B_{nlm_l,\vec{k}}$ can be obtained from the continuous conditions of $\varphi_{\vec{k}}$ and its derivative on the surfaces of atomic spheres, and $R_{nl}(r, E_{nl})$ and $\frac{\partial R_{nl}(r, E_{nl})}{\partial E}$ can be obtained by numerically solving the Schrödinger equation. The Bloch wave is

$$\Phi_{\vec{k}}(\vec{r}) = \sum_{\vec{K}_i} C_{\vec{K}_i}(\vec{k}) \varphi_{\vec{k}+\vec{K}_i}(\vec{r}), \quad (3.201)$$

where the sum is taken in the finite range of $|\vec{K}_i| < K_{\text{mx}}$ with appropriately selected value of K_{mx} . From the variation of the total energy we get a set of simultaneous linear equations of $C_{\vec{K}_i}(\vec{k})$. The eigenenergy $E_{\vec{k}}$ for each $\vec{k}$ can be obtained by solving the secular equation

$$| \langle \varphi_{\vec{k}+\vec{K}_i} | \hat{H} | \varphi_{\vec{k}+\vec{K}_j} \rangle - E_{\vec{k}} \langle \varphi_{\vec{k}+\vec{K}_i} | \varphi_{\vec{k}+\vec{K}_j} \rangle | = 0, \quad (|\vec{K}_i|, |\vec{K}_j| < K_{\text{mx}}) \quad (3.202)$$

and $\{C_{\vec{K}_i}(\vec{k})\}$ can be obtained by substituting $E_{\vec{k}}$ into the linear equations. The number of $\vec{k}$ -points should be large enough to get a fine enough band structure (smooth DOS curve).

Fig. 3.32 The band structures of Fe and Ni metals calculated by use of GW (approximation used in KKR method), LSDA and static COHSEX(Coulomb-hole-plus-screened-exchange) methods. Solid lines: majority spin; Dotted lines: minority spin. The energy is with respect to the Fermi energy level shown by the dotted vertical line [20]

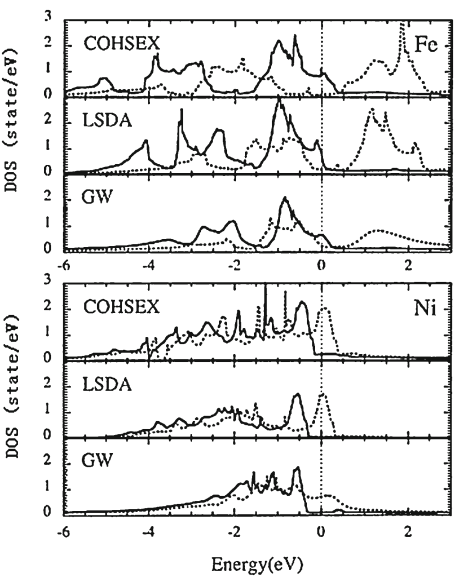


Table 3.6 Values of magnetic polarization moments of Fe, Co, and Ni atoms in the metals [21]

	p_J/μ_B	
	Calculation	Experiment
Fe	2.29	2.22
Co	1.61	1.72
Ni	0.62	0.61

3.8.8 Examples of Band Structures

3.8.8.1 DOS of Fe and Ni Metals

Figure 3.32 demonstrates the band structures of ferromagnetic Fe and Ni metals calculated by different methods. The Fermi energy level is within the valence band which corresponds to its current conductive property.

3.8.8.2 Atomic Magnetic Moments of Fe, Co, and Ni in the Metals

Table 3.6 demonstrates the values of magnetic polarization moments of Fe, Co, and Ni atoms in the pure metals calculated by GGA and LAPW methods in the framework of LSDA, which are compared with the experimental values.

3.8.8.3 DOS of NiO

NiO at low temperatures has the cubic structure of MnO (Fig.3.9). Figure 3.33a and b demonstrate the spin-resolved and total DOS calculated by applying so-called unoccupied-states potential correction in the LSDA formalism. The full and broken curves in Fig.3.33a represent the E_g and T_g (Fig. 3.26) contribution, respectively. Figure 3.33c shows the experimental spectra of a photoemission spectroscopy (PES) and BIS, one of inverse photoemission spectroscopy (IPES). The fully filled valence band is separated by an energy gap from the completely void conduction band, which corresponds to its insulating property. The calculated energy gap of 3.9 eV is in agreement with the experimental value of 4–4.3 eV. The peaks of (D, E) are of 3d, and (B, C) are of purely O2p or mixed (Ni3d-O2p). The calculations reproduce all energies of the peaks well. The calculated magnetic polarization moment of Ni atom is $1.68\mu_B$ compared to the experimental values of $1.64\mu_B$ and $1.77\mu_B$.

In the experiment of PES, a light beam of photon energy $\hbar\omega$ is irradiated onto the sample, and photoelectrons of varying kinetic energy E_T are emitted. By recording the photoelectron count n_e as a function of E_T , the kinetic energy spectrum $n_e(E_T)$ can be obtained.

$$E_T = \hbar\omega - (\varepsilon_{vm} - \varepsilon) - \Phi, \quad (3.203)$$

where ε_{vm} is the maximum energy level of the valence band, ε is the energy of the electron in the sample before it is emitted, and Φ is the work function which corresponds to the minimum amount of energy to remove an electron of valence band maximum energy from the insulator. The value of ε corresponding to E_T can be obtained from the relation of (3.203), and the energy spectrum $n_e(\varepsilon)$ is constructed from $n_e(E_T)$. $n_e(\varepsilon)$ among other factors is proportional to the total DOS $n(E)$ of the filled valence band.

In the experiment of IPES, a well-collimated electron beam of well-defined kinetic energy E_T is irradiated onto the sample. These electrons couple to high-lying unfilled electronic states and decay to low-lying unfilled states of energy levels ε by emitting photons of energies $\hbar\omega$. Each ε relates with corresponding $\hbar\omega$ through the relation

$$\varepsilon = E_T - \hbar\omega. \quad (3.204)$$

The photons emitted in the decay process are recorded, from which an energy spectrum, photon counts n_p versus ω , is generated. The energy spectrum $n_p(\varepsilon)$ is constructed from the spectrum $n_p(\omega)$. $n_p(\varepsilon)$ among other factors is proportional to the total DOS of non-filled conduction band.

Note 1

Let

$$\varphi_\alpha(\vec{r} + \vec{a}_j) = C_j \varphi_\alpha(\vec{r}). \quad (C_j : \text{undetermined constant}) \quad (3.205)$$

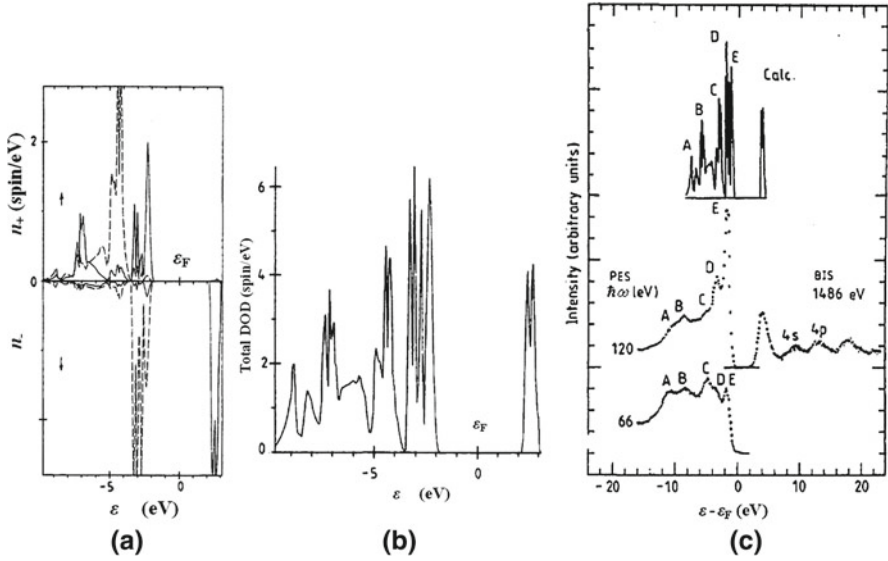


Fig. 3.33 Spin-resolved DOS (a), total DOS (b) and PES and BIS spectra (c) for NiO [22]

Since $|\varphi_\alpha(\vec{r} + \vec{a}_j)|^2 = |\varphi_\alpha(\vec{r})|^2$ and $\varphi_\alpha(\vec{r} + N_j \vec{a}_j) = \varphi_\alpha(\vec{r})$ it holds

$$C_j C_j^* = 1, C_j^{N_j} = 1, \quad (3.206)$$

from which we get

$$C_j = \exp(ik_j) \equiv C_j(k_j), \quad k_j = \frac{2\pi}{N_j} \times \text{integer}. \quad (3.207)$$

Let $\varphi_{\vec{k}}$ represent the φ_α of $\{k_j\}$ ($j=1, 2, 3$), then

$$\begin{aligned} \varphi_{\vec{k}}(\vec{r} + \vec{R}_n) &= C_1^{n_1}(k_1) C_2^{n_2}(k_2) C_3^{n_3}(k_3) \varphi_{\vec{k}}(\vec{r}) \\ &= \exp\left(i \sum_{j=1,2,3} k_j n_j\right) \varphi_{\vec{k}}(\vec{r}) = \exp(i\vec{k} \cdot \vec{R}_n) \varphi_{\vec{k}}(\vec{r}), \end{aligned} \quad (3.208)$$

$$u_{\vec{k}}(\vec{r} + \vec{R}_n) = \exp[-i\vec{k} \cdot (\vec{r} + \vec{R}_n)] \varphi_{\vec{k}}(\vec{r} + \vec{R}_n) \quad (3.150)$$

$$\begin{aligned} &= \exp[-i\vec{k} \cdot (\vec{r} + \vec{R}_n)] \exp(i\vec{k} \cdot \vec{R}_n) \varphi_{\vec{k}}(\vec{r}) \\ &= \exp(-i\vec{k} \cdot \vec{r}) \varphi_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r}). \end{aligned} \quad (3.209)$$

Note 2

The integral of $\varphi_{\vec{k}'}^*(\vec{r})\varphi_{\vec{k}}(\vec{r})$ in a hexahedron of unit length edges parallel to $\{\vec{a}_\alpha\}$ is

$$\begin{aligned} \int \varphi_{\vec{k}'}^*(\vec{r})\varphi_{\vec{k}}(\vec{r})d\mathbf{v} &= \int u_{\vec{k}'}(\vec{r})u_{\vec{k}}(\vec{r})\exp[i(\vec{k}-\vec{k}')\cdot\vec{r}]d\mathbf{v} \\ &= \sum_n^{1,2,\dots,N} \int_{\text{unit cell}} u_{\vec{k}'}(\vec{r})u_{\vec{k}}(\vec{r})\exp[i(\vec{k}-\vec{k}')\cdot(\vec{r}+\vec{R}_n)]d\mathbf{v} \quad (N=N_1N_2N_3) \\ &= \int u_{\vec{k}'}(\vec{r})u_{\vec{k}}(\vec{r})\exp[i(\vec{k}-\vec{k}')\cdot\vec{r}]d\mathbf{v} \sum_n^{1,2,\dots,N} \exp[i(\vec{k}-\vec{k}')\cdot\vec{R}_n]. \quad (3.210) \end{aligned}$$

$$\text{If } \vec{k} \neq \vec{k}', \vec{k}-\vec{k}' = \sum_j^{1,2,3} \frac{2\pi m_j}{N_j} \vec{b}_j \neq 0,$$

$$\sum_n^{1,2,\dots,N} \exp[i(\vec{k}-\vec{k}')\cdot\vec{R}_n] = \prod_j \left[\sum_{n_j}^{1,2,\dots,N_j} \exp \left(i \sum_j^{1,2,3} \frac{2\pi m_j}{N_j} n_j \right) \right] = 0. \quad (3.211)$$

3.9 Hyperfine Interactions in Solids**3.9.1 Hamiltonian of a Nucleus in a Magnetic Field**

The Hamiltonian of a nucleus in a magnetic field $\vec{H}$ is the sum of the Zeeman energy $\hat{H}_H$ and the hyperfine interactions $\hat{H}_{\text{hf}}$,

$$\hat{H} = \hat{H}_H + \hat{H}_{\text{hm}} + \hat{H}_{\text{q}} + \hat{H}_{\text{e0}}, \quad (2.215) \quad (3.212)$$

$$\hat{H}_H = -g_N\mu_N\hat{I}\cdot\vec{H}, \quad (2.192) \quad (3.213)$$

$$\hat{H}_{\text{hm}} = -g_N\mu_N\hat{I}\cdot\vec{H}_{\text{hm}}, \quad (2.199) \quad (3.214)$$

$$\hat{H}_{\text{q}} = \frac{|e|}{2} \sum_p^{1,\dots,Z} \sum_{\alpha,\beta}^{x,y,z} V_{\alpha\beta} \alpha_p \beta_p, \quad (2.213) \quad (3.215)$$

$$\hat{H}_{e0} = \frac{3Ze^2}{10\epsilon_0} |\Psi(0)|^2 r_N^2. \quad (2.214), |\Psi(0)|^2 = \sum_{(i,\sigma)} |\psi_{i,\sigma}(0)|^2,$$

$$\text{sum } \sum_{(i,\sigma)} \text{ is over all electrons at the nucleus site } r = 0) \quad (3.216)$$

In solids a nucleus interacts not only with the electrons of the central ion but also with the external electrons and nuclei, thereby the hyperfine parameters $\vec{H}_{\text{hm}}$, $V_{\alpha\beta}$, and $|\Psi(0)|^2$ in the above equations are different from those of the free ion. The hyperfine parameters provide some microscopic information about the physical and chemical environment of the central ion along with the state of the ion itself.

The matrix consisted of nine components $\{V_{\alpha\beta}\}$ is called electric field gradient (EFG). $V_{\alpha\beta}$ being real and $V_{\alpha\beta} = V_{\beta\alpha}$, the matrix is Hermitian and hence can be diagonalized in an appropriate symmetrical coordinate x' , y' , and z' (A4.2.4):

$$(V') = \begin{pmatrix} V_{x'x'} & 0 & 0 \\ 0 & V_{y'y'} & 0 \\ 0 & 0 & V_{z'z'} \end{pmatrix}. \quad (3.217)$$

The principal x' , y' , and z' axes are selected by the conditions of $|V_{x'x'}| \leq |V_{y'y'}| \leq |V_{z'z'}|$. The asymmetry parameter of EFG is defined by the relation of

$$\eta \equiv \frac{V_{x'x'} - V_{y'y'}}{V_{z'z'}}. \quad (0 \leq \eta \leq 1) \quad (3.218)$$

Since

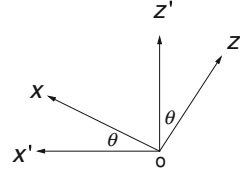
$$V_{x'x'} + V_{y'y'} + V_{z'z'} = -\nabla \cdot \vec{E} = 0, \quad (\vec{E} : \text{electric field produced by the electric charge outside the nucleus}) \quad (3.219)$$

$$V_{x'x'} = -\frac{1}{2}(1 - \eta)V_{z'z'}, \quad V_{y'y'} = -\frac{1}{2}(1 + \eta)V_{z'z'}, \quad (3.220)$$

that is, the two parameters of $V_{z'z'}$ and η provide all information about the EFG. One source of EFG is the neighbor electric charges. The second is the distorted fully electric subshells of the central ion. The third is the partially filled electric subshell of the central ion. For the third source take a high-spin state $\text{Fe}^{+2}(3d^6)$ ion as an example. The electron cloud of five 3d electrons of parallel spins is spherically symmetrical and does not produce EFG if not distorted. The remaining 3d electron of opposite spin direction produces a significant EFG.

The hyperfine parameters can be measured by use of nuclear magnetic resonance (NMR) and Mössbauer spectroscopies.

Fig. 3.34 xyz and $x'y'z'$ coordinate



3.9.2 Hyperfine Energy Eigenvalue

In a magnetic ordered medium of spontaneous magnetization not very small, the electric-quadrupole interaction $\hat{H}_q$ in general is one order of magnitude smaller than the hyperfine magnetic interaction $\hat{H}_{hm}$ (Fig.3.24) and can be treated as perturbation.

Assume that $\vec{H} // \vec{H}_{hm} // z$ axis. The eigenstate of $\hat{H} - \hat{H}_q$ is $|\alpha, I, M_I\rangle$, and the eigenenergy is

$$\begin{aligned} E(I, M_I) - E_q(I, M_I) &= \left\langle \alpha, I, M_I \left| -g_N \mu_N (H + H_{hm}) \hat{I}_z + \frac{3Ze^2}{10\epsilon_0} |\Psi(0)|^2 r_N^2 \right| \alpha, I, M_I \right\rangle \\ &= -g_N \mu_N (H + H_{hm}) M_I + \frac{3Ze^2}{10\epsilon_0} |\Psi(0)|^2 r_{NI}^2, \\ (M_I &= -I, -I+1, \dots, I, (3.212)) \end{aligned} \quad (3.221)$$

where g_{NI} and r_{NI} are the g_N and r_N for the spin state of I .

The expression of $\hat{H}_q$ in the frame of EFG principal axes is

$$\hat{H}_q = \frac{|e|}{2} \left(V_{x'x'} \sum_p^{1,\dots,Z} x_p'^2 + V_{y'y'} \sum_p^{1,\dots,Z} y_p'^2 + V_{z'z'} \sum_p^{1,\dots,Z} z_p'^2 \right). \quad (3.222)$$

To calculate the perturbation energy, the above representation should be transformed into that in the frame of the same x, y, z axes of $|\alpha, I, M_I\rangle$. Let θ denote the angle between z' and z axes and take the x axis in the $x'z'$ plane (Fig.3.34). The relations between the coordinates (x', y', z') and (x, y, z) are

$$x' = x \cos \theta - z \sin \theta, \quad y' = y, \quad z' = x \sin \theta + z \cos \theta. \quad (3.223)$$

Inserting (3.223) and (3.220) into (3.222), transforming the latter into the linear combination of the product of the components of irreducible tensor $\{Y_{2m_2}\}$ and r_p^2 , and then calculating the average of the latter over the $|\alpha, I, M_I\rangle$ state, we get the perturbation energy

$$E_q(I, M_I) = \frac{|e|}{2} \left\langle \alpha, I, M_I \left| V_{x'x'} \sum_p^{1,\dots,Z} x_p'^2 + V_{y'y'} \sum_p^{1,\dots,Z} y_p'^2 + V_{z'z'} \sum_p^{1,\dots,Z} z_p'^2 \right. \right.$$

$$\begin{aligned}
& \times \sum_p^{1,\dots,Z} z_p^2 \left| \alpha, I, M_I \right\rangle \\
& = \frac{|e|}{2} V_{z'z'} \left\langle I, M_I \left| \left[-\frac{1}{2}(1-\eta) \cos^2 \vartheta + \sin^2 \theta \right] \sum_p^{1,\dots,Z} x_p^2 - \frac{1}{2}(1+\eta) \right. \right. \\
& \quad \times \sum_p^{1,\dots,Z} y_p^2 + \left[-\frac{1}{2}(1-\eta) \sin^2 \theta + \cos^2 \theta \right] \sum_p^{1,\dots,Z} z_p^2 \\
& \quad \left. + \left[\frac{1}{2}(1-\eta) + 1 \right] 2 \sin \theta \cos \theta \sum_p^{1,\dots,Z} z_p x_p \right| I, M_I \right\rangle \\
& = \frac{|e|}{2} V_{z'z'} \left\langle I, M_I \left| \frac{1}{8} [(3+\eta) \sin^2 \theta + 2\eta \cos^2 \theta] \sum_p^{1,\dots,Z} [(x_p + iy_p)^2 \right. \right. \\
& \quad \left. + (x_p - iy_p)^2] \right. \\
& \quad \left. + \frac{1}{2}(3-\eta) \sin \theta \cos \theta \sum_p^{1,\dots,Z} [z_p(x_p + iy_p) + z_p(x_p - iy_p)] \right. \\
& \quad \left. + \frac{1}{2} \left[\cos^2 \theta - \frac{1}{2}(1-\eta) \sin^2 \theta \right] \sum_p^{1,\dots,Z} (3z_p^2 - r_p^2) \right| I, M_I \right\rangle \\
& = \begin{cases} 0, & (I = \frac{1}{2}) \\ \frac{|e|Q_I V_{z'z'}}{4I(2I-1)} [\cos^2 \theta - \frac{1}{2}(1-\eta) \sin^2 \theta] [3M_I^2 - I(I+1)]. & (I > \frac{1}{2}) \end{cases} \quad (3.224)
\end{aligned}$$

Inserting (3.224) into (3.221), we get the total eigenenergy

$$E(I, M_I) = \begin{cases} -g_{N\frac{1}{2}} \mu_N (H + H_{\text{hm}}) M_I + \frac{3Ze^2}{10\epsilon_0} |\Psi(0)|^2 r_{N\frac{1}{2}}^2, & (I = \frac{1}{2}) \\ -g_{NI} \mu_N (H + H_{\text{hm}}) M_I + \frac{3Ze^2}{10\epsilon_0} |\Psi(0)|^2 r_{NI}^2 \\ \quad + \frac{|e|Q_I V_{z'z'}}{4I(2I-1)} \left[\cos^2 \theta - \frac{1}{2}(1-\eta) \sin^2 \theta \right] \\ \quad \times [3M_I^2 - I(I+1)]. & (I > \frac{1}{2}) \end{cases} \quad (3.225)$$

3.9.3 Hyperfine Magnetic Field

If $\vec{H}=0$, the time average of magnetization of a nonmagnetic medium, like paramagnetic medium, is zero and $\vec{H}_{\text{hm}}=0$. But in a magnetic ordered medium, the magnetic ion has a spin magnetic moment and residual or complete orbital magnetic moment, which produces a hyperfine magnetic field. In addition, the 3d and

Table 3.7 Values of $\mu_0 H_{\text{hm}}$ in some magnetic materials

Material	Atom	Crystal site	$\mu_0 H_{\text{hm}}/\text{T}$	Temperature/K	Magnetism
Fe metal	Fe		33.0	300	Ferromagnetic
Fe ₃ O ₄	Fe	A	48.4	300	Ferrimagnetic
		B	45.9	300	
Nd ₂ Fe ₁₄ B (Fig.10.17)	Fe	c	28.3	300	
		e	27.6	300	
		j ₁	27.6	300	
		j ₂	34.2	300	
		k ₁	28.9	300	
		k ₂	30.2	300	
		f,g average	354	4.2	
SmCo ₅ (Fig.5.3)	Sm		342	4.2	Ferromagnetic

4f magnetic electrons polarize the s electrons through exchange interactions giving rise to the difference in $|\varphi_{n00}(0)|^2$ for different spin electrons and hence hyperfine magnetic field of the contact term (2.210).

In the case of isolated atom,

$$H_{\text{hm}} \propto \langle J, M_J | \hat{L}_z | J, M_J \rangle \propto \langle J, M_J | \hat{s}_z | J, M_J \rangle \propto \langle J, M_J | \hat{J}_z | J, M_J \rangle, \quad ((2.211), \text{A4.6, (a4.35)}) \quad (3.226)$$

that is, the hyperfine magnetic field is proportional to the magnetic moment of the atom. The hyperfine magnetic field in a solid is also nearly proportional to the magnetic moment of the central ion. The hyperfine magnetic field of a 3d ion mainly arises from the contact term and the value of $\mu_0 H_{\text{hm}}$ is tens of T. The field for a 4f ion arises from both electron orbital and spin magnetic moments, and the values are several hundred T (Table 3.7).

3.9.4 Principle of NMR Spectroscopy

There are two experimental methods: continuous wave method and Fourier transform (spin echo) method. The latter is dominating nowadays. The principle of NMR will be explained through analysis of the continuous wave method for weak magnetic media. The sample is held in a strong static magnetic field. A small low frequency alternating magnetic field parallel to the static field is superimposed so that the total magnetic field H is modulated in magnitude around the static field. A coil normal to the field direction is wound around the sample. A radio frequency current of angular frequency ω flows the coil. When the energy of the photon $\hbar\omega$ emitted by the coil equals the energy gap between the excited and ground states of the nucleus of sample,

that is,

$$\hbar\omega = |E(I, M_I \pm 1) - E(I, M_I)|, \quad (3.227)$$

some nuclei absorb the photons to transit from the ground state to an excited state. Consuming the energy of the electromagnetic wave, it causes increase in the electric impedance of the coil. Thus some absorption peaks are observed in the curve of the impedance versus H . By analyzing (3.227) and (3.225) with the experimental value of the resonance field H we can get some information about the hyperfine parameters.

Different from the weak magnetic media, magnetic ordered media have their own strong hyperfine magnetic fields and in general no field is applied. In this case the impedance of the coil is measured as a function of ω . A resonance absorb peak is observed when the frequency satisfies (3.227).

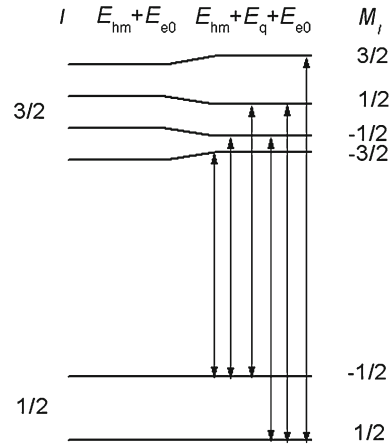
3.9.5 Principle of Mössbauer Spectroscopy

Take the most widely used ^{57}Fe Mössbauer spectroscopy as an example. Radioisotope ^{57}Co of 272 day half-life decays into the second excited state $I = 5/2$ of ^{57}Fe by trapping an electron, then transits to the first excited state $I = 3/2$ of ^{57}Fe (10^{-7} second half-life) by 91% probability followed by transition to the ground state $I = 1/2$, or directly transit from $I = 5/2$ state to the ground state $I = 1/2$ by 9% probability. The Mössbauer spectroscopy uses the γ -ray emitted during the transition from $I = 3/2$ to $I = 1/2$ state of energy level difference $\Delta E = 14.4$ keV. When the emission source, such as ^{57}Co containing Pd-Co alloy, emits the γ -ray, it may accompany the transition between the lattice vibration eigenstates caused by the recoil. But there is a large probability, about 100% at low temperatures, that the lattice vibration eigenstate remains unchanged. In such case the energy lost by the γ -ray is only the kinetic energy of the whole source of mass M . Let $\hbar\omega$ is the energy of the γ -ray, then the momentum of the ray is $\hbar\omega/c$ in which c is the light speed in vacuum. The recoil momentum and kinetic energy acquired by the emission source are $-\hbar\omega/c$ and $(\hbar\omega)^2/2Mc^2$. M being strikingly large the recoil kinetic energy is so small that it can be neglected and it holds

$$\Delta E = \hbar\omega + (\hbar\omega)^2/2Mc^2 = \hbar\omega. \quad (3.228)$$

The γ -ray is irradiated onto a thin sample containing ^{57}Fe (2.19% nuclei of natural Fe atom is ^{57}Fe). Each energy level of the state of $I = 1/2$ and $3/2$ in an ordered magnetic medium is split into $2I+1$ energy levels of different M_I under the hyperfine interactions. The γ -ray permeated through the sample reaches the recorder. The emission source vibrates by variable speed with respect to the sample making the frequency of the γ -ray ω Doppler scanned. The γ -ray strength recorded by the recorder as a function of the emission source speed is called Mössbauer spectrum. In most cases no magnetic field is applied for the measurement of the spectrum, and

Fig. 3.35 Energy level splitting of the $I=3/2$ and $1/2$ states of ^{57}Fe and the Mössbauer transitions

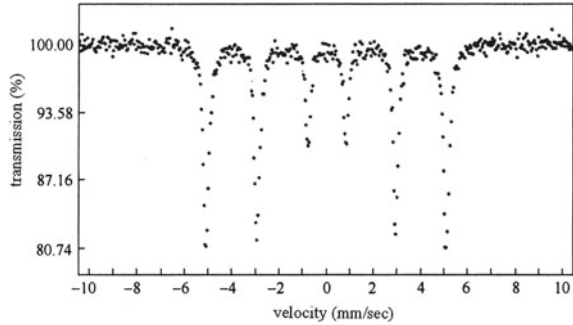


when the resonance conditions of transition between the $I = 1/2$ and $3/2$ states are satisfied, that is, (Fig. 3.35)

$$\begin{aligned}
 \hbar\omega &= -g_{N\frac{3}{2}}\mu_N H_{hm} M_{\frac{3}{2}} + \frac{3Ze^2}{10\epsilon_0} |\Psi(0)|^2 r_{N\frac{3}{2}}^2 \\
 &\quad + \frac{|e|Q_{\frac{3}{2}}V_{z'z'}}{4\frac{3}{2}(2\frac{3}{2}-1)} \left[\cos^2\theta - \frac{1}{2}(1-\eta)\sin^2\theta \right] \left(3M_{\frac{3}{2}}^2 - \frac{3 \cdot 5}{2 \cdot 2} \right) \\
 &\quad - \left[-g_{N\frac{1}{2}}\mu_N H_{hm} M_{\frac{1}{2}} + \frac{3Ze^2}{10\epsilon_0} |\Psi(0)|^2 r_{N\frac{1}{2}}^2 \right] \\
 &= -\mu_N H_{hm} (g_{N\frac{3}{2}} M_{\frac{3}{2}} - g_{N\frac{1}{2}} M_{\frac{1}{2}}) \\
 &\quad + \frac{3Ze^2 < r_N > \Delta r_N}{5\epsilon_0} |\Psi(0)|^2 \\
 &\quad + \frac{|e|Q_{\frac{3}{2}}V_{z'z'}}{12} \left[\cos^2\theta - \frac{1}{2}(1-\eta)\sin^2\theta \right] \left(3M_{\frac{3}{2}}^2 - \frac{15}{4} \right), \\
 (\langle r_N \rangle &\equiv \frac{1}{2}(r_{N\frac{3}{2}} + r_{N\frac{1}{2}}), \Delta r_N \equiv r_{N\frac{3}{2}} - r_{N\frac{1}{2}}, M_I = -I, -I+1, \dots, I)
 \end{aligned}
 \tag{3.229}$$

a part of the ray is absorbed by the ^{57}Fe nuclei of the sample giving rise to some absorption peaks in the spectrum. From the positions of the peaks we can get the values of the parameters H_{hm} , $V_{z'z'}$, η , and $|\Psi(0)|^2$. The relative strengths of the peaks also provide some other information. Let $|\Psi(0)|_s^2$ be the value for a standard sample such as Fe metal. The difference between the second terms of the last expressions of (3.229) for the sample and the standard sample

Fig. 3.36 Mössbauer spectrum of Fe metal. 1mm/s corresponds to 4.80×10^{-8} eV



$$\delta = \frac{3Ze^2 \langle r_N \rangle^2}{5\epsilon_0} \frac{\Delta r_N}{\langle r_N \rangle} (|\Psi(0)|^2 - |\Psi(0)|_s^2) \quad (3.230)$$

is called isomer shift. The value of δ reflects the electron density of s electrons at the nucleus $|\Psi(0)|^2$ which is affected by the distribution of the electrons of the atom and the chemical bond. Figure 3.36 demonstrates the Mössbauer spectrum of Fe metal at R.T..

3.9.6 Examples of NMR and Mössbauer Spectroscopy Application

3.9.6.1 Magnetic Field Measurement

Water contains abundant hydrogen. The nucleus ^1H (proton) has no quadrupole but has a large nuclear magnetic moment the value of which is very precisely known (Table 2.4). The hyperfine magnetic field of ^1H is very small, and its value is averaged to zero in water. The resonance condition in a magnetic field H is

$$\hbar\omega = E\left(\frac{1}{2}, -\frac{1}{2}\right) - E\left(\frac{1}{2}, \frac{1}{2}\right) = g_N\mu_N H. \quad (3.231)$$

The gyromagnetic ratio of the nucleus being $\gamma = g_N\mu_N/\hbar$ (2.192), (3.231) coincides with (3.121) of macroscopic theory. The resonance frequency can be measured very precise, therefore the NMR of water is used for precise measurement of H .

3.9.6.2 Magnetic Resonance Imaging

About 70 % of human body is water. Magnetic resonance imaging (MRI) (also called NMR imaging) is primarily a medical imaging technique exploiting NMR of ^1H .

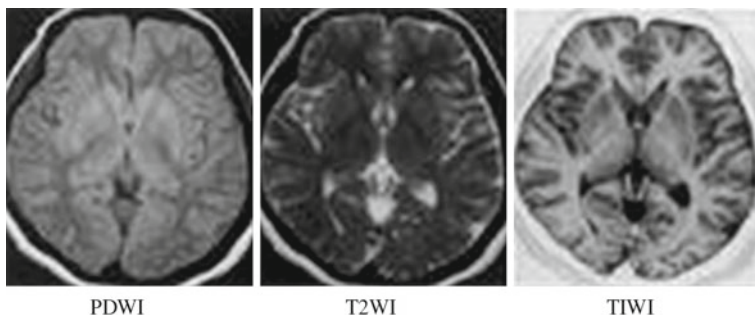


Fig. 3.37 MRI of head. PDWI: proton density image, T2w1 T_2 image, T1w1: T_1 image [23]

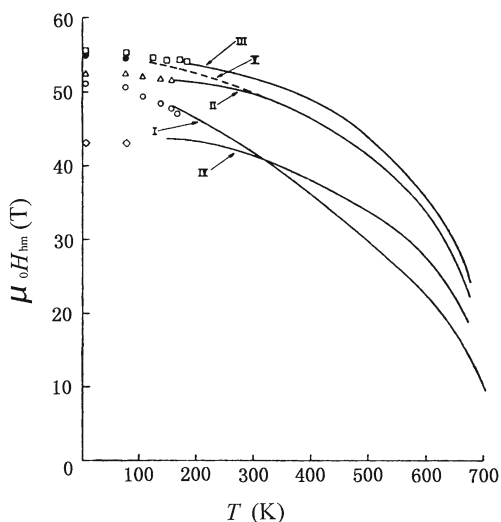
An MRI scanner constitutes of magnetic field, radio wave, and image reproduction systems. A superconducting electromagnet tube produces a magnetic field of a couple of T strength. The patient is placed in the tube. Additional gradient magnetic field is applied during the scan by solenoids known as gradient coils to make the magnetic field strength depend on the position within the patient. The set of the gradient coils can produce the gradient field in any direction. The radio frequency transmitter is briefly turned on and emits photons of angular frequency ω , and NMR takes place in the small section of the patient where the static magnetic field satisfies the resonance condition of (3.231). By absorbing the photons some spins of protons in the section flip to the excited state. After the field is turned off, the protons decay to the original ground state releasing photons. It is these electromagnetic signals that the scanner detects. The currents through the gradient coils are adjusted to change the resonance section and repeat the above pulse sequences until enough data of the signal from the wanted area are accumulated.

An image can be constructed from the data set because the signals from different tissues, including different pathological tissues, are different. Figure 3.37 demonstrates three images on the same section of a head constructed by using the signal strength (proton density image) and relaxation characteristics of T_1 and T_2 (Sect. 3.6.7.4).

3.9.6.3 Molecular Structure Analyses

Ninety percent of the job of NMR spectroscopy for weak magnetic media is for analysis of molecular structure, including small and large and chemical and biological molecules. The nuclei mostly used are ^1H and ^{13}C followed by ^{19}F and ^{31}P . The investigation of ^{15}N and ^{14}N NMR is increasingly becoming active in the biological field. The molecules are magnetized by an applied magnetic field and hyperfine magnetic fields are produced by the magnetic moments of the ions. Although the hyperfine magnetic interactions are very small, they are different for different atomic sites of different environment and many very closely distributed sharp absorption peaks can

Fig. 3.38 $\mu_0 H_{\text{hm}}$ at five Fe sites in $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$ versus temperature. Lines: by ME [24] dots: by NMR [25]



be observed by a high resolution (large magnetic field) NMR spectroscopy. Through analyses of the structure of the spectrum, including the relaxation processes, some information about the molecular structure can be obtained. Super-high-resolution NMR spectroscopy (largest ever $\mu_0 H$ is ~ 23 T) and X-ray structure analysis are the two most effective experimental methods complementing each other for exploration of large biological molecular structure.

3.9.6.4 Temperature Dependences of Atomic Magnetic Moments of Different Sublattices

Exploiting that hyperfine magnetic field is proportional to the magnetic moment of the ion, the values of magnetic moments of ions on different crystal sites, their dependences on temperature, and magnetic transition temperature can be measured. Figure 3.38 demonstrates $\mu_0 H_{\text{hm}}$ at the five Fe sites in $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$ (Fig. 3.13) as a function of temperature measured by NMR and Mössbauer spectroscopy methods.

3.9.6.5 Distribution of the Value of Atomic Magnetic Moment in Alloys

Figure 3.39 demonstrates the Mössbauer spectrum and restored from it hyperfine magnetic field distribution $p(H_{\text{hm}})$ for ordered Fe_3Si alloy (a) and disordered $\text{Fe}_{75}\text{Si}_{25}$ alloy (b), respectively.

The unit cell of the ordered Fe_3Si is constituted of $2 \times 2 \times 2$ bcc. The body centers of four next neighbor bcc (refer shaded cubes in Fig. 3.12b) are occupied by Si and the other lattice points by Fe atoms. Thus, one kind of Fe atom has 8 nearest

Fig. 3.39 Mössbauer spectrum and $\mu_0 H_{\text{hm}}$ distribution deduced from the spectrum.

a ordered Fe_3Si alloy.

b disordered $\text{Fe}_{75}\text{Si}_{25}$ alloy

[26]

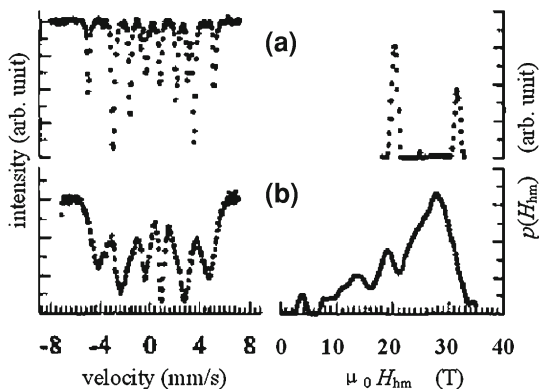
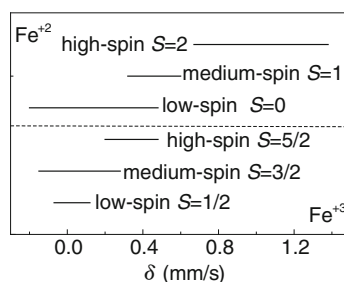


Fig. 3.40 Relation between S and δ (with respect to Fe metal) for Fe^{+2} and Fe^{+3} ion.



neighbor Fe atoms and another kind of Fe atom 4 Fe and 4 Si nearest neighbor atoms. Correspondingly, the Mössbauer spectrum consists of two sextets and the $p(H_{\text{hm}})$ curve is consisted of two sharp peaks at $\mu_0 H_{\text{hm}}=32$ T and 20 T (Fig. 3.39a). Apparently, $\mu_0 H_{\text{hm}}=32$ T is the hyperfine magnetic field of the Fe which has 8 nearest neighbor Fe. The value is a bit smaller than 33 T of pure Fe metal of atomic magnetic polarization moment $2.2 \mu_B$ revealing that the effects of the next neighbor atoms are not negligible. The value of the atomic magnetic polarization moment of the two kinds of Fe atoms are about $2.2 \times 32/33=2.1 \mu_B$ and $2.2 \times 20/33= 1.3 \mu_B$.

For disordered $\text{Fe}_{75}\text{Si}_{25}$, the peaks of the Mössbauer spectrum are much broader which can be fitted by a set of a number of sextets. The surrounding environment being widely different the value of the magnetic moment and hence the hyperfine magnetic field of Fe atoms distribute in a wide range between 3 and 33 T (Fig. 3.39b).

3.9.6.6 Empirical Relations between Total Spin and Isomer Shift for Fe^{+2} and Fe^{+3} Ions

Figure 3.40 shows empirical relations between spin S and isomer shift δ for Fe^{+2} and Fe^{+3} ions.

The spin state of an ion is explained below by taking an Fe^{+3} in a cubic CEF as an example: If the CEF interaction is much smaller than the inter-3d electron exchange

interaction, the spins of the five 3d electrons of $\text{Fe}^{+3}(3d^5)$ are aligned parallel, and it becomes a high-spin ($S = 5/2$) state. Three electrons half fill the T_{2g} orbits and another two half fill the E_g orbits (Fig.3.26). If the CEF interaction is much stronger than the inter-3d exchange interaction and T_{2g} is the ground orbital state, all of the five electrons fill the T_{2g} orbits, the spins of three electrons are parallel, and the spins of the other two electrons are antiparallel to the above spins. If E_g is the ground orbital state, the four E_g orbits are fully filled by four 3d electrons. Another one electron fills the T_{2g} orbital state. In both cases, the total spin being 1/2, it becomes the low-spin state. If the CEF and exchange interactions are competitive, it becomes a medium-spin state.

It can be seen from Fig.3.40 that if δ is measured very large, the Fe ion can be considered bivalent and is at the high-spin state of $S=2$.

3.9.6.7 Detection of Phase Transformation from $V_{z'z'}(T)$ Curve

The characteristics of the temperature dependence of $V_{z'z'}$ being different for different phases of a compound, the phase transformation can be detected and the transformation temperature can be measured from the temperature where the slope of $V_{z'z'}(T)$ becomes discontinuous.

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Chapter 4

Exchange Interaction

As was shown in Sect. 3.4, spontaneous magnetization arises through exchange interactions. There are different detailed mechanisms of exchange interaction in solids. Classic expression of exchange energy is in common use in magnetism. This chapter introduces main theoretical models of the mechanisms and the classic expression, and contains the sections of Direct exchange interaction in solid; Superexchange interaction; RKKY exchange interaction; Double exchange interaction; and Classic expression of exchange energy.

4.1 Direct Exchange Interaction in Solid

Heisenberg (1928) first analyzed exchange interactions in solid. Consider N isolated atoms. Each atom has a magnetic electron. Let $\varphi_\alpha(\vec{r})$ and ε denote the orbital and eigenenergy of the electron and $u_\alpha(\vec{r})$ the core potential in atom α .

$$\left[\frac{\hat{p}^2}{2m} + u_\alpha(\vec{r}) \right] \varphi_\alpha(\vec{r}) = \varepsilon \varphi_\alpha(\vec{r}) \quad (\alpha = 1, 2, \dots, N). \quad (4.1)$$

The N atoms approach each other to form a solid. Suppose each magnetic electron remains localized within its atom.

4.1.1 Hamiltonian of One Magnetic Electron Atom System

Let $\hat{n}_{\alpha,\pm}$ denote the number operator of $\pm$ spin (A5.1) of the electron in atom α . Since each atom has a magnetic electron,

$$\hat{n}_{\alpha,+} + \hat{n}_{\alpha,-} = 1. \quad (4.2)$$

The Hamiltonian of the electron system is

$$\hat{H} = \hat{H}_1 + \hat{H}_2, \quad (4.3)$$

$$\hat{H}_1 = \sum_i^{1,\dots,N} \left[\frac{\hat{p}_i^2}{2m} + \sum_{\alpha}^{1,\dots,N} u_{\alpha}(\vec{r}_i) \right], \quad (4.4)$$

$$\hat{H}_2 = \frac{1}{2} \sum_{i,j}^{1,\dots,N; j \neq i} \frac{e^2}{4\pi\epsilon_0 r_{ij}}. \quad (4.5)$$

The orbitals of neighbor atoms are approximately orthogonal but not strictly. In the below, orthogonal approximation is taken for less important two-particle Hamiltonian $\hat{H}_2$ but not for the most important one-particle Hamiltonian $\hat{H}_1$.

4.1.2 Exchange Hamiltonian in $\hat{H}_2$

Consider the average of $\hat{H}_2$ in the state of the electron system $\Psi = |1, 2, \dots, N\rangle$. $\hat{H}_2$ in this case is

$$\hat{H}_2 = \frac{1}{2} \sum_{\alpha,\beta}^{\alpha \neq \beta} \sum_{\sigma,\sigma'}^{\pm} \left(g_{\alpha\beta\beta\alpha} \hat{a}_{\alpha,\sigma}^+ \hat{a}_{\beta,\sigma'}^+ \hat{a}_{\beta,\sigma'} \hat{a}_{\alpha,\sigma} + g_{\alpha\beta\alpha\beta} \hat{a}_{\alpha,\sigma}^+ \hat{a}_{\beta,\sigma'}^+ \hat{a}_{\alpha,\sigma'} \hat{a}_{\beta,\sigma} \right) \quad ((a5.34))$$

$$= \frac{1}{2} \sum_{\alpha,\beta}^{\alpha \neq \beta} \sum_{\sigma,\sigma'}^{\pm} \left(K_{2\alpha\beta} \hat{n}_{\alpha,\sigma} \hat{n}_{\beta,\sigma'} + J_{A2\alpha\beta} \hat{a}_{\alpha,\sigma}^+ \hat{a}_{\beta,\sigma'}^+ \hat{a}_{\alpha,\sigma'} \hat{a}_{\beta,\sigma} \right) \quad ((a5.17)-(a5.18))$$

$$= \frac{1}{2} \sum_{\alpha,n}^{\alpha \neq \beta} \left(K_{2\alpha\beta} + J_{A2\alpha\beta} \sum_{\sigma,\sigma'}^{\pm} \hat{a}_{\alpha,\sigma}^+ \hat{a}_{\beta,\sigma'}^+ \hat{a}_{\alpha,\sigma'} \hat{a}_{\beta,\sigma} \right), \quad (4.2) \quad (4.6)$$

in which

$$K_{2\alpha\beta} \equiv g_{\alpha\beta\beta\alpha} \equiv \int \frac{e^2}{4\pi\epsilon_0 r_{12}} |\varphi_{\alpha}(\vec{r}_1)|^2 |\varphi_{\beta}(\vec{r}_2)|^2 d\nu_1 d\nu_2, \quad (4.7)$$

$$J_{A2\alpha\beta} \equiv g_{\alpha\beta\alpha\beta} \equiv \int \frac{e^2}{4\pi\epsilon_0 r_{12}} \varphi_{\alpha}^*(\vec{r}_1) \varphi_{\beta}^*(\vec{r}_2) \varphi_{\alpha}(\vec{r}_2) \varphi_{\beta}(\vec{r}_1) d\nu_1 d\nu_2, \quad (4.8)$$

$$\begin{aligned} & \sum_{\sigma,\sigma'}^{\pm} \hat{a}_{\alpha,\sigma}^+ \hat{a}_{\beta,\sigma'}^+ \hat{a}_{\alpha,\sigma'} \hat{a}_{\beta,\sigma} \\ &= (\hat{a}_{\alpha,+}^+ \hat{a}_{\beta,+}^+ \hat{a}_{\alpha,+} \hat{a}_{\beta,+} + \hat{a}_{\alpha,-}^+ \hat{a}_{\beta,-}^+ \hat{a}_{\alpha,-} \hat{a}_{\beta,-}) \\ &+ (\hat{a}_{\alpha,+}^+ \hat{a}_{\beta,-}^+ \hat{a}_{\alpha,-} \hat{a}_{\beta,+} + \hat{a}_{\alpha,-}^+ \hat{a}_{\beta,+}^+ \hat{a}_{\alpha,+} \hat{a}_{\beta,-}) \end{aligned}$$

$$\begin{aligned}
&= -(\hat{n}_{\alpha,+}\hat{n}_{\beta,+} + \hat{n}_{\alpha,-}\hat{n}_{\beta,-}) - (\hat{a}_{\alpha,+}^+\hat{a}_{\alpha,-}\hat{a}_{\beta,-}^+\hat{a}_{\beta,+} + \hat{a}_{\alpha,-}^+\hat{a}_{\alpha,+}\hat{a}_{\beta,+}^+\hat{a}_{\beta,-}) \\
&\quad ((a5.17)-(a5.18)) \\
&= -\frac{1}{2}[(\hat{n}_{\alpha,+} + \hat{n}_{\alpha,-})(\hat{n}_{\beta,+} + \hat{n}_{\beta,-}) + (\hat{n}_{\alpha,+} - \hat{n}_{\alpha,-})(\hat{n}_{\beta,+} - \hat{n}_{\beta,-})] \\
&\quad - (\hat{s}_{+\alpha}\hat{s}_{-\beta} + \hat{s}_{-\alpha}\hat{s}_{+\beta}) \quad ((a5.39)-(a5.40)) \\
&= -\frac{1}{2}2\hat{s}_{z\alpha}\hat{s}_{z\beta} - (\hat{s}_{+\alpha}\hat{s}_{-\beta} + \hat{s}_{-\alpha}\hat{s}_{+\beta}) = -\frac{1}{2}2\hat{s}_{\alpha} \cdot \hat{s}_{\beta}. \quad ((4.2), (a5.41))
\end{aligned} \tag{4.9}$$

The first term in the last expression of (4.6) being Coulomb interaction irrelevant to spin, it is taken out of consideration. The second term gives rise to the exchange interaction

$$\hat{H}_{\text{ex2}} = -\frac{1}{2} \sum_{\alpha}^{1,2,\dots,N} \sum_{\beta}^{n(\alpha)} 2J_{A2} \hat{s}_{\alpha} \cdot \hat{s}_{\beta}. \tag{4.10}$$

The sum of $\sum_{\beta}^{n(\alpha)}$ is taken over the nearest neighbors of atom α and J_{A2} is the $J_{A2\alpha\beta}$ of nearest neighbor atoms. The exchange interaction between non-nearest neighbor atoms is neglected.

4.1.3 Exchange Hamiltonian in $\hat{H}_1$

The expression of (a5.24) for second quantized operator of $\hat{H}_1$ is deduced under the condition of orthonormality of $\{\varphi_{\alpha}\}$ and is not applicable for the atomic wave functions which are not orthogonal. Let $\psi_{\alpha,\sigma_{\alpha}}$ denote the spin-orbital of electron of spin σ_{α} in atom α . The average of $\hat{H}_1$ is

$$\begin{aligned}
&\langle N, \dots, 2, 1 | \hat{H}_1 | 1, 2, \dots, N \rangle \\
&= \frac{N}{N!} \int \begin{vmatrix} \psi_{1,\sigma_1}^+(1) & \psi_{2,\sigma_2}^+(1) & \cdots & \psi_{N,\sigma_N}^+(1) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_{1,\sigma_1}^+(i) & \psi_{2,\sigma_2}^+(i) & \cdots & \psi_{N,\sigma_N}^+(i) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_{1,\sigma_1}^+(N) & \psi_{2,\sigma_2}^+(N) & \cdots & \psi_{N,\sigma_N}^+(N) \end{vmatrix} \left[\frac{\hat{p}_1^2}{2m} + \sum_{\gamma}^{1,\dots,N} u_{\gamma}(\vec{r}_1) \right] \\
&\quad \times \begin{vmatrix} \psi_{1,\sigma_1}(1) & \psi_{2,\sigma_2}(1) & \cdots & \psi_{N,\sigma_N}(1) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_{1,\sigma_1}(i) & \psi_{2,\sigma_2}(i) & \cdots & \psi_{N,\sigma_N}(i) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_{1,\sigma_1}(N) & \psi_{2,\sigma_2}(N) & \cdots & \psi_{N,\sigma_N}(N) \end{vmatrix} dv_1 dv_2 \cdots dv_N \\
&= \frac{N}{N!} \int (N-2)! \sum_{\alpha < \beta}^{1,\dots,N} \sum_i^{2,\dots,N} \begin{vmatrix} \psi_{\alpha,\sigma_{\alpha}}^+(1) & \psi_{\beta,\sigma_{\beta}}^+(1) \\ \psi_{\alpha,\sigma_{\alpha}}^+(i) & \psi_{\beta,\sigma_{\beta}}^+(i) \end{vmatrix}
\end{aligned}$$

$$\begin{aligned}
& \times \left[\frac{\hat{p}_1^2}{2m} + \sum_{\gamma}^{1, \dots, N} u_{\gamma}(\vec{r}_1) \right] \left| \begin{array}{cc} \psi_{\alpha, \sigma_{\alpha}}(1) & \psi_{\beta, \sigma_{\beta}}(1) \\ \psi_{\alpha, \sigma_{\alpha}}(i) & \psi_{\beta, \sigma_{\beta}}(i) \end{array} \right| dv_1 dv_i \\
& = \frac{1}{2} \int \sum_{\alpha \neq \beta}^{1, \dots, N} \left| \begin{array}{cc} \psi_{\alpha, \sigma_{\alpha}}^{+}(1) & \psi_{\beta, \sigma_{\beta}}^{+}(1) \\ \psi_{\alpha, \sigma_{\alpha}}^{+}(2) & \psi_{\beta, \sigma_{\beta}}^{+}(2) \end{array} \right| \left[\frac{\hat{p}_1^2}{2m} + \sum_{\gamma}^{1, \dots, N} u_{\gamma}(\vec{r}_1) \right] \left| \begin{array}{cc} \psi_{\alpha, \sigma_{\alpha}}(1) & \psi_{\beta, \sigma_{\beta}}(1) \\ \psi_{\alpha, \sigma_{\alpha}}(2) & \psi_{\beta, \sigma_{\beta}}(2) \end{array} \right| dv_1 dv_2.
\end{aligned} \tag{4.11}$$

By neglecting the terms except linear terms of overlap integral of nearest neighbor atoms, the terms relevant to spins are

$$\begin{aligned}
& - \frac{1}{2} \sum_{\alpha}^{1, \dots, N} \sum_{\beta}^{n(\alpha)} \int [u_{\alpha}(\vec{r}_1) \psi_{\alpha, \sigma_{\alpha}}^{+}(1) \psi_{\beta, \sigma_{\beta}}^{+}(2) \psi_{\alpha, \sigma_{\alpha}}(2) \psi_{\beta, \sigma_{\beta}}(1) \\
& + u_{\beta}(\vec{r}_1) \psi_{\alpha, \sigma_{\alpha}}^{+}(2) \psi_{\beta, \sigma_{\beta}}^{+}(1) \psi_{\alpha, \sigma_{\alpha}}(1) \psi_{\beta, \sigma_{\beta}}(2)] dv_1 dv_2 \\
& = - \frac{1}{2} \sum_{\alpha}^{1, \dots, N} \sum_{\beta}^{n(\alpha)} \delta(\sigma_{\alpha}, \sigma_{\beta}) \int [u_{\alpha}(\vec{r}_1) + u_{\beta}(\vec{r}_2)] \varphi_{\alpha}^{*}(\vec{r}_1) \varphi_{\beta}^{*}(\vec{r}_2) \varphi_{\alpha}(\vec{r}_2) \varphi_{\beta}(\vec{r}_1) dv_1 dv_2 \\
& = - \frac{1}{2} \sum_{\alpha}^{1, \dots, N} \sum_{\beta}^{n(\alpha)} 2\delta(\sigma_{\alpha}, \sigma_{\beta}) J_{A1},
\end{aligned} \tag{4.12}$$

$$J_{A1} = \int \frac{u_{\alpha}(\vec{r}_1) + u_{\beta}(\vec{r}_2)}{2} \varphi_{\alpha}^{*}(\vec{r}_1) \varphi_{\beta}^{*}(\vec{r}_2) \varphi_{\alpha}(\vec{r}_2) \varphi_{\beta}(\vec{r}_1) dv_1 dv_2.$$

(α, β : nearest neighbors) (4.13)

Equation (4.12) shows that the exchange energy of parallel spin state of nearest neighbor atoms is smaller than that of the antiparallel spin state by twice the exchange integral, $2J_{A1}$, as in the cases of atom He ((2.153), (2.155)) and molecule H_2 (2.182), (2.184)). Therefore, the exchange Hamiltonian of (4.12) is ((2.159)–(2.161))

$$\hat{H}_{ex1} = - \frac{1}{2} \sum_{\alpha}^{1, \dots, N} \sum_{\beta}^{n(\alpha)} 2J_{A1} \hat{s}_{\alpha} \cdot \hat{s}_{\beta}. \tag{4.14}$$

4.1.4 Total Exchange Hamiltonian

The total exchange Hamiltonian is the sum of (4.10) and (4.14):

$$\hat{H}_{ex} = - \frac{1}{2} \sum_{\alpha}^{1, \dots, N} \sum_{\beta}^{n(\alpha)} 2J_{A1} \hat{s}_{\alpha} \cdot \hat{s}_{\beta}, \tag{4.15}$$

$$J_A = \int \left[\frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{u_m(\vec{r}_1) + u_n(\vec{r}_2)}{2} \right] \varphi_\alpha^*(\vec{r}_1) \varphi_\beta^*(\vec{r}_2) \varphi_\alpha(\vec{r}_2) \varphi_\beta(\vec{r}_1) d\mathbf{v}_1 d\mathbf{v}_2. \quad (4.16)$$

(α, β : nearest neighbors)

The expression of exchange Hamiltonian between the two atoms in solid is the same in form with those in He atom (2.162) and H₂ molecule (2.189). $\varphi_\alpha^*(\vec{r}_1) \varphi_\beta^*(\vec{r}_2) \varphi_\alpha(\vec{r}_2) \varphi_\beta(\vec{r}_1)$ in J_A is also the same in form, but its coefficient $\frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{u_m(\vec{r}_1) + u_n(\vec{r}_2)}{2}$ is different from $\frac{e^2}{4\pi\epsilon_0 r_{12}}$ (2.157) of He atom and $\frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{12}} - \frac{1}{r_{1a}} - \frac{1}{r_{2b}} \right)$ (2.178) of H₂ molecule.

4.1.5 Interatomic Exchange Hamiltonian in Multi Magnetic Electron Atom System

In a multi magnetic electron atom system the spins of magnetic electrons in each atom are coupled to total spin $\hat{S}$ through strong intraatomic exchange interaction (Sect. 2.5). By extending the relation of (4.15) deduced for one magnetic electron atom system to multi magnetic electron atom system we get the exchange Hamiltonian of atom α with nearest neighbor atoms as

$$\hat{H}_{\text{ex}}(n) = -2J_A \hat{S}_\alpha \cdot \sum_{\beta}^{n(\alpha)} \hat{S}_\beta. \quad (J_A : \text{average of (4.16)}) \quad (4.17)$$

4.1.6 Exchange Integral as a Function of Distance Between a Pair of Atoms

During the 1930s, Néel, Slater, Bethe et al. analyzed the conditions of appearance of ferromagnetism, that is, $J_A > 0$. In the middle of the α and β atoms $\varphi_\alpha^*(\vec{r}_1) \varphi_\beta^*(\vec{r}_2) \varphi_\alpha(\vec{r}_2) \varphi_\beta(\vec{r}_1)$ is positive. The condition of $J_A > 0$ can be realized if $\varphi_\alpha(\vec{r})$ and $\varphi_\beta(\vec{r})$ are large in the middle of the pair separated by distance a and small near the nuclei so that the positive term $e^2/4\pi\epsilon_0 r_{12}$ is larger than the absolute values of negative term $[u_\alpha(\vec{r}_1) + u_\beta(\vec{r}_2)]/2 \sim -(e^2/4\pi\epsilon_0)(1/r_{1\alpha} + 1/r_{2\beta})/2$. To satisfy such conditions, the average orbital radius of the magnetic electron subshell r should roughly be half of a .

Slater proposed that the exchange integral as a function of a/r for Mn, Fe, Co, Ni metals should be that of Fig. 4.1 [1].

The 3d electrons in metals and alloys being itinerant, it is only anticipated that the Hisenberg's theory based on the localized model can explain the magnetism qualitatively.

Fig. 4.1 J_A as a function of a/r for Mn, Fe, Co and Ni metals

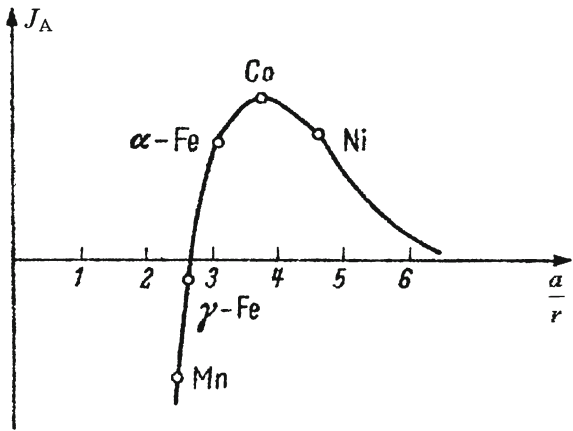


Table 4.1 Néel temperatures of typical ferrites [2]

Type of crystal	Composition	T_N/K
Spinel	$MnO \cdot Fe_2O_3$	573
	Fe_3O_4	858
Garnet	$3Y_2O_3 \cdot 5Fe_2O_3$	553
	$3Gd_2O_3 \cdot 5Fe_2O_3$	564
Magnetoplumbite	$BaO \cdot 6Fe_2O_3$	723
	$SrO \cdot 6Fe_2O_3$	733

4.2 Superexchange Interaction

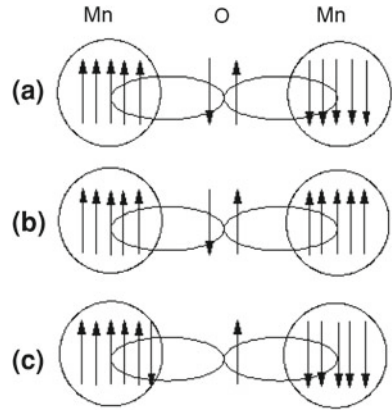
In a magnetic oxide, neighbor magnetic ions being separated by an oxygen ion (Figs. 3.9 and 3.12), the distance between them is large and superposition of the electrons of neighbor magnetic ions is very small. Therefore, the direct exchange interaction should be very small.

Many ferrites, however, have fairly high Néel temperatures (Table 4.1) revealing that the exchange interactions between them are not small. The superexchange interaction model proposed by Kramers (1934) and refined by Anderson (1950–1963) explains the exchange interaction mechanism.

4.2.1 Physical Picture of Superexchange Interaction

Consider the Mn–O–Mn ion system arranged on a [100] crystal axis (x -axis) in an anti-ferromagnetic MnO (Figs. 3.9 and 4.2). In each $Mn^{+2}(3d^5)$ five 3d orbits are half filled by same spin 3d electrons. In each $O^{-2}(2p^6)$ all 2p orbits $R_{21}Y_{1m_1}$ ($m_1 = 0, \pm 1$) are fully filled by spin-up and -down electrons. For convenience of analysis take the real functions

Fig. 4.2 Mn–O–Mn system.
(a) and (b): ground states (c):
excited state



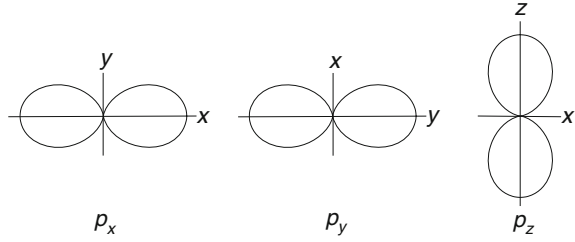
$$\begin{aligned}
 p_x &= -\frac{1}{\sqrt{2}}(Y_{11} - Y_{1-1}) = \sqrt{\frac{3}{4\pi}} \frac{x}{r}, \\
 p_y &= \frac{i}{\sqrt{2}}(Y_{11} + Y_{1-1}) = \sqrt{\frac{3}{4\pi}} \frac{y}{r}, \\
 p_z &= Y_{10} = \sqrt{\frac{3}{4\pi}} \frac{z}{r}
 \end{aligned} \tag{4.18}$$

instead of $\{Y_{1m_1}\}$ as the basis vectors. Figure 4.3 shows the angular distribution of the electron density p_α^2 ($\alpha = x, y, z$). It has the rotational symmetry about the α axis. When all the p electrons are in the O ion there is no relevance between the spins of two side Mn^{+2} ions making the energies of parallel and antiparallel spin states of them the same. The p_x orbit stretches toward the Mn^{+2} ions and heavily superposes with the 3d orbits of the Mn^{+2} ions, so there is a large opportunity for the p_x electron to transfer to the Mn ions. The p_y and p_z orbits superposing with the 3d orbit only slightly the opportunity of the migration is small for the electrons. The effects of p_y and p_z orbits, therefore, will be neglected hereafter. The p_x electron which has the opposite spin to the spins of left side Mn^{+2} ion can transfer to the 3d orbit of the ion and stay there for a while. During the stay the remaining in the O ion p_x electron directly exchange interacts with the 3d electrons of the right side of Mn^{+2} . If the exchange integral is negative, the spins of the Mn^{+2} are coupled antiparallel with the p_x electron spin and hence coupled antiparallel with the left side Mn^{+2} ion spins indirectly (Fig. 4.2c).

4.2.2 Semi-Quantitative Analysis of Superexchange Interaction

Consider $\text{M}_1\text{--O--M}_2$ system arranged in the same way as the above Mn–O–Mn system. M_1 and M_2 have a magnetic electron d_1 and d_2 , respectively. The two p_x electrons

Fig. 4.3 Angular distribution of p_x^2 , p_y^2 and p_z^2



in the O ion are denoted by p and p' . By neglecting the spin-orbit interaction, take the Coulomb interactions $\hat{H}_{CF}$ between the ions as perturbation. The Hamiltonian being irrelevant to the spins, the eigenfunction of the four electron system is the product of orbital and spin functions.

First analyze the ground states and lower energy level excited states in the absence of the perturbation. At the ground state, the opposite spin p and p' electrons remain in the O ion. The total spin of the two electron system $S(p, p')$ is zero. The state is denoted by $(p, p')^{2S(p, p')+1} = (p, p')^1$ in which the superscript is the spin degeneracy. Since there is no spin relevance between d_1 and d_2 , their spins are either antiparallel or parallel with corresponding state $(d_1, d_2)^1$ or $(d_1, d_2)^3$. The ground states of the four electrons system, therefore, are

$$\Psi_g^1 = [(d_1 d_2)^1 (p' p)^1]^1, \quad (4.19)$$

$$\Psi_g^3 = [(d_1 d_2)^3 (p' p)^1]^3, \quad (4.20)$$

where the superscripts of Ψ and the brackets are the degeneracy of the total spin $2S(d_1, d_2, p, p') + 1$.

An excited state is that of p' electron transferred to the M_1 ion and becomes d'_1 . There are many ways to describe the state of the four electron system. We will first couple d_1 and d'_1 to form the state $(d_1 d'_1)^{2S(d_1 d'_1)+1}$ and p and d_2 form the state $(p d_2)^{2S(p d_2)+1}$, and then couple the two systems to the state of the four-electron system:

$$\Psi_a^1 = [(d_1 d'_1)^1 (p d_2)^1]^1, \quad (4.21)$$

$$\Psi_b^3 = [(d_1 d'_1)^1 (p d_2)^3]^3, \quad (4.22)$$

$$\Psi_c^3 = [(d_1 d'_1)^3 (p d_2)^1]^3, \quad (4.23)$$

$$\Psi_d^1 = [(d_1 d'_1)^3 (p d_2)^3]^1, \quad (4.24)$$

$$\Psi_d^3 = [(d_1 d'_1)^3 (p d_2)^3]^3, \quad (4.25)$$

$$\Psi_d^5 = [(d_1 d'_1)^3 (p d_2)^3]^5. \quad (4.26)$$

The energy of the excited state with respect to the ground energy level constitutes of two parts. One is the transfer energy of p' to M_1 ion. Let $E(\uparrow\uparrow)$ and $E(\uparrow\downarrow)$ denote the energy when the spins of d'_1 and d_1 are parallel and antiparallel, respectively.

Another is the direct exchange energy between p remaining in the O ion and d_2 in the M_2 ion. When the spins of them are parallel or antiparallel, the energy is negative or positive exchange integral J_A . Thus, the energies of the states of (4.21)–(4.26) are

$$E_a^1 = E(\uparrow\downarrow) + J_A \equiv E_a, \quad (4.27)$$

$$E_b^3 = E(\uparrow\downarrow) - J_A \equiv E_b, \quad (4.28)$$

$$E_c^3 = E(\uparrow\uparrow) + J_A \equiv E_c, \quad (4.29)$$

$$E_d^1 = E_d^3 = E_d^5 = E(\uparrow\uparrow) - J_A \equiv E_d. \quad (4.30)$$

Now analyze the effects of the perturbation $\hat{H}_{CF}$. $\hat{H}_{CF}$ being irrelevant to the spins and the two ground states have different spin states, the matrix elements $\langle \Psi_g^i | \hat{H}_{CF} | \Psi_g^j \rangle (i, j = 1, 3)$ are diagonalized:

$$\langle \Psi_g^1 | \hat{H}_{CF} | \Psi_g^3 \rangle = \langle \Psi_g^3 | \hat{H}_{CF} | \Psi_g^1 \rangle = 0, \quad (4.31)$$

$$\langle \Psi_g^1 | \hat{H}_{CF} | \Psi_g^1 \rangle = \langle \Psi_g^3 | \hat{H}_{CF} | \Psi_g^3 \rangle \equiv E_{CF1}. \quad (4.32)$$

The perturbation energy is (Appendix 6)

$$E^i = E_{CF1} + \sum_{\nu}^{a,b,c,d} \frac{|\langle \Psi_g^i | \hat{H}_{CF} | \Psi_{\nu}^i \rangle|^2}{-E_{\nu}}. \quad (i = 1, 3) \quad (4.33)$$

To calculate the matrix elements in the right of above equation, transform the $[(d_1 d_2)^{1S(d_1 d_2)+1}(p' p)^{2S(p' p)+1}]^i$ representations of Ψ_g^i ((4.19)–(4.20)) to the $[(d_1 p')^{2S(d_1 p')+1}(p d_2)^{2S(p d_2)+1}]^i$ representations of Ψ_{ν}^i ((4.21)–(4.26)) as below.

$$\Psi_g^1 = C_{11}[(d_1 p')^1(p d_2)^1]^1 + C_{12}[(d_1 p')^3(p d_2)^3]^1, \quad (4.34)$$

$$\Psi_g^3 = C_{31}[(d_1 p')^1(p d_2)^3]^3 + C_{32}[(d_1 p')^3(p d_2)^1]^3 + C_{33}[(d_1 p')^3(p d_2)^3]^3. \quad (4.35)$$

From the normal conditions of Ψ_g^1 and Ψ_g^3 we get

$$\langle \Psi_g^1 | \Psi_g^1 \rangle = |C_{11}|^2 + |C_{12}|^2 = 1, \quad (4.36)$$

$$\langle \Psi_g^3 | \Psi_g^3 \rangle = |C_{31}|^2 + |C_{32}|^2 + |C_{33}|^2 = 1. \quad (4.37)$$

At the ground states Ψ_g^1 and Ψ_g^3 , the spins of d_1 and p' and those of p and d_2 are irrelevant, so the averages of $\hat{s}_{d_1} \cdot \hat{s}_{p'}$ and $\hat{s}_p \cdot \hat{s}_{d_2}$ on these states are zero, i.e.,

$$\begin{aligned} \langle \Psi_g^1 | \hat{s}_{d_1} \cdot \hat{s}_{p'} | \Psi_g^1 \rangle &= \langle C_{11}[(d_1 p')^1(p d_2)^1]^1 + C_{12}[(d_1 p')^3(p d_2)^3]^1 \\ &\quad \times \hat{s}_{d_1} \cdot \hat{s}_{p'} | C_{11}[(d_1 p')^1(p d_2)^1]^1 + C_{12}[(d_1 p')^3(p d_2)^3]^1 \rangle \end{aligned}$$

$$\begin{aligned}
&= |C_{11}|^2 \langle (d_1 p')^1 | \hat{s}_{d_1} \cdot \hat{s}_{p'} | (d_1 p')^1 \rangle + |C_{12}|^2 \langle (d_1 p')^3 | \hat{s}_{d_1} \cdot \hat{s}_{p'} | (d_1 p')^3 \rangle \\
&= |C_{11}|^2 \left\langle s = \frac{1}{2}, s = \frac{1}{2}, S = 0, M_s = 0 | \hat{s}_{d_1} \cdot \hat{s}_{p'} | \frac{1}{2}, \frac{1}{2}, 0, 0 \right\rangle \\
&\quad + |C_{12}|^2 \left\langle \frac{1}{2}, \frac{1}{2}, 1, M_s | \hat{s}_{d_1} \cdot \hat{s}_{p'} | \frac{1}{2}, \frac{1}{2}, 1, M_s \right\rangle \\
&= |C_{11}|^2 \left\langle \frac{1}{2}, \frac{1}{2}, 0, 0 \left| \frac{\hat{S}^2 - 2\hat{s}^2}{2} \right| \frac{1}{2}, \frac{1}{2}, 0, 0 \right\rangle \\
&\quad + |C_{12}|^2 \left\langle \frac{1}{2}, \frac{1}{2}, 1, M_s \left| \frac{\hat{S}^2 - 2\hat{s}^2}{2} \right| \frac{1}{2}, \frac{1}{2}, 1, M_s \right\rangle \\
&= -|C_{11}|^2 \frac{3}{4} + |C_{12}|^2 \frac{1}{4} = 0,
\end{aligned} \tag{4.38}$$

$$\begin{aligned}
&\langle \Psi_g^3 | \hat{s}_{d_1} \cdot \hat{s}_{p'} | \Psi_g^3 \rangle = \langle C_{31} [(d_1 p')^1 (pd_2)^3]^3 + C_{32} [(d_1 p')^3 (pd_2)^1]^3 \\
&\quad + C_{33} [(d_1 p')^3 (pd_2)^3]^3 | \hat{s}_{d_1} \cdot \hat{s}_{p'} | C_{31} [(d_1 p')^1 (pd_2)^3]^3 \\
&\quad + C_{32} [(d_1 p')^3 (pd_2)^1]^3 + C_{33} [(d_1 p')^3 (pd_2)^3]^3 \rangle \\
&= |C_{31}|^2 \left\langle \frac{1}{2}, \frac{1}{2}, 0, 0 | \hat{s}_{d_1} \cdot \hat{s}_{p'} | \frac{1}{2}, \frac{1}{2}, 0, 0 \right\rangle \\
&\quad + (|C_{32}|^2 + |C_{33}|^2) \left\langle \frac{1}{2}, \frac{1}{2}, 1, M_s | \hat{s}_{d_1} \cdot \hat{s}_{p'} | \frac{1}{2}, \frac{1}{2}, 1, M_s \right\rangle \\
&= |C_{31}|^2 \frac{-3}{4} + (|C_{32}|^2 + |C_{33}|^2) \frac{1}{4} = 0,
\end{aligned} \tag{4.39}$$

$$\begin{aligned}
&\langle \Psi_g^3 | \hat{s}_p \cdot \hat{s}_{d_2} | \Psi_g^3 \rangle = \langle C_{31} [(d_1 p')^1 (pd_2)^3]^3 + C_{32} [(d_1 p')^3 (pd_2)^1]^3 \\
&\quad + C_{33} [(d_1 p')^3 (pd_2)^3]^3 | \hat{s}_{d_2} \cdot \hat{s}_p | C_{31} [(d_1 p')^1 (pd_2)^3]^3 \\
&\quad + C_{32} [(d_1 p')^3 (pd_2)^1]^3 + C_{33} [(d_1 p')^3 (pd_2)^3]^3 \rangle \\
&= (|C_{31}|^2 + |C_{33}|^2) \frac{1}{4} - |C_{32}|^2 \frac{3}{4} = 0.
\end{aligned} \tag{4.40}$$

From (4.36)–(4.40) we get

$$|C_{11}|^2 = |C_{31}|^2 = |C_{32}|^2 = \frac{1}{4}, \quad |C_{33}|^2 = \frac{1}{2}, \quad |C_{12}|^2 = \frac{3}{4}. \tag{4.41}$$

Thereby, the values of non-zero matrices in the second term in the right of (4.33) are

$$|\langle \Psi_g^1 | \hat{H}_{CF} | \Psi_a^1 \rangle|^2 = |\langle \Psi_g^3 | \hat{H}_{CF} | \Psi_b^3 \rangle|^2 = |\langle \Psi_g^3 | \hat{H}_{CF} | \Psi_c^3 \rangle|^2 = \frac{|b|^2}{4}, \quad (4.42)$$

$$|\langle \Psi_g^1 | \hat{H}_{CF} | \Psi_d^1 \rangle|^2 = |C_{12}|^2 |b|^2 = \frac{3|b|^2}{4}, \quad (4.43)$$

$$|\langle \Psi_g^3 | \hat{H}_{CF} | \Psi_d^3 \rangle|^2 = |C_{33}|^2 |b|^2 = \frac{|b|^2}{2}, \quad (4.44)$$

$$b \equiv \langle d'_1 | \hat{H}_{CF} | p' \rangle. \quad (4.45)$$

b is called transfer integral. Inserting the above results and (4.27)–(4.30) into (4.33) we get

$$E^1 = E_{CF1} - \frac{|b|^2}{4} \left(\frac{3}{E(\uparrow\uparrow) - J_A} + \frac{1}{E(\uparrow\downarrow) + J_A} \right), \quad (4.46)$$

$$\begin{aligned} E^3 &= E_{CF1} - \frac{|b|^2}{4} \left(\frac{2}{E(\uparrow\uparrow) - J_A} + \frac{1}{E(\uparrow\uparrow) + J_A} + \frac{1}{E(\uparrow\downarrow) - J_A} \right) \\ &\approx E^1 - 2 \frac{|b|^2}{4} J_A \left(\frac{1}{E^2(\uparrow\downarrow)} - \frac{1}{E^2(\uparrow\uparrow)} \right). \quad (E(\uparrow\uparrow), E(\uparrow\downarrow) \gg |J_A|) \end{aligned} \quad (4.47)$$

That is, under the Coulomb interaction between the ions, the energy of the system becomes dependent on the spin quantum number of the M_1 -O- M_2 system. Since p' can also transfer to M_2 ion, and p to transfer to M_1 and M_2 , the energy term including $|b|^2$ should be multiplied by 4. By employing the relations of

$$\begin{aligned} \langle S, M_S | 2\vec{s}_{d1} \cdot \hat{s}_{d2} | S, M_S \rangle &= S(S+1) - 2s(s+1) \quad (\hat{S} = \hat{s}_{d1} + \hat{s}_{d2}) \\ &= \begin{cases} 2 - \frac{3}{2} = \frac{1}{2}, & (S=1) \\ -\frac{3}{2}, & (S=0) \end{cases} \end{aligned} \quad (4.48)$$

equations (4.46) and (4.47), each multiplied by 4, can be formulated in a unified form of

$$E^i = \langle S, M_S | \hat{H}_{ex} | S, M_S \rangle + \text{constant}, \quad (4.49)$$

$$\hat{H}_{ex}(d_1, d_2) \equiv -2J_{A \text{ sup}} \hat{s}_{d1} \cdot \hat{s}_{d2}, \quad (4.50)$$

$$J_{A \text{ sup}} = |b|^2 J_A \left(\frac{1}{E^2(\uparrow\downarrow)} - \frac{1}{E^2(\uparrow\uparrow)} \right) \quad (4.51)$$

just in the same way as the exchange Hamiltonian was deduced for He atom ((2.158)–(2.161)). $J_{A \text{ sup}}$ is called superexchange integral. It depends not only on the exchange integral between p_x and d but also on the transfer energy of p_x to M ion. Here p_x electrons of the non-magnetic oxygen ion play an intermediary between the spins of M_1 and M_2 ions.

4.2.3 Anderson's Potential and Kinetic Exchanges

Anderson's theory explains the ferro- and anti-ferromagnetic coupling between the ion spins in oxides reasonably [3].

4.2.3.1 Hamiltonian of a Magnetic Electron System in Wannier Function Representation

Let $\{\varphi_{\vec{k}}(\vec{r})\}$ denote the Bloch waves of the electrons of all spins parallel in a 3d energy band. Wannier function is a convenient tool to analyze the problems where the localization of electron plays an important role. Consider the case in which there are N 3d ions in a unit volume and a 3d band is filled by N electrons. The Wannier function $W_{\alpha}(\vec{r}) \equiv W(\vec{r} - \vec{R}_{\alpha})$ of the 3d electron at the magnetic ion site $\vec{R}_{\alpha}$ is defined by the Fourier transformation of the Bloch wave $\varphi_{\vec{k}}(\vec{r})$ as

$$W_{\alpha}(\vec{r}) = |\alpha\rangle = \frac{1}{\sqrt{N}} \sum_{\vec{k}} \exp(-i\vec{k} \cdot \vec{R}_{\alpha}) \varphi_{\vec{k}}(\vec{r}), \quad (4.52)$$

where the sum $\sum_{\vec{k}}$ is over the first Brillouin zone (Sect. 3.8.2). It can be easily proved that $\{W_{\alpha}(\vec{r})\}$ is orthonormal as well as $\{\varphi_{\vec{k}}(\vec{r})\}$. $W_{\alpha}(\vec{r})$ is characterized by its localization around the $\vec{R}_{\alpha}$ site such as in the case of $\varphi_{\vec{k}}(\vec{r})$ is a plane wave $\exp(i\vec{k} \cdot \vec{r})$ of constant electron density the Wannier function is overwhelmingly localized at $\vec{R}_{\alpha}$ as $W_{\alpha}(\vec{R}_{\alpha}) = \sqrt{N}$ and

$$W_{\alpha}(\vec{R}_{\beta \neq \alpha}) = (1/\sqrt{N}) \sum_{\vec{k}} \exp[i\vec{k} \cdot (\vec{R}_{\beta \neq \alpha} - \vec{R}_{\alpha})] = 0.$$

The Hamiltonian of the electron system in the Wannier function representation is

$$\hat{H} = \hat{H}_1^0 + \hat{H}_1' + \hat{H}_1'' + \hat{H}_2, \quad (4.53)$$

$$\hat{H}_1^0 = \sum_{\alpha} \sum_{\sigma}^{\pm} h_{\alpha\alpha} \hat{a}_{\alpha,\sigma}^+ \hat{a}_{\alpha,\sigma}, \quad (4.54)$$

$$\hat{H}_1' = \sum_{\alpha} \sum_{\sigma}^{\pm} h_{\alpha\alpha} \hat{a}_{\alpha,\sigma}^+ \hat{a}_{\alpha,-\sigma}, \quad \hat{H}_1'' = \sum_{\alpha \neq \beta} \sum_{\sigma, \sigma'}^{\pm} h_{\alpha\beta} \hat{a}_{\alpha,\sigma}^+ \hat{a}_{\beta,\sigma'}, \quad (\text{a5.24}) \quad (4.55)$$

$$h_{\alpha\beta} = \int W_{\alpha}^*(\vec{r}) \hat{h}(\vec{r}) W_{\beta}(\vec{r}) d\vec{r}, \quad (4.56)$$

$$\hat{h}(\vec{r}) = \frac{\hat{p}^2(\vec{r})}{2m} + V(\vec{r}), \quad (V(\vec{r}) : \text{external potential}) \quad (4.57)$$

$$\hat{H}_2 = \frac{1}{2} \sum_{\alpha, \beta, \gamma, \delta} \sum_{\sigma, \sigma', \sigma'', \sigma'''}^{\pm} g_{\alpha\beta\gamma\delta} \hat{a}_{\alpha, \sigma}^+ \hat{a}_{\beta, \sigma'}^+ \hat{a}_{\gamma, \sigma''} \hat{a}_{\delta, \sigma'''} \quad (\text{a5.34}) \quad (4.58)$$

$$g_{\alpha\beta\gamma\delta} \equiv \int W_{\alpha}^*(\vec{r}_1) W_{\beta}^*(\vec{r}_2) g(\vec{r}_1, \vec{r}_2) W_{\gamma}(\vec{r}_2) W_{\delta}(\vec{r}_1) dv_1 dv_2, \quad (4.59)$$

$$g(\vec{r}_1, \vec{r}_2) = \frac{e^2}{4\pi\epsilon_0 r_{12}}. \quad (2.12)$$

A ground spin-orbital state $|g\rangle$ (g : Arabic) is an eigenfunction of $\hat{H}_1^0$ in which every ion site has a localized 3d electron.

$$\hat{H}_1^0 |g\rangle = \sum_{\alpha} \sum_{\sigma}^{\pm} h_{\alpha\alpha} \hat{a}_{\alpha, \sigma}^+ \hat{a}_{\alpha, \sigma} |g\rangle = \left(\sum_{\alpha} h_{\alpha\alpha} \right) |g\rangle = E_g |g\rangle. \quad (4.60)$$

Since $h_{\alpha\alpha}$ is irrelevant to spin, σ of $W_{\alpha}(\vec{r})\chi_{\alpha}(\sigma)$ is arbitrary and $|g\rangle$ is multifold spin degenerate.

4.2.3.2 Potential Exchange

Consider the first-order perturbation of $\hat{H}_2$. Equation (4.2) holds for the ground states and the problem is quite similar to that of the direct exchange interaction (Sect. 4.1.1 and 4.1.2). By neglecting the interactions between non-neighbor ions and repeating the same procedures of (4.6)–(4.10), $\hat{H}_2$ of (4.58) gives rise to Hamiltonian including the exchange Hamiltonian as

$$\begin{aligned} \hat{H}_2 &= \frac{1}{2} \sum_{\alpha} \sum_{\beta}^{n(\alpha)} \sum_{\sigma, \sigma'}^{\pm} g_{\alpha\beta\beta\alpha} \hat{a}_{\alpha, \sigma}^+ \hat{a}_{\beta, \sigma'}^+ \hat{a}_{\beta, \sigma'} \hat{a}_{\alpha, \sigma} + \frac{1}{2} \sum_{\alpha} \sum_{\beta}^{n(\alpha)} \sum_{\sigma, \sigma'}^{\pm} g_{\alpha\beta\alpha\beta} \hat{a}_{\alpha, \sigma}^+ \hat{a}_{\beta, \sigma'}^+ \hat{a}_{\alpha, \sigma'} \hat{a}_{\beta, \sigma} \\ &= \frac{1}{2} \sum_{\alpha} \sum_{\beta}^{n(\alpha)} K_{2\alpha\beta} + \frac{1}{2} \sum_{\alpha} \sum_{\beta}^{n(\alpha)} \left(-\frac{1}{2} - 2J_{A2} \hat{s}_{\alpha} \cdot \hat{s}_{\beta} \right), \\ &\quad \left(\sum_{\beta}^{n(\alpha)} : \text{sum over the neighbors of } \alpha \text{ atom} \right) \end{aligned} \quad (4.61)$$

$$K_{2\alpha\beta} \equiv \int W_{\alpha}^*(\vec{r}_1) W_{\alpha}^*(\vec{r}_2) \frac{e^2}{4\pi\epsilon_0 r_{12}} W_{\alpha}(\vec{r}_2) W_{\alpha}(\vec{r}_1) dv_1 dv_2, \quad (4.62)$$

$$J_{A2} = \int W_{\alpha}^*(\vec{r}_1) W_{\beta}^*(\vec{r}_2) \frac{e^2}{4\pi\epsilon_0 r_{12}} W_{\alpha}(\vec{r}_2) W_{\beta}(\vec{r}_1) dv_1 dv_2. \quad (\alpha, \beta : \text{neighbors}) \quad (4.63)$$

The exchange interaction $(1/2) \sum_{\alpha} \sum_{\beta}^{n(\alpha)} (-2J_{A2} \hat{s}_{\alpha} \cdot \hat{s}_{\beta})$ in (4.61) is called potential exchange. Since the exchange integral J_{A2} is positive (2.166) the potential exchange couples the spins parallel.

4.2.3.3 Kinetic Exchange

The excited states in which a 3d electron of an ion site is transferred to a neighbor ion site will be considered. Let $\{|\mu\rangle\}$ and E_e represent the states and eigenenergy. Consider the diagonal term of the second-order perturbation of $\hat{H}_1''$

$$\sum_{\mu} \frac{\langle l | \hat{H}_1'' | \mu \rangle \langle \mu | \hat{H}_1'' | l \rangle}{E - E_e}. \quad (\text{a6.8}) \quad (4.64)$$

By approximating $E - E_e$ by $E_g - E_e = -U$ ($U > 0$) (4.64) simplifies to

$$\begin{aligned} & -\frac{1}{U} \sum_{\mu} \langle l | \sum_{\alpha} \sum_{\beta}^{n(\alpha)} \sum_{\sigma, \sigma'}^{\pm} h_{\alpha\beta} \hat{a}_{\alpha, \sigma}^+ \hat{a}_{\beta, \sigma'} | \mu \rangle \langle \mu | \sum_{\alpha} \sum_{\beta}^{n(\alpha)} \sum_{\sigma, \sigma'}^{\pm} h_{\alpha\beta} \hat{a}_{\alpha, \sigma}^+ \hat{a}_{\beta, \sigma'} | l \rangle \\ &= -\frac{1}{U} \langle l | \sum_{\alpha} \sum_{\beta}^{n(\alpha)} \sum_{\sigma, \sigma'}^{\pm} h_{\alpha\beta} \hat{a}_{\alpha, \sigma}^+ \hat{a}_{\beta, \sigma} h_{\beta\alpha} \hat{a}_{\beta, \sigma'}^+ \hat{a}_{\alpha, \sigma'} | l \rangle \quad (\langle \mu | \mu' \rangle = \delta(\mu, \mu'), \text{ so} \\ & \sum_{\mu} |\mu\rangle \langle \mu | \mu' \rangle = |\mu'\rangle \text{ for arbitrary } |\mu'\rangle, \text{ thus } \sum_{\mu} |\mu\rangle \langle \mu | = 1) \\ &= -\frac{|h|^2}{U} \sum_{\alpha} \sum_{\beta}^{n(\alpha)} \sum_{\sigma, \sigma'}^{\pm} \langle l | \hat{a}_{\alpha, \sigma}^+ \hat{a}_{\beta, \sigma'}^+ \hat{a}_{\alpha, \sigma'} \hat{a}_{\beta, \sigma} | l \rangle. \quad (h \equiv h_{\alpha, n(\alpha)}) \end{aligned} \quad (4.65)$$

The last expression gives rise to the exchange Hamiltonian of

$$-\frac{|h|^2}{U} \sum_{\alpha} \sum_{\beta}^{n(\alpha)} \sum_{\sigma, \sigma'}^{\pm} \hat{a}_{\alpha, \sigma}^+ \hat{a}_{\beta, \sigma'}^+ \hat{a}_{\alpha, \sigma'} \hat{a}_{\beta, \sigma} = \frac{|h|^2}{U} \sum_{\alpha} \sum_{\beta}^{n(\alpha)} 2\hat{s}_{\alpha} \cdot \hat{s}_{\beta}. \quad ((4.6) - (4.10)) \quad (4.66)$$

This exchange interaction is called kinetic exchange. Contrary to that the potential exchange couples the spins parallel, the kinetic exchange couples the spins anti-parallel.

4.3 RKKY Exchange Interaction

In rare-earth metals, the distances between the nearest neighbor ions (~ 0.35 nm) being far larger than the orbital radii of the 4f subshells (~ 0.035 nm) overlap of the 4f electrons with those of the neighbor atoms is very small, so the direct 4f–4f exchange

interaction should be very small. But these metals have 10–300 K range Néel or Curie temperatures, which show that the exchange interactions are not small in many metals. The 4f subshell is imbedded inner side enclosed by the full $5s^2 5p^6$ subshells while the outermost $5d^1 6s^2$ electrons itinerate the whole metal as conduction electrons. The RKKY theory (Ruderman, Kittel(1954), Kasuya(1956), Yoshida(1957)) explains the 4f–4f exchange interaction [4]. It considers that the conduction electron spins are magnetized through direct exchange interactions with the 4f electrons. The 4f ions couple each other indirectly through intermediary of the conduction electrons bringing about the magnetic ordering.

Below, the wave function of each conduction electron is approximated by (3.134) of free electron.

4.3.1 *f-s Exchange Hamiltonian $\hat{H}_{\text{ex}}$*

N conduction electrons in a unit volume are under the direct exchange interactions from the 4f ions. The exchange Hamiltonian is

$$\hat{H}_{\text{ex}} = \sum_i^{1,2,\dots,N} \sum_n -2J_A(\vec{r}_i - \vec{R}_n) \vec{S}_n \cdot \hat{s}_i, \quad (4.67)$$

where $\vec{S}_n$ and $\vec{R}_n$ are the spin and position vector of the n^{th} rare-earth ion, $\hat{s}_i$ and $\vec{r}_i$ are the spin and position vector of i^{th} conduction electron, and $J_A(\vec{r}_i - \vec{R}_n)$ the exchange integral of the i^{th} conduction electron and n^{th} rare-earth ion. The second quantized representation of the Hamiltonian of (4.67) is

$$\begin{aligned} \hat{H}_{\text{ex}} &= \sum_{\vec{k}, \vec{k}'} \sum_{\sigma, \sigma'}^{\pm} \langle \vec{k}, \sigma | \sum_n -2J_A(\vec{r} - \vec{R}_n) \vec{S}_n \cdot \hat{s} | \vec{k}', \sigma' \rangle \hat{a}_{\vec{k}, \sigma}^{\pm} \hat{a}_{\vec{k}', \sigma'}^{\pm} \quad (\text{a5.24}) \\ &= - \sum_{\vec{k}, \vec{k}'} \sum_n \int \exp[-i(\vec{k} - \vec{k}') \cdot \vec{r}] J_A(\vec{r} - \vec{R}_n) d\vec{v} \sum_{\sigma, \sigma'}^{\pm} \\ &\quad \times \langle \sigma | 2S_{zn} \hat{s}_z + S_{+n} \hat{s}_- + S_{-n} \hat{s}_+ | \sigma' \rangle \hat{a}_{\vec{k}, \sigma}^{\pm} \hat{a}_{\vec{k}', \sigma'}^{\pm} \\ &= - \sum_{\vec{k}, \vec{k}'} \sum_n \exp[-i(\vec{k} - \vec{k}') \cdot \vec{R}_n] J_{A, \vec{k} - \vec{k}'} \\ &\quad \times \sum_{\sigma, \sigma'}^{\pm} \langle \sigma | S_{zn} (\hat{a}_+^{\dagger} \hat{a}_+ - \hat{a}_-^{\dagger} \hat{a}_-) + S_{+n} \hat{a}_-^{\dagger} \hat{a}_+ + S_{-n} \hat{a}_+^{\dagger} \hat{a}_- | \sigma' \rangle \hat{a}_{\vec{k}, \sigma}^{\pm} \hat{a}_{\vec{k}', \sigma'}^{\pm} \\ &\quad ((\text{a539})-(\text{a541})) \end{aligned}$$

$$\begin{aligned}
&= - \sum_{\vec{k}, \vec{k}'} \sum_n \exp \left[-i(\vec{k} - \vec{k}') \cdot \vec{R}_n \right] J_{A, \vec{k} - \vec{k}'} \left[S_{zn} \left(\hat{a}_{\vec{k}, +}^+ \hat{a}_{\vec{k}', +} - \hat{a}_{\vec{k}, -}^+ \hat{a}_{\vec{k}', -} \right) \right. \\
&\quad \left. + S_{+n} \hat{a}_{\vec{k}, -}^+ \hat{a}_{\vec{k}', +} + S_{-n} \hat{a}_{\vec{k}, +}^+ \hat{a}_{\vec{k}', -} \right], \quad (4.68)
\end{aligned}$$

$$J_{A, \vec{k} - \vec{k}'} \equiv \int \exp[-i(\vec{k} - \vec{k}') \cdot \vec{r}] J_A(\vec{r}) d\vec{r}. \quad (4.69)$$

$J_A(\vec{r})$ is the quantity depending on the overlap of the orbits of conduction and 4f electrons. The overlap in a finite space is approximated by the infinite overlap on the center of the ion as

$$J_A(\vec{r}) = J_A \delta(\vec{r}). \quad (\delta(\vec{r}) : \text{Dirac delta}) \quad (4.70)$$

Under this approximation (4.69) and (4.68) simplify to

$$J_{A, \vec{k} - \vec{k}'} = J_A, \quad (4.71)$$

$$\begin{aligned}
\hat{H}_{\text{ex}} &= -J_A \sum_{\vec{k}, \vec{k}'} \sum_n \exp[-i(\vec{k} - \vec{k}') \cdot \vec{R}_n] [S_{zn} (\hat{a}_{\vec{k}, +}^+ \hat{a}_{\vec{k}', +} - \hat{a}_{\vec{k}, -}^+ \hat{a}_{\vec{k}', -}) \\
&\quad + S_{+n} \hat{a}_{\vec{k}, -}^+ \hat{a}_{\vec{k}', +} + S_{-n} \hat{a}_{\vec{k}, +}^+ \hat{a}_{\vec{k}', -}]. \quad (4.72)
\end{aligned}$$

4.3.2 First-Order Perturbation of $\hat{H}_{\text{ex}}$

From the first-order perturbation secular equation of the exchange interaction (Appendix 6)

$$\begin{aligned}
&\begin{vmatrix} \langle \vec{k}, + | \hat{H}_{\text{ex}} | \vec{k}, + \rangle - \varepsilon^{(1)} & \langle \vec{k}, + | \hat{H}_{\text{ex}} | \vec{k}, - \rangle \\ \langle \vec{k}, - | \hat{H}_{\text{ex}} | \vec{k}, + \rangle & \langle \vec{k}, - | \hat{H}_{\text{ex}} | \vec{k}, - \rangle - \varepsilon^{(1)} \end{vmatrix} \\
&= \begin{vmatrix} -J_A \sum_n S_{zn} - \varepsilon^{(1)} & -J_A \sum_n S_{-n} \\ -J_A \sum_n S_{+n} & J_A \sum_n S_{zn} - \varepsilon^{(1)} \end{vmatrix} = 0 \quad (4.73)
\end{aligned}$$

we get the first-order perturbation energy $\varepsilon^{(1)}$ for each conduction electron:

$$\varepsilon^{(1)} = \pm \Delta, \quad \Delta \equiv -J_A \sqrt{\left(\sum_n \vec{S}_n \right) \cdot \left(\sum_n \vec{S}_n \right)} = -J_A \sqrt{\sum_{n,m} \vec{S}_n \cdot \vec{S}_m}. \quad (4.74)$$

The zero's order approximate eigenstates are $|\vec{k}, \pm\rangle$. $\varepsilon^{(1)}$ depends on the spin but not on $\vec{k}$, and the spin-up and spin-down energy band shifts upward and downward by Δ , respectively (Fig. 3.28b). To decrease the energy of the system, the electrons of spin-up above the Fermi level transfer into the vacant states of spin-down band below the Fermi level by changing the spin and $\vec{k}$ simultaneously (Fig. 3.28c). $k_F^- - k_F = k_F - k_F^+ \ll k_F$ where k_F^- and k_F^+ are the new Fermi radii for the spin-down and spin-up bands. The change of the electron numbers of spin-up and spin-down bands are

$$\mp \frac{dN}{2} = \mp n(\varepsilon_F) \Delta, \quad (\text{Fig. 3.28}) \quad (4.75)$$

and the change of the energy of the system is

$$E^{(1)} = -\frac{dN}{2} \Delta = -n(\varepsilon_F) \Delta^2 = -\frac{3N J_A^2}{4\varepsilon_F} \sum_{m,n} \vec{S}_m \cdot \vec{S}_n. \quad (4.76)$$

The state of ferromagnetic coupling between all rare-earth ions has the lowest energy regardless the sign of J_A . Total spin of conduction electrons is parallel with those of rare-earth ions if $J_A > 0$ or antiparallel if $J_A < 0$.

4.3.3 Oscillatory Decay of Conduction Electron Magnetization

4.3.3.1 First-Order Approximate Spin-Orbital of Conduction Electron

The spin-orbital is

$$\begin{aligned} \psi'_{\vec{k},\pm} &= \psi_{\vec{k},\pm} + \sum_{\vec{k}'} \sum_{\sigma}^{\pm} \frac{\langle \vec{k}', \sigma | \hat{H}_{\text{ex}} | \vec{k}, \pm \rangle}{\varepsilon_{\vec{k}} - \varepsilon_{\vec{k}'}} \psi_{\vec{k}',\sigma} \quad (\text{Appendix 6}) \\ &= \psi_{\vec{k},\pm} - J_A \sum_{\vec{k}'}^{\vec{k}' \neq \vec{k}} \frac{2m}{\hbar^2(k^2 - k'^2)} \sum_{\sigma}^{\pm} \sum_n \langle \vec{k}', \sigma | \sum_{\vec{k}'', \vec{k}'''} \exp[-i(\vec{k}'' - \vec{k}''') \cdot \vec{R}_n] \\ &\quad \times [S_{zn} (\hat{a}_{\vec{k}'',+}^+ \hat{a}_{\vec{k}'',+} - \hat{a}_{\vec{k}'',-}^+ \hat{a}_{\vec{k}'',-}) \\ &\quad + S_{+n} \hat{a}_{\vec{k}'',-}^+ \hat{a}_{\vec{k}'',+} + S_{-n} \hat{a}_{\vec{k}'',+}^+ \hat{a}_{\vec{k}'',-}] | \vec{k}, \pm \rangle \psi_{\vec{k}',\sigma} \quad ((3.135), (4.72)) \\ &= \psi_{\vec{k},\pm} - J_A \sum_{\vec{k}'}^{\vec{k}' \neq \vec{k}} \frac{2m}{\hbar^2(k^2 - k'^2)} \sum_n \exp[-i(\vec{k}' - \vec{k}) \cdot \vec{R}_n] \\ &\quad \times (\pm S_{zn} \psi_{\vec{k}',\pm} + S_{\pm n} \psi_{\vec{k}',\mp}). \end{aligned} \quad (4.77)$$

4.3.3.2 Conduction Electron Densities of $\pm$ Spins

Let

$$F(x) \equiv \frac{x \cos x - \sin x}{x^4}, \quad (\text{called RKKY function}) \quad (4.78)$$

$$\vec{q} \equiv \vec{k}' - \vec{k}, \quad (k'_\alpha, k_\alpha = 2\pi \times \text{integer}, \quad \alpha = x, y, z) \quad (4.79)$$

$$f(q) \equiv 1 + \frac{4k_F^2 - q^2}{4k_F q} \ln \left| \frac{q + 2k_F}{q - 2k_F} \right| = f(-q), \quad (q \neq 0) \quad (4.80)$$

$$f(0) \equiv \lim_{q \rightarrow 0} f(q) = 2, \quad (4.81)$$

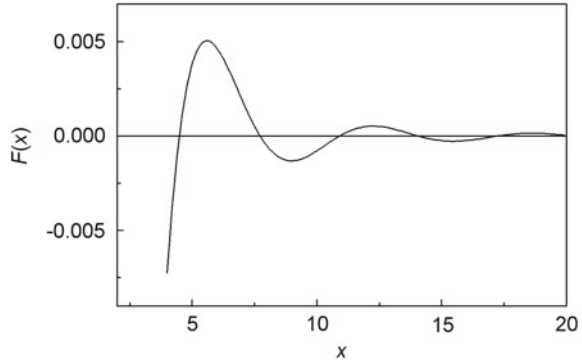
then

$$\sum_{\vec{k}}^{\vec{k}+\vec{q} \neq |\vec{k}| \leq k_F} \frac{1}{\vec{k}^2 - (\vec{k} + \vec{q})^2} = -\frac{k_F}{16\pi^2} f(q), \quad (q \neq 0. \text{ Note 1 of this section}) \quad (4.82)$$

$$\sum_{\vec{q}} f(q) \exp(i\vec{q} \cdot \vec{R}) = -12N\pi F(2k_F R). \quad (\text{sum } \sum_{\vec{q}} \text{ is over all } \vec{q} \text{ including } 0. \text{ Note 2 of this section}) \quad (4.83)$$

The conduction electron densities of $\pm$ spins are

$$\begin{aligned} \rho^\pm(\vec{r}) &= \sum_{\vec{k}}^{\vec{k} \leq k_F^\pm} |\psi'_{\vec{k}, \pm}(\vec{r})|^2 = \sum_{\vec{k}}^{\vec{k} \leq k_F^\pm} |\psi_{\vec{k}, \pm}(\vec{r})|^2 \\ &\mp \frac{2mJ_A}{\hbar^2} \sum_{\vec{k}}^{\vec{k} \leq k_F} \sum_{\vec{k}'}^{\vec{k}' \neq \vec{k}} \frac{1}{\vec{k}^2 - \vec{k}'^2} \sum_n [\exp[i(\vec{k} - \vec{k}') \cdot (\vec{r} - \vec{R}_n)] \\ &+ \exp[-i(\vec{k} - \vec{k}') \cdot (\vec{r} - \vec{R}_n)]] S_{zn} \\ &\left(\text{in the last term of the last expression the approximation of } \sum_{\vec{k}}^{\vec{k} \leq k_F} \text{ replaced } \sum_{\vec{k}}^{\vec{k} \leq k_F^\pm} \right) \\ &= \frac{N}{2} \pm \frac{3NJ_A}{8\varepsilon_F} \sum_n 2S_{zn} \pm \frac{mJ_A k_F}{4\hbar^2 \pi^2} \sum_{\vec{q}} \sum_n^{\neq 0} f(q) \exp[i\vec{q} \cdot (\vec{r} - \vec{R}_n)] S_{zn} \left(\sum_n S_{zn} \gg \sum_n S_{\pm n} \right), \\ &\sum_{\vec{k}}^{\vec{k} \leq k_F^\pm} |\psi_{\vec{k}, \pm}(\vec{r})|^2 \approx \frac{N}{2} \pm \frac{3NJ_A}{4\varepsilon_F} \sum_n S_{zn}, \quad (4.74) - (4.75), (3.142), (4.82) \\ &= \frac{N}{2} \pm \frac{3NJ_A}{8\varepsilon_F} \sum_{\vec{q}} \sum_n f(q) \exp[i\vec{q} \cdot (\vec{r} - \vec{R}_n)] S_{zn} \quad ((3.139), (3.140)) \end{aligned}$$

Fig. 4.4 RKKY function

$$= \frac{N}{2} \mp \frac{(3N)^2 \pi J_A}{2\varepsilon_F} \sum_n F(2k_F |\vec{r} - \vec{R}_n|) S_{zn}. \quad (4.84)$$

$F(x)$ is an oscillatory decaying function (Fig. 4.4). Equation (4.84) shows that under the exchange interaction with the n^{th} ion the density of conduction electron of $\pm$ spins makes oscillatory decay around the average density $N/2$ with increase of the distance $|\vec{r} - \vec{R}_n|$.

4.3.4 Indirect Exchange Interaction Between Rare-Earth Ions

4.3.4.1 Second-Order Perturbation Energy of $\hat{H}_{\text{ex}}$

The second-order perturbation energy is

$$\begin{aligned} E^{(2)} &= \sum_{\vec{k}} \sum_{\substack{|\vec{k}'| \leq k_F \\ |\vec{k}'| \neq |\vec{k}|}} \sum_{\sigma, \sigma'} \frac{\pm |\langle \vec{k}, \sigma | \hat{H}_{\text{ex}} | \vec{k}', \sigma' \rangle|^2}{\varepsilon_{\vec{k}} - \varepsilon_{\vec{k}'}} \quad ((\text{a6.8})-(\text{a6.9})) \\ &= \sum_{\vec{k}} \sum_{\substack{|\vec{k}'| \leq k_F \\ |\vec{k}'| \neq |\vec{k}|}} \frac{J_A^2}{\varepsilon_{\vec{k}} - \varepsilon_{\vec{k}'}} \sum_{m,n} \left\{ \langle \vec{k}, + | \exp[-i(\vec{k} - \vec{k}') \cdot \vec{R}_n] S_{zn} \hat{a}_{\vec{k},+}^+ \hat{a}_{\vec{k}',+} | \vec{k}', + \rangle \right. \\ &\quad \times \langle \vec{k}', + | \exp[-i(\vec{k}' - \vec{k}) \cdot \vec{R}_m] S_{zm} \hat{a}_{\vec{k}',+}^+ \hat{a}_{\vec{k},+} | \vec{k}, + \rangle \\ &\quad + \langle \vec{k}, + | \exp[-i(\vec{k} - \vec{k}') \cdot \vec{R}_n] S_{-n} \hat{a}_{\vec{k},+}^+ \hat{a}_{\vec{k}',-} | \vec{k}', - \rangle \\ &\quad \times \langle \vec{k}', - | \exp[-i(\vec{k}' - \vec{k}) \cdot \vec{R}_m] S_{+m} \hat{a}_{\vec{k}',-}^+ \hat{a}_{\vec{k},+} | \vec{k}, + \rangle \\ &\quad + \langle \vec{k}, - | \exp[-i(\vec{k} - \vec{k}') \cdot \vec{R}_n] S_{+n} \hat{a}_{\vec{k},-}^+ \hat{a}_{\vec{k}',+} | \vec{k}', + \rangle \\ &\quad \times \langle \vec{k}', + | \exp[-i(\vec{k}' - \vec{k}) \cdot \vec{R}_m] S_{-m} \hat{a}_{\vec{k}',+}^+ \hat{a}_{\vec{k},-} | \vec{k}, - \rangle \end{aligned}$$

$$\begin{aligned}
& + \langle \vec{k}, - | \exp[-i(\vec{k} - \vec{k}') \cdot \vec{R}_n] S_{zn} \hat{a}_{\vec{k}',-}^+ \hat{a}_{\vec{k},-} | \vec{k}, - \rangle \\
& \times \langle \vec{k}', - | \exp[-i(\vec{k}' - \vec{k}) \cdot \vec{R}_m] S_{zm} \hat{a}_{\vec{k},-}^+ \hat{a}_{\vec{k}',-} | \vec{k}, - \rangle \} \quad (4.72) \\
& = \frac{2mJ_A^2}{\hbar^2} \sum_{\vec{q}}^{\neq 0} \sum_{\vec{k}}^{|\vec{k}+\vec{q}| \neq |\vec{k}| \leq k_F} \sum_{m,n} \frac{\exp[i\vec{q} \cdot (\vec{R}_m - \vec{R}_n)]}{\vec{k}^2 - (\vec{k} + \vec{q})^2} (2\vec{S}_m \cdot \vec{S}_n) \\
& = -\frac{3NJ_A^2}{8\varepsilon_F} \sum_{\vec{q}}^{\neq 0} \sum_{m,n} f(q) \exp[i\vec{q} \cdot (\vec{R}_m - \vec{R}_n)] \vec{S}_m \cdot \vec{S}_n. \\
& ((4.82), (3.139), (3.140)) \quad (4.85)
\end{aligned}$$

4.3.4.2 Total Exchange Energy

$$\begin{aligned}
E^{(1)} + E^{(2)} &= -\frac{3NJ_A^2}{4\varepsilon_F} \sum_{m,n}^{m \neq n} \vec{S}_m \cdot \vec{S}_n \\
&\quad - \frac{3NJ_A^2}{8\varepsilon_F} \sum_{\vec{q}}^{\neq 0} \sum_{m,n}^{m \neq n} f(q) \exp[i\vec{q} \cdot (\vec{R}_m - \vec{R}_n)] \vec{S}_m \cdot \vec{S}_n \\
&= -\frac{3NJ_A^2}{8\varepsilon_F} \sum_{\vec{q}} \sum_{m,n}^{m \neq n} f(q) \exp[i\vec{q} \cdot (\vec{R}_m - \vec{R}_n)] \vec{S}_m \cdot \vec{S}_n \quad (4.81) \\
&= \frac{(3NJ_A)^2 \pi}{2\varepsilon_F} \sum_{m,n}^{m \neq n} F(2k_F |\vec{R}_m - \vec{R}_n|) \vec{S}_m \cdot \vec{S}_n. \quad (4.83) \quad (4.86)
\end{aligned}$$

It has the form of exchange interactions between the spins of rare-earth ions and can be explained as the rare-earth ions are exchange interacting each other through the intermediary of the conduction electrons. The effective exchange integral of a pair of the ions decays oscillatory with increase of the distance between them, becoming positive in some distance intervals and negative in other distance intervals. The RKKY exchange interaction is a somewhat long range interaction in contrast to that the direct exchange interaction is a short range interaction.

4.3.5 Curie Temperature and de Gennes Factor

The exchange energy of $\vec{S}_m$ with the other spins of rare-earth ions $\frac{(3NJ_A)^2 \pi}{2\varepsilon_F} \vec{S}_m \cdot \sum_n^{n \neq m} F(2k_F |\vec{R}_m - \vec{R}_n|) \vec{S}_n$ can be considered as the potential energy of the magnetic polarization moment of the ion $-g_J \vec{J}_m \mu_B$ (2.98) in the molecular field

$-wNg_J\mu_B \sum_n \vec{J}_n/\mu_0$ (3.15). Consider the simple ferromagnetic case of $\vec{S}_n = \vec{S}$. It holds

$$\frac{(3NJ_A)^2\pi}{2\varepsilon_F} S^2 \sum_n F(2k_F|\vec{R}_m - \vec{R}_n|) \propto (g_J - 1)^2 J^2 \propto wg_J^2 J^2. \quad (2.111) \quad (4.87)$$

Inserting the last relation into (3.21) we get

$$T_C = \frac{wNg_J^2 J(J+1)}{3\mu_0 k_B} \propto (g_J - 1)^2 J(J+1), \quad (4.88)$$

that is T_C of 4f metals and the compounds constituted of 4f and non-magnetic elements is proportional to $(g_J - 1)^2 J(J+1)$. $(g_J - 1)^2 J(J+1)$ is called de Gennes factor.

Figure 4.5 demonstrates $CJ(J+1)(g_J - 1)^2$ as a function of R^{+3} ion, which is compared with the experimental values of T_C for ferromagnetic RAI_2 compounds (The compounds of $R = Ce$ and Eu are anti-ferromagnetic, and La^{+3} , Yb^{+3} and Lu^{+3} have no magnetic moment). The value of the coefficient C is fitted to make the calculated value for Gd^{+3} ion to coincide with the experimental value of $GdAl_2$. The theoretical values, which are deduced by neglecting the excited multiplets, are apparently smaller for the light rare-earth ions and slightly larger for the heavy rare-earth ions. If the excited multiplets are taken into account, the discrepancies should be reduced. In fact, first, the values of $J (= |L - S|)$ of the ground multiplets for light rare-earth ions are smaller than $J (= L + S)$ for heavy rare-earth ions, which in general results in the smaller energy gaps between the energy levels of excited and ground multiplets for the light rare-earth ions than those for heavy rare-earth ions (2.70), Fig. 2.3). Therefore, the effects of the excited multiplet terms are larger for light rare-earth ions than heavy rare-earth ions. Second, the values of J of excited multiplets are larger than that of the ground multiplet for light rare-earth ions while they are smaller for heavy rare-earth ions. So the mixing of the excited multiples increases the theoretical values of T_C for the light rare-earth ions while it decreases T_C for the heavy rare-earth ions. For Gd^{+3} ion the energy level of the excited multiplet being very large (Fig. 2.3) the mixing has little effects on the T_C .

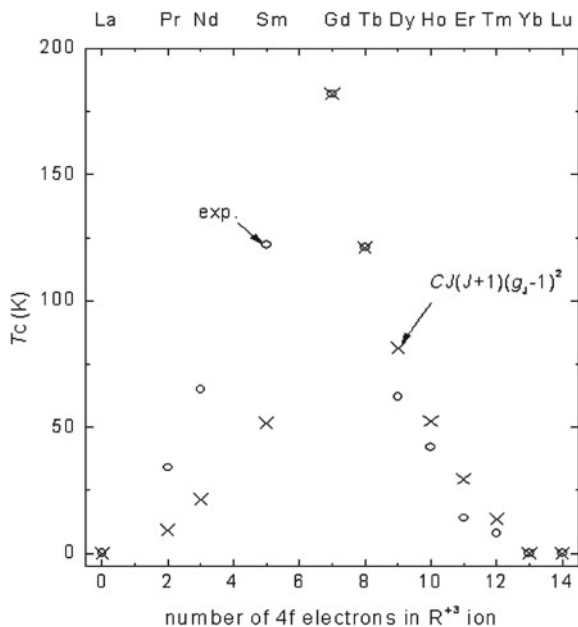
Note 1

Exploiting the relations of

$$\int_0^\pi \frac{\sin \theta d\theta}{(a + b \cos \theta)} = \frac{-1}{b} \ln \left| \frac{a - b}{a + b} \right|,$$

(if it happens that the denominator in the integrand of first expression becomes zero at some points, the integration should skip the points such as if

Fig. 4.5 $CJ(J+1)(g_J-1)^2$ of R^{+3} ion and T_C of RAl_2 [5] versus number of 4f electrons



$$a + b \cos \theta_c = 0, \quad \int_0^\pi \frac{\sin \theta d\theta}{(a + b \cos \theta)} = \int_0^{\theta_c^-} \frac{\sin \theta d\theta}{(a + b \cos \theta)} + \int_{\theta_c^+}^\pi \frac{\sin \theta d\theta}{(a + b \cos \theta)}.$$

The same is applicable below) (4.89)

$$\int_a^b \ln |x| dx = b(\ln |b| - 1) - a(\ln |a| - 1), \quad (4.90)$$

$$\lim_{x \rightarrow 0} x \ln x = 0, \quad (4.91)$$

$$\int_a^b x \ln |x| dx = b^2 \left(\frac{1}{2} \ln |b| - \frac{1}{4} \right) - a^2 \left(\frac{1}{2} \ln |a| - \frac{1}{4} \right), \quad (4.92)$$

we get

$$\sum_{\vec{k}}^{\vec{k} + \vec{q} \neq \vec{k} \leq k_F} \frac{1}{\vec{k}^2 - (\vec{k} + \vec{q})^2} = \frac{1}{(2\pi)^3} \int_0^{k_F} \int_0^\pi \frac{2\pi k^2 \sin \theta d\theta dk}{-(q^2 + 2qk \cos \theta)}$$

$$\begin{aligned}
& (\theta : \text{angle between } \vec{q} (\neq 0) \text{ and } \vec{k}) \\
&= \frac{1}{2(2\pi)^2 q} \int_0^{k_F} k \ln \left| \frac{2k - q}{2k + q} \right| dk \\
&= \frac{1}{2(2\pi)^2 q} \int_0^{k_F} \left[\left(k - \frac{q}{2}\right) \ln \left|k - \frac{q}{2}\right| - \left(k + \frac{q}{2}\right) \ln \left|k + \frac{q}{2}\right| \right. \\
&\quad \left. + \frac{q}{2} \ln \left|k - \frac{q}{2}\right| + \frac{q}{2} \ln \left(k + \frac{q}{2}\right) \right] dk \\
&= \frac{1}{2(2\pi)^2 q} \left\{ \left(k_F - \frac{q}{2}\right)^2 \left(\frac{\ln |k_F - q/2|}{2} - \frac{1}{4} \right) \right. \\
&\quad \left. - \left(k_F + \frac{q}{2}\right)^2 \left(\frac{\ln(k_F + q/2)}{2} - \frac{1}{4} \right) \right. \\
&\quad \left. + \frac{q}{2} \left[\left(k_F - \frac{q}{2}\right) \ln \left|k_F - \frac{q}{2}\right| + \frac{q}{2} \ln \frac{q}{2} - k_F \right] \right. \\
&\quad \left. + \frac{q}{2} \left[\left(k_F + \frac{q}{2}\right) \ln \left(k_F + \frac{q}{2}\right) - \frac{q}{2} \ln \frac{q}{2} - k_F \right] \right\} \\
&= -\frac{k_F}{16\pi^2} \left(1 + \frac{4k_F^2 - q^2}{4k_F q} \ln \left| \frac{2k_F + q}{2k_F - q} \right| \right). \tag{4.93}
\end{aligned}$$

Note 2

Some characteristics of complex functions

(1) Analytical function

If a complex function $\Psi(z)$ is differentiable at any point in the region D , $\Psi(z)$ is called analytical function in D .

(2) Jordan auxiliary theorem

Let CR be an arc $z = R \exp(i\phi)$ centered at the origin, $0 \leq \alpha \leq \phi \leq \beta \leq \pi$ (Fig.4.6). If $\Psi(z)$ is continuous on the CR of $R \geq R_0$ (R_0 : arbitrary finite positive real number) and $\lim_{R \rightarrow \infty} \Psi(z) = 0$, it holds

$$\lim_{R \rightarrow \infty} \int_{\text{CR}} \psi(z) \exp(imz) dz = 0. \quad (m : \text{arbitrary positive real number}) \tag{4.94}$$

(3) Cauchy theorem

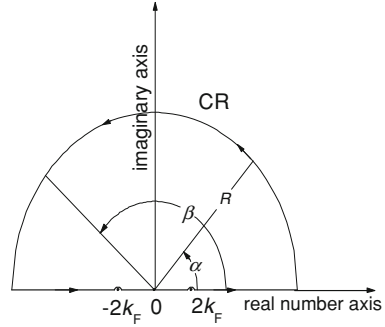
Let C be an arbitrary closed circuit in D . If $\Psi(z)$ is analytical in D , it holds

$$\oint_C \psi(z) dz = 0. \tag{4.95}$$

(4)

$$\ln(-1) = i\pi. \quad (\exp(i\pi) = -1) \tag{4.96}$$

Fig. 4.6 Integration path in the complex q plane



Deduction of (4.83)

Let θ denote the angle between $\vec{q}$ and $\vec{R}$.

(1)

$$\begin{aligned}
 F_1 &\equiv \frac{k_F}{2\pi} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(q) \exp(i\vec{q} \cdot \vec{R}) d^3q \\
 &= \frac{1}{2\pi} \int_0^{\infty} \int_0^{\pi} 2\pi q^2 \sin \theta \exp(iq R \cos \theta) \left(k_F + \frac{4k_F^2 - q^2}{4q} \ln \left| \frac{q + 2k_F}{q - 2k_F} \right| \right) d\theta dq \\
 &\quad ((4.80)-(4.81)) \\
 &= \frac{1}{iR} \int_0^{\infty} q [-\exp(iq R \cos \theta)]_0^{\pi} \left(k_F + \frac{4k_F^2 - q^2}{4q} \ln \left| \frac{q + 2k_F}{q - 2k_F} \right| \right) dq \\
 &= \frac{1}{iR} \int_0^{\infty} q [\exp(iq R) - \exp(-iq R)] \left(k_F + \frac{4k_F^2 - q^2}{4q} \ln \left| \frac{q + 2k_F}{q - 2k_F} \right| \right) dq \\
 &= \frac{1}{iR} \int_{-\infty}^{\infty} q \exp(iq R) \left(k_F + \frac{4k_F^2 - q^2}{4q} \ln \left| \frac{q + 2k_F}{q - 2k_F} \right| \right) dq. \quad (4.97)
 \end{aligned}$$

$|(q + 2k_F)/(q - 2k_F)|$ in the integrand is not an analytical function at $q = \pm 2k_F$. But $[(4k_F^2 - q^2)/(4q)] \ln |(q + 2k_F)/(q - 2k_F)| \rightarrow 0$ when $q \rightarrow \pm 2k_F$. To make the integrand analytical at every point, expand the real q to complex number and replace the infinitely small segment of the straight integration path centered at the points $\pm 2k_F$ by half circles above the points (Fig. 4.6).

(2)

$$F_2 \equiv \frac{1}{iR} \int_{-\infty}^{\infty} q \exp(iqR) \left(k_F + \frac{4k_F^2 - q^2}{4q} \ln \frac{q + 2k_F}{q - 2k_F} \right) dq \\ + \frac{1}{iR} \lim_{|q| \rightarrow \infty} \int_{CR} q \exp(iqR) \left(k_F + \frac{4k_F^2 - q^2}{4q} \ln \frac{q + 2k_F}{q - 2k_F} \right) dq \quad (4.98)$$

in which the integration path of the first integration along the real number axis of q is the same with F_1 , and that of the second integration is along the half circle CR of infinite radius R above the real number axis from $q = \infty (\alpha = 0)$ to $q = -\infty (\beta = \pi)$. The sum of the paths of the first and second integrations constitutes a closed circuit and hence according to the Cauchy theorem (4.95) it holds

$$F_2 = 0. \quad (4.99)$$

(3)

$$\lim_{|q| \rightarrow \infty} q \left(k_F + \frac{4k_F^2 - q^2}{4q} \ln \frac{q + 2k_F}{q - 2k_F} \right) \\ = \lim_{|q| \rightarrow \infty} \left\{ qk_F + \frac{4k_F^2 - q^2}{4} 2 \left[\frac{2k_F}{q} + \frac{1}{3} \left(\frac{2k_F}{q} \right)^3 + \dots \right] \right\} = 0, \quad (4.100)$$

hence, according to the Jordan auxiliary theorem (4.94)

$$\frac{1}{iR} \lim_{|q| \rightarrow \infty} \int_{CR} q \exp(iqR) \left(k_F + \frac{4k_F^2 - q^2}{4q} \ln \frac{q + 2k_F}{q - 2k_F} \right) dq = 0, \quad (4.101)$$

thus

$$\frac{1}{iR} \int_{-\infty}^{\infty} q \exp(iqR) \left(k_F + \frac{4k_F^2 - q^2}{4q} \ln \frac{q + 2k_F}{q - 2k_F} \right) dq = 0. \quad ((4.98), (4.101)) \quad (4.102)$$

- (4) Since $\ln[(q + 2k_F)/(q - 2k_F)] = \ln |(q + 2k_F)/(q - 2k_F)|$ in the regions of $q > 2k_F$ and $q < -2k_F$, and $(q + 2k_F)/(q - 2k_F) = -|(q + 2k_F)/(q - 2k_F)|$ in the region of $-2k_F < q < 2k_F$,

$$\begin{aligned}
F_1 &= F_1 - F_2 = \frac{1}{iR} \int_{-\infty}^{\infty} \exp(iqR) \left(k_F^2 - \frac{q^2}{4} \right) \left(\ln \left| \frac{q+2k_F}{q-2k_F} \right| - \ln \frac{q+2k_F}{q-2k_F} \right) dq \\
&= \frac{1}{iR} \int_{-2k_F}^{2k_F} \exp(iqR) \left(k_F^2 - \frac{q^2}{4} \right) \left(\ln \left| \frac{q+2k_F}{q-2k_F} \right| - \ln \frac{q+2k_F}{q-2k_F} \right) dq \\
&= \frac{1}{iR} \int_{-2k_F}^{2k_F} \exp(iqR) \left(k_F^2 - \frac{q^2}{4} \right) \left\{ \ln \left| \frac{q+2k_F}{q-2k_F} \right| - \left[\ln \left| \frac{q+2k_F}{q-2k_F} \right| - \ln(-1) \right] \right\} dq \\
&= \frac{\pi}{R} \int_{-2k_F}^{2k_F} \exp(iqR) \left(k_F^2 - \frac{q^2}{4} \right) dq. \quad (4.96)
\end{aligned} \tag{4.103}$$

$$(5) \quad L(R) \equiv \int_{-2k_F}^{2k_F} \exp(iqR) dq = \frac{2 \sin(2k_F R)}{R}. \tag{4.104}$$

$$\begin{aligned}
F_1 &= \frac{\pi}{R} \int_{-2k_F}^{2k_F} \exp(iqR) \left(k_F^2 - \frac{q^2}{4} \right) dq = \frac{\pi}{R} \left(k_F^2 + \frac{1}{4} \frac{d^2}{dR^2} \right) L(R) \\
&= \frac{\pi}{R} \left(\frac{\sin(2k_F R)}{R^3} - \frac{2k_F \cos(2k_F R)}{R^2} \right) = -(2k_F)^4 \pi F(2k_F R). \quad (4.78)
\end{aligned} \tag{4.105}$$

$$(6) \quad \sum_{\vec{q}} f(q) \exp(i\vec{q} \cdot \vec{R}) = \frac{1}{(2\pi)^3} \int_0^{\infty} f(q) \exp(i\vec{q} \cdot \vec{R}) dq^3 = \frac{1}{(2\pi)^3} \frac{2\pi F_1}{k_F} \tag{4.97}$$

$$= -\frac{4k_F^3}{\pi} F(2k_F R) = -12N\pi F(2k_F R). \quad (3.139) \tag{4.106}$$

4.4 Double Exchange Interaction

The perovskite structure (Fig. 3.14) LaMnO_3 is anti-ferromagnetic insulator. In contrast, the doped compounds of $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ ($\text{A} = \text{Ca}, \text{Sr or Ba}, 0.2 < x < 0.4$) in which some La ions are replaced by A ions are ferromagnetic with $T_C = 300\text{--}370\text{ K}$ and good electric conductivity.

The double exchange model, first proposed by Zener (1951), can explain the correlation between the magnetism and electric conductivity.

$\text{La}^{+3}(4f^0)$ and $\text{O}^{-2}(2p^6)$ ions are nonmagnetic and the 3d electrons in the $\text{Mn}^{+3}(3d^4)$ ion are localized within the ion under the strong correlation interactions making LaMnO_3 a Mott insulator (The insulator which is expected to be conductive by the band theory based on the mean field approximation). The Mn ion is at the crystal site of cubic symmetry surrounded by six nearest O^{-2} ions (Fig. 3.14) just in the same way as the octahedral site of spinel ferrite (Figs. 3.12, 3.25). The strong intraatomic exchange interactions maintain the 3d electron spins parallel inside each ion. The term energy level of $3d^1$ ion is split into the energy levels of threefold degenerate ground orbital state T_{2g} and twofold degenerate excited orbital state E_g (Sect. 3.6.3, Fig. 3.26). Three 3d electrons of the Mn^{+3} ion fill half of the T_{2g} orbits, and the remaining one fills the E_g orbits. The antiferromagnetism arises from the superexchange interactions.

If some trivalent La^{+3} ions are substituted by divalent A^{+2} ions, the same amount of trivalent $\text{Mn}^{+3}(3d: T_{2g}^3 E_g^1)$ ions are replaced by tetravalent $\text{Mn}^{+4}(3d: T_{2g}^3 E_g^0)$ ions to preserve the electrical neutrality of the compound. Both of the E_g orbits of Mn ion and the p_x, p_y and p_z orbits of the nearest $\text{O}^{-2}(3p^6)$ ion being stretched in the $\langle 100 \rangle$ directions (Figs. 3.27, 4.3), they overlap each other. The large probability of wandering of the p electrons onto the vacant E_g orbits of $\text{Mn}^{+4}(3d: T_{2g}^3 E_g^0)$ and the E_g electrons of $\text{Mn}^{+3}(3d: T_{2g}^3 E_g^1)$ ions onto the p orbits transforms the insulator to an electrical conductor. The exchange interaction between the conductive electrons and the revised localized T_{2g} electrons couples the magnetic moments of the T_{2g} electrons parallel (Fig. 4.7b). If the strength of the double exchange interaction of parallel coupling is larger than the superexchange interaction of antiparallel coupling, the compound becomes ferromagnetic.

4.5 Classic Expressions of Exchange Energy

4.5.1 Exchange Energy in Cubic Crystals

First consider a ferromagnetic simple cubic crystal of lattice constant a constituted of single magnetic element. The spin of the atom $\vec{S}$ varies slowly with position $(n_x, n_y, n_z)a$ ($n_j (j = x, y, z)$: integer). The exchange interactions between not nearest neighbor atoms will be neglected. Let $\{\alpha_i(n_x, n_y, n_z)\}$ ($i = x, y, z$) denote the direction cosines of $\vec{S}(n_x, n_y, n_z)$. The exchange energy of the atom at (n_x, n_y, n_z) with its two side neighbor atoms on the x -axis is

$$\varepsilon_x(n_x, n_y, n_z) = -2J_A \vec{S}(n_x, n_y, n_z) \cdot [\vec{S}(n_x+1, n_y, n_z) + \vec{S}(n_x-1, n_y, n_z)] \quad (4.17)$$

$$= -2J_A S^2 \sum_{i=x,y,z} \alpha_i(n_x, n_y, n_z) [\alpha_i(n_x+1, n_y, n_z) + \alpha_i(n_x-1, n_y, n_z)]. \quad (4.107)$$

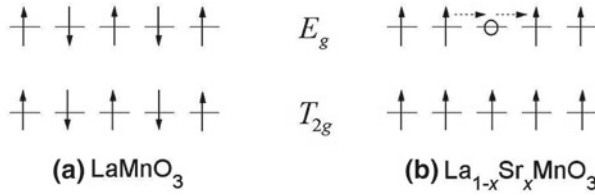


Fig. 4.7 The relation between the magnetism and electric conductivity caused by double exchange interaction. **a** anti-ferromagnetic insulator; **b** ferromagnetic metal

Inserting the Taylor expansion of $\alpha_i(n_x \pm 1, n_y, n_z)$ about $\alpha_i(n_x, n_y, n_z)$

$$\alpha_i(n_x \pm 1, n_y, n_z) = \alpha_i(n_x, n_y, n_z) \pm a \frac{\partial \alpha_i}{\partial x} \bigg|_{(n_x, n_y, n_z)} + \frac{a^2}{2} \frac{\partial^2 \alpha_i}{\partial x^2} \bigg|_{(n_x, n_y, n_z)} \quad (4.108)$$

into the last expression of (4.107) we get

$$\varepsilon_x(n_x, n_y, n_z) = -2J_A S^2 \sum_i^{x,y,z} \left[2\alpha_i^2(n_x, n_y, n_z) + a^2 \alpha_i(n_x, n_y, n_z) \frac{\partial^2 \alpha_i}{\partial x^2} \bigg|_{(n_x, n_y, n_z)} \right]. \quad (4.109)$$

The first term in the right of (4.109) is a constant and will be neglected. In the same way we get similar expressions for $\varepsilon_y(n_x, n_y, n_z)$ and $\varepsilon_z(n_x, n_y, n_z)$. The sum of them is

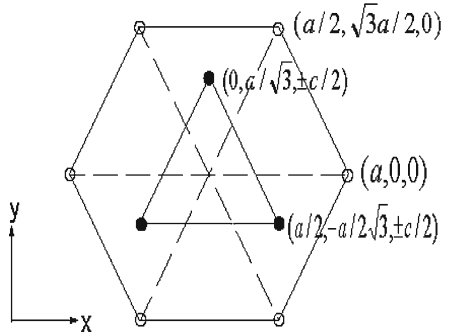
$$\sum_i^{x,y,z} \varepsilon_i(n_x, n_y, n_z) = -2J_A S^2 a^2 \sum_i^{x,y,z} \alpha_i(n_x, n_y, n_z) \nabla^2 \alpha_i(n_x, n_y, n_z). \quad (4.110)$$

Adding (4.110) for all lattice points $\{n_x, n_y, n_z\}$ in the volume v , dividing the sum by 2 (in the sum the exchange interaction for a pair of adjacent ions is calculated twice), and substituting the discrete sum $\sum_i$ with integration, we get the exchange energy as

$$\begin{aligned} & -\frac{J_A S^2 a^2}{a^3} \int \sum_i^{x,y,z} \alpha_i(\vec{r}) \nabla^2 \alpha_i(\vec{r}) dv \\ & = \frac{J_A S^2}{a} \left\{ \int_v \sum_i^{x,y,z} [\nabla \alpha_i(\vec{r})]^2 dv - \oint_{\text{surface}} \sum_i^{x,y,z} \alpha_i(\nabla \alpha_i) \cdot d\vec{S} \right\}. \quad (a3.28) \quad (4.111) \end{aligned}$$

The surface integration in the right of (4.111) is over the surface covering the volume v and $d\vec{S}$ is the differential of the surface vector. From the above equation we get the expressions of exchange energy volume density:

Fig. 4.8 Coordinates of lattice points in hcp crystal



$$F_{\text{ex}} = -\frac{J_A S^2}{a} \sum_i^{x,y,z} \alpha_i \nabla^2 \alpha_i = -\frac{J_A S^2}{a} \frac{\vec{M}_s \cdot \nabla^2 \vec{M}_s}{M_s^2} = \frac{J_A S^2}{a} \sum_i^{x,y,z} (\nabla \alpha_i)^2. \quad (4.112)$$

In the same way, it is deduced that the energy density for bcc and fcc crystals is twice and four times of (4.112), respectively. Summing up the above results, the exchange energy density of cubic crystals is expressed in a general form of

$$F_{\text{ex}} = -A \sum_i^{x,y,z} \alpha_i \nabla^2 \alpha_i = -A \frac{\vec{M}_s \cdot \nabla^2 \vec{M}_s}{M_s^2} = A \sum_i^{x,y,z} (\nabla \alpha_i)^2, \quad (4.113)$$

where coefficient A is called exchange stiffness constant or exchange constant.

4.5.2 Exchange Energy in Non-Cubic Crystals

First consider a hcp crystal of lattice constants a and c (Fig. 3.11) as an example. The atom at the lattice point $(0, 0, 0)$ has 12 nearest neighbor atoms. Six of them are on the same c -plane distant a from the center. Their coordinates are $(a \cos \theta, a \sin \theta, 0)$ ($\theta = 2\pi n/6, n = 0, 1, 2, \dots, 5$). The other six atoms are on the $\pm c/2$ planes $\sqrt{a^2/3 + c^2/4}$ away from the center. Their coordinates are $(0, a/\sqrt{3}, \pm c/2)$ and $(\pm a/2, -a/(2\sqrt{3}), \pm c/2)$ (Fig. 4.8). Suppose the exchange integral for a pair of nearest neighbor atoms depends on the distance between them. Let J_A and J'_A denote the exchange integral for the central atom and the atoms of the first and second group, respectively. By using the same method used in the preceding Sect. 4.5.1 we get the exchange energy for the 12 pairs of the adjacent atoms as

$$-2J_A S^2 \sum_i^{x,y,z} \alpha_i(0, 0, 0) \frac{3}{2} \left(\frac{\partial^2 \alpha_i}{\partial x^2} \Big|_{(0,0,0)} + \frac{\partial^2 \alpha_i}{\partial y^2} \Big|_{(0,0,0)} \right) a^2$$

$$\begin{aligned}
& -2J'_A S^2 \sum_i^{x,y,z} \alpha(0,0,0) \frac{1}{2} \left[\left(\frac{\partial^2 \alpha_i}{\partial x^2} \Big|_{(0,0,0)} + \frac{\partial^2 \alpha_i}{\partial y^2} \Big|_{(0,0,0)} \right) a^2 + \frac{\partial^2 \alpha_i}{\partial z^2} \Big|_{(0,0,0)} \frac{3c^2}{2} \right] \\
& = -(3J_A + J'_A) S^2 a^2 \sum_i^{x,y,z} \alpha_i(0,0,0) \nabla^2 \alpha_i(0,0,0) \\
& - \left[-(3J_A + J'_A) a^2 + J'_A \frac{3c^2}{2} \right] S^2 \sum_i^{x,y,z} \alpha_i(0,0,0) \frac{\partial^2 \alpha_i}{\partial z^2} \Big|_{(0,0,0)}. \tag{4.114}
\end{aligned}$$

The first term in the last expression has the same form with that of cubic crystal (4.111) and is isotropic. The second term has the axial anisotropy which vanishes if the distance of the second group atoms from the center $\sqrt{a^2/3 + c^2/4}$ equals to that of the atom of the first group a , and hence J'_A is equal to J_A . Co metal ($a = 0.2502$ nm, $c = 0.4061$ nm, $\sqrt{a^2/3 + c^2/4} = 0.996a$) belongs to this case, and the exchange energy density can be expressed by (4.113) of cubic crystal. In general the exchange energy of an atom located at a non-cubic symmetry crystal site has anisotropic term but it is very small. In some cases, however, the anisotropic term can not be neglected (Sects. 5.2.4.2, 5.2.5).

Examples of A values: $A = 2.4 \times 10^{-11}$ J/m and 4.7×10^{-11} J/m for Fe and Co metals.

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Chapter 5

Magnetic Anisotropy

A crystal with a certain crystal structure is anisotropic. Therefore, the free energy of a magnetic crystal depends on the direction of the spontaneous magnetization vector $\vec{M}_s$ with respect to the lattice axes. The anisotropy is called magnetocrystalline anisotropy. The magnetostatic energy of a non-spherical magnetic body also depends on the $\vec{M}_s$ direction. The anisotropy is called shape anisotropy. Additional magnetic anisotropy may be induced through some treatment in some magnetic media. Such anisotropy is called induced magnetic anisotropy. Magnetic atoms in amorphous alloys have magnetic anisotropies with randomly distributed easy-axis directions. Such anisotropy is called random anisotropy.

This chapter introduces typical phenomena and basic theories of the anisotropies. It contains the sections of Magnetocrystalline anisotropy; Mechanisms of magnetocrystalline anisotropy; Shape anisotropy; Induced magnetic anisotropy; and Random anisotropy and effective anisotropy.

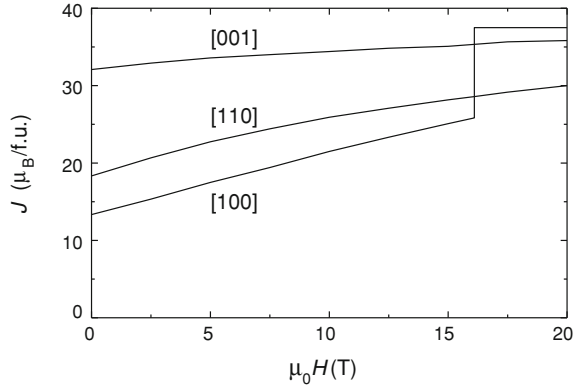
5.1 Magnetocrystalline Anisotropy

5.1.1 Anisotropy of Magnetization Curve of Crystal and Concept of Magnetocrystalline Anisotropy

Figure 5.1 demonstrates the magnetization curves of tetragonal $\text{Nd}_2\text{Fe}_{14}\text{B}$ crystal measured in the [100], [110], and [001] axes directions [1].

For a serious measurement of a magnetization curve, the sample is first thermally demagnetized (Sect. 3.1.4) by cooling from a paramagnetic state down to the measurement temperature in the absence of magnetic field. By use of this method an ideal demagnetized state of well-distributed domains is achieved. The demagnetized state can also be realized through alternating field demagnetization process: first the amplitude of the field is set to be large enough for magnetization to saturation which is followed by gradual decrease to zero. Compared with the thermal demagnetization,

Fig. 5.1 Magnetization curves of $\text{Nd}_2\text{Fe}_{14}\text{B}$ crystal in the [100], [110] and [001] axis directions measured at 4.2 K



the domain distribution is less even and the magnetization curve is a bit different, but the difference in many cases is small. The method is simple and widely used if not very high quality of measurement is needed or just to put a magnetic component to a non-magnetized state.

A static magnetization curve is measured by increasing applied magnetic field very slowly or step-by-step so that the magnetization at each field is measured at equilibrium state.

The work done on a unit volume medium for magnetization from demagnetized state to saturation is

$$W = \int_0^{J_s} H dJ, \quad (5.1)$$

which is equal to the area surrounded by the $J(H)$ curve, the J axis, and the line of $J = J_s$ parallel to the H axis. This area depends on the direction of the magnetization, so it is anisotropic implicating that the energy of the saturated state is a function of the magnetization direction.

The magnetization energy spent for rotating the saturated magnetic polarization vector $\vec{J}_s$ from a certain direction to another direction α is called magnetocrystalline anisotropy energy in the α direction which will be denoted by F_K .

5.1.2 Phenomenological Expressions of F_K

Let $\{\alpha_i\} (i = x, y, z)$ represent the direction cosines of $\vec{J}_s$ direction in the crystal orthogonal coordinate in which the [001] and [100] axes are the z and x axes. The phenomenological expression of F_K as a function of $\{\alpha_i\}$ can be obtained from the condition that the energy should have the crystal symmetry.

First analyze the expression of F_K for cubic crystals.

- ① Expand F_K into a power series of α_x, α_y , and α_z ;
- ② F_K should remain unchanged under the reflection operations against the {100} planes; therefore, F_K is a function of α_i to the power of 2, i.e., $F_K = F_K(\alpha_x^2, \alpha_y^2, \alpha_z^2)$;
- ③ F_K should remain unchanged under the reflection operations against the {110} planes, therefore any exchange between α_i and α_j ($j \neq i = x, y, z$) does not change F_K .

From the above results and using the relation of $\alpha_x^2 + \alpha_y^2 + \alpha_z^2 = 1$ and neglecting the constant term we get the phenomenological expression of F_K as

$$\begin{aligned}
 F_K &= B_{21}(\alpha_x^2 + \alpha_y^2 + \alpha_z^2) + B_{41}(\alpha_x^4 + \alpha_y^4 + \alpha_z^4) + B_{42}(\alpha_x^2\alpha_y^2 + \alpha_y^2\alpha_z^2 + \alpha_z^2\alpha_x^2) \\
 &\quad + B_{61}(\alpha_x^6 + \alpha_y^6 + \alpha_z^6) + B_{62}(\alpha_x^2\alpha_y^4 + \alpha_y^2\alpha_z^4 + \alpha_z^2\alpha_x^4) + B_{63}\alpha_x^2\alpha_y^2\alpha_z^2 + \dots \\
 &= K_1(\alpha_x^2\alpha_y^2 + \alpha_y^2\alpha_z^2 + \alpha_z^2\alpha_x^2) + K_2\alpha_x^2\alpha_y^2\alpha_z^2 + \dots, \quad (5.2)
 \end{aligned}$$

where B_{mn} and K_i are the expansion constants.

In the same way, the expressions of F_K for tetragonal and hexagonal crystals can be deduced as

$$F_K = K_1 \sin^2 \theta + K_2 \sin^4 \theta + K_3 \sin^4 \theta \cos(4\phi) + \dots, \quad (5.3)$$

$$F_K = K_1 \sin^2 \theta + K_2 \sin^4 \theta + K_3 \sin^6 \theta + K_4 \sin^6 \theta \cos(6\phi) + \dots, \quad (5.4)$$

where θ and ϕ are the zenith and azimuth angles of $\vec{J}_s$ direction. The expansions in the right of (5.2)–(5.4) are infinite, but in real the first few terms is enough to get good coincidence with experiment. K_i ($i = 1, 2, \dots$) are called magnetocrystalline anisotropy constants. The direction (or crystal axis) along which F_K is minimum or maximum is called easy direction (or easy axis) or hard direction (or hard axis), respectively. For example, for Fe metal $K_1 > 0$ and $K_2 > 0$, therefore the {100} axes are the easy axes and {111} axes the hard axes. If no anisotropy exists in the c plane (K_3 in (5.3) or K_4 in (5.4) is zero), the anisotropy is called uniaxial anisotropy. If the easy direction of tetragonal and hexagonal crystals is along the c axis ([001] axis), or between the c axis and c plane, or in the c plane, the anisotropy is called easy axis anisotropy, or easy cone anisotropy, or easy plane anisotropy, respectively. Figure 5.2 demonstrates the temperature dependences of K_1 , K_2 , and K_3 of $\text{Nd}_2\text{Fe}_{14}\text{B}$. The K_2 is positive at any temperature and K_1 is positive above ~ 135 K and negative below this temperature. Thus, the anisotropy is of easy axis above ~ 135 K and easy cone below ~ 135 K. The cone angle, the angle between the easy axis and the c axis, increases from 0 at ~ 135 K to $\sim 32^\circ$ at 4.2 K. The transition temperatures between the easy axis, easy cone, and easy plane anisotropies are called spin reorientation temperatures. All magnetocrystalline anisotropy constants become zero as well as J_s at Curie or Néel temperature. Table 5.1 presents the values of magnetocrystalline anisotropy constants at R.T. for some magnetic materials.

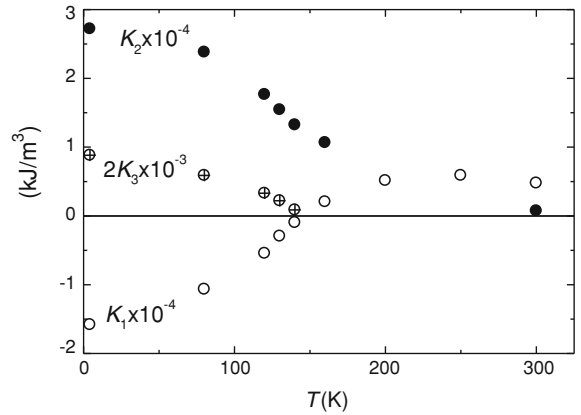


Fig. 5.2 Temperature dependences of K_1 , K_2 and K_3 of $\text{Nd}_2\text{Fe}_{14}\text{B}$ [2]

Table 5.1 The values of K_1 and K_2 for some magnetic materials

Material	Crystal structure	$K_1/(\text{kJ}/\text{m}^3)$	$K_2/(\text{kJ}/\text{m}^3)$
Fe-80 at%Ni [3]	Cubic	0.3	—
Fe-44%Co [4]	Cubic	−0.2	−220
$\text{MnO} \cdot \text{Fe}_2\text{O}_3$ [3]	Cubic	−3	−2.5
Ni [5]	Cubic	−5.6	—
$\text{NiO} \cdot \text{Fe}_2\text{O}_3$ [3]	Cubic	−7	—
Fe_3O_4 [3]	Cubic	−9	0.12
Fe [5]	Cubic	48	—
$\text{CoO} \cdot \text{Fe}_2\text{O}_3$ [3]	Cubic	260	—
$\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$ [3]	Hexagonal	320	—
$\text{SrO} \cdot 6\text{Fe}_2\text{O}_3$ [6]	Hexagonal	350	140
Co [5]	Hexagonal	410	—
$\text{Nd}_2\text{Fe}_{14}\text{B}$ [3]	Tetragonal	5,000	—
SmCo_5 [3]	Hexagonal	11,000–20,000	—

The symmetry around the atom in the surface atomic layer is different from that of inside the magnetic body, so the magnetization direction dependence of the magnetocrystalline anisotropy energy of the surface atomic layer is different from (5.2)–(5.4). Take the (001) surface layer of a cubic crystal as an example. It is easily deduced that the expression is

$$F_K = K_{1s}\alpha_z^2 + K_{2s}\alpha_z^4 + K_{3s}\alpha_x^2\alpha_y^2 + \dots \quad (5.5)$$

The energy band calculations show that the Fe (100) single atomic layer film has easy plane anisotropy [7].

5.1.3 Magnetic Anisotropy Field

Let (θ_0, ϕ_0) and $(\theta = \vartheta_0 + \Delta\theta, \phi = \phi_0 + \Delta\phi)$ denote the zenith and azimuth angles of easy direction and $\vec{J}_s$ direction, respectively. If the angle δ between them is small, the magnetocrystalline anisotropy energy relative to that in the easy direction can be expressed in the form of a potential energy of $\vec{J}_s$ in the effective magnetic field $\vec{H}_K$ called magnetocrystalline anisotropy field or tersely magnetic anisotropy field. In many cases the direction of $\vec{H}_K$ is selected in the easy direction, and in few cases it is taken normal to the easy axis. The two cases will be discussed separately.

5.1.3.1 The Case of $\vec{H}_K // \text{easy direction}$

The Taylor expansion of $F_K(\theta, \phi)$ about the easy direction (θ_0, ϕ_0) is

$$\begin{aligned} F_K(\theta, \phi) &= F_K(\theta_0, \phi_0) + \frac{1}{2} \left[\frac{\partial^2 F_K}{\partial \theta^2} \Big|_{\theta_0, \phi_0} (\Delta\theta)^2 + 2 \frac{\partial^2 F_K}{\partial \theta \partial \phi} \Big|_{\theta_0, \phi_0} \Delta\theta \Delta\phi \right. \\ &\quad \left. + \frac{\partial^2 F_K}{\partial \phi^2} \Big|_{\theta_0, \phi_0} (\Delta\phi)^2 \right] \\ &\equiv F_K(\theta_0, \phi_0) + \frac{1}{2} \left[F_K^{\theta\theta}(\Delta\theta)^2 + 2F_K^{\theta\phi} \Delta\theta \Delta\phi + F_K^{\phi\phi} (\Delta\phi)^2 \right], \end{aligned} \quad (5.6)$$

from which we get

$$\frac{\partial F_K(\theta, \phi)}{\partial \theta} = F_K^{\theta\theta} \Delta\theta + F_K^{\theta\phi} \Delta\phi, \quad (5.7)$$

$$\frac{\partial F_K(\theta, \phi)}{\partial \phi} = F_K^{\theta\phi} \Delta\theta + F_K^{\phi\phi} \Delta\phi. \quad (5.8)$$

According to the definition of magnetocrystalline anisotropy field, it holds

$$-J_s H_K (\cos \delta - 1) = F_K(\theta, \phi) - F_K(\theta_0, \phi_0). \quad (5.9)$$

From the derivative of (5.9) with respect δ

$$\begin{aligned} J_s H_K \sin \delta &\approx J_s H_K \delta = \frac{\partial F_K(\theta, \phi)}{\partial \theta} \frac{d\theta}{d\delta} + \frac{\partial F_K(\theta, \phi)}{\partial \phi} \frac{d\phi}{d\delta} \\ &= \left(F_K^{\theta\theta} \Delta\theta + F_K^{\theta\phi} \Delta\phi \right) \frac{d\theta}{d\delta} + \left(F_K^{\theta\phi} \Delta\theta + F_K^{\phi\phi} \Delta\phi \right) \frac{d\phi}{d\delta} \end{aligned} \quad (5.10)$$

we get the general expression of H_K as

$$H_K = \frac{1}{J_s} \left[F_K^{\theta\theta} \left(\frac{d\theta}{d\delta} \right)^2 + 2F_K^{\theta\phi} \frac{d\theta}{d\delta} \frac{d\phi}{d\delta} + F_K^{\phi\phi} \left(\frac{d\phi}{d\delta} \right)^2 \right]. \quad (5.11)$$

H_K in general depends on the deviation direction $(\Delta\theta, \Delta\phi)$. Let H_K^θ and H_K^ϕ denote the H_K for $\delta = \Delta\theta$ ($\Delta\phi = 0$) and $\delta = \sin\theta_0\Delta\phi$ ($\Delta\theta = 0$), respectively, then

$$H_K^\theta = \frac{1}{J_s} F_K^{\theta\theta}, \quad (5.12)$$

$$H_K^\phi = \begin{cases} 0, & (\theta_0 = 0) \\ \frac{1}{J_s \sin^2\theta_0} F_K^{\phi\phi}, & (\theta_0 \neq 0) \end{cases} \quad (5.13)$$

When $\theta_0 = 0$

$$H_K = H_K^\theta = \frac{1}{J_s} F_K^{\theta\theta}. \quad (5.14)$$

Examples of H_K expression:

① Uniaxial anisotropy in the case of $K_{i>1} = 0$.

If $K_1 > 0$, $\theta_0 = 0$ or π ,

$$F_K = K_1 \sin^2(\Delta\theta) \approx K_1(\Delta\theta)^2, \quad (5.15)$$

$$H_K = \frac{2K_1}{J_s}. \quad (5.16)$$

② Cubic anisotropy in the case of $K_{i>1} = 0$.

If $K_1 > 0$, the easy axes are $\langle 100 \rangle$ axes. Take $\theta_0 = 0$, then $F_K \approx K_1(\alpha_x^2 + \alpha_y^2)\alpha_z^2 = K_1 \sin^2(\Delta\theta) \cos^2(\Delta\theta) \approx K_1(\Delta\theta)^2$, and (5.16) holds.

If $K_1 < 0$, $\cos^2\theta_0 = 1/3$, $\cos^2\phi_0 = \sin^2\phi_0 = 1/2$,

$$H_K^\theta = H_K^\phi = -\frac{4K_1}{3J_s}. \quad (5.17)$$

③ Easy plane hexagonal anisotropy.

If $K_1 + 2K_2 + 3K_3 + 3K_4 < 0$ and $K_4 < 0$, $\theta_0 = \pi/2$ and $\cos(6\phi_0) = 1$,

$$H_K^\theta = -2 \frac{K_1 + 2K_2 + 3K_3 + 3K_4}{J_s}, \quad (5.18)$$

$$H_K^\phi = -\frac{36K_4}{J_s}. \quad (5.19)$$

5.1.3.2 The Case of $\vec{H}_K \perp$ Easy Direction

Take an example of uniaxial and cubic anisotropy of $K_1 > 0$ and $K_{i>1} = 0$. $\theta_0 = 0$ or π . According to the definition of anisotropy field,

$$-\vec{J}_s \cdot \vec{H}_K = F_K = K_1(\alpha_x^2 + \alpha_y^2), \quad (5.20)$$

$$\vec{H}_K = -\frac{dF_K}{d\vec{J}_s} = -\sum_i^{x,y} \frac{\partial F_K}{J_s \partial \alpha_i} \vec{e}_i = -H_K(\alpha_x \vec{e}_x + \alpha_y \vec{e}_y), \quad (5.21)$$

that is, the value of H_K is the same with that of (5.16) of the case of $\vec{H}_K$ is along the easy direction. The direction is opposite to the projection of the magnetization vector on the xy plane.

5.2 Mechanisms of Magnetocrystalline Anisotropy

Magnetocrystalline anisotropy is explained on the basis of the localized electron theory for the localized magnetic electrons or on the basis of the itinerant electron theory for the itinerant magnetic electrons. This section introduces the localized electron models of the mechanisms including the magnetic moment interaction model, single-ion model, and two-ion model.

5.2.1 Magnetic Moment Interaction Model

The magnetic moment interaction energy of a couple of magnetic polarization moments $\vec{p}_{J1}$ and $\vec{p}_{J2}$ separated by $\vec{r}$ is

$$\frac{1}{4\pi\mu_0} \left[\frac{\vec{p}_{J1} \cdot \vec{p}_{J2}}{r^3} - \frac{3(\vec{p}_{J1} \cdot \vec{r})(\vec{p}_{J2} \cdot \vec{r})}{r^5} \right]. \quad ((1.46), (1.75)) \quad (5.22)$$

It is anisotropic and is one of the origin of magnetocrystalline anisotropy. This interaction is very small and in general is neglected if the other mechanisms also contribute to the anisotropy.

5.2.2 Single-Ion Model

This model can explain the magnetocrystalline anisotropy of the 3d ions in insulators, such as ferrites, and of the 4f (rare earth) ions in alloys and compounds. It considers

that the anisotropy of the ions arises from the CEF, exchange, and spin–orbit interactions. In usual the spin–orbit interaction is much smaller than the CEF interaction for 3d ions while it is much larger for 4f ions (Fig. 3.24), therefore the details of the single-ion model for the two kinds of the ions are somewhat different and will be discussed separately.

5.2.3 Single-Ion Model for 3d Ion

In a CEF the ground term energy level of 3d ion splits into several levels (Sect. 3.6). The ground energy level will be taken zero. Since CEF Hamiltonian is irrelevant to spin, the eigenstate in the CEF is a product of the orbital eigenfunction and the spin eigenfunction $|S_m\rangle \equiv |S, m\rangle$ (S : spin quantum number of the term; $m \equiv M_S = -S, -S+1, \dots, S$). Suppose the exchange interaction with the other ions is much weaker than the CEF interaction. The perturbation of the spin–orbit interaction and exchange interaction on the state produces the magnetocrystalline anisotropy. First analyze the case of non-degenerate ground orbital state.

5.2.3.1 The Case of Ground Energy Level in CEF is Nondegenerate in Orbital State

When the perturbation is absent, the ground orbital state is nondegenerate, but is degenerate in spin state. Let $|g\rangle$ (Arabic) denote the ground orbital and $|\mu\rangle$ (Greek) and ε_μ the excited orbital and its energy level.

The perturbation secular equation is (a6.7)

$$\left| \langle g, S_l | \hat{H}_{\text{eff}} | g, S_k \rangle - \varepsilon \delta(S_l, S_k) \right| = 0. \quad (l, k = -S, -S+1, \dots, S) \quad (5.23)$$

① Spin Hamiltonian of spin–orbit interaction.

The matrix element for perturbation $\hat{H}' = \lambda \hat{\vec{L}} \cdot \hat{\vec{S}}$ in (5.23) is ((a6.8), $\varepsilon_0 = 0$)

$$\begin{aligned} \left| \langle g, S_l | \hat{H}_{\text{eff}} | g, S_k \rangle \right. &= \langle g, S_l | \lambda \hat{\vec{L}} \cdot \hat{\vec{S}} | g, S_k \rangle \\ &+ \sum_{\mu} \sum_m \frac{\langle g, S_l | \lambda \hat{\vec{L}} \cdot \hat{\vec{S}} | \mu, S_m \rangle \langle \mu, S_m | \lambda \hat{\vec{L}} \cdot \hat{\vec{S}} | g, S_k \rangle}{\varepsilon - \varepsilon_\mu} \\ &+ \sum_{\mu, \nu} \sum_{m, n} \frac{\langle g, S_l | \lambda \hat{\vec{L}} \cdot \hat{\vec{S}} | \mu, S_m \rangle \langle \mu, S_m | \lambda \hat{\vec{L}} \cdot \hat{\vec{S}} | \nu, S_n \rangle \langle \nu, S_n | \lambda \hat{\vec{L}} \cdot \hat{\vec{S}} | g, S_k \rangle}{(\varepsilon - \varepsilon_\mu)(\varepsilon - \varepsilon_\nu)} + \dots \end{aligned} \quad (5.24)$$

Each term in the right of above equation can be expressed by corresponding matrix element of spin operator Hamiltonian with respect to the spin state $\langle S_l | \hat{H}_{si} | S_k \rangle (i = 1, 2, \dots)$ as below.

The first term is $\langle S_l | \hat{H}_{s1} | S_k \rangle = \lambda \sum_{\alpha}^{x,y,z} \langle g | \hat{L}_{\alpha} | g \rangle \langle S_l | \hat{S}_{\alpha} | S_k \rangle = 0$ (3.96), therefore $\hat{H}_{s1} = 0$.

In the second term,

$$\begin{aligned}
 & \sum_{\mu} \sum_m \frac{\langle g, S_l | \hat{L}_{\alpha} \hat{S}_{\alpha} | \mu, S_m \rangle \langle \mu, S_m | \hat{L}_{\beta} \hat{S}_{\beta} | g, S_k \rangle}{\varepsilon - \varepsilon_{\mu}} \quad (\alpha, \beta = x, y, z) \\
 &= \sum_{\mu} \sum_m \frac{\langle g | \hat{L}_{\alpha} | \mu \rangle \langle \mu | \hat{L}_{\beta} | g \rangle \langle S_l | \hat{S}_{\alpha} | S_m \rangle \langle S_m | \hat{S}_{\beta} | S_k \rangle}{\varepsilon - \varepsilon_{\mu}} \\
 &= \sum_{\mu} \frac{\langle g | \hat{L}_{\alpha} | \mu \rangle \langle \mu | \hat{L}_{\beta} | g \rangle \langle S_l | \hat{S}_{\alpha} \hat{S}_{\beta} | S_k \rangle}{\varepsilon - \varepsilon_{\mu}}, \quad \left(\sum_m |S_m\rangle \langle S_m| = 1 \right) \quad (5.25)
 \end{aligned}$$

so

$$\begin{aligned}
 \hat{H}_{s2} &= \sum_{\alpha, \beta}^{x,y,z} D_{\alpha\beta} \hat{S}_{\alpha} \hat{S}_{\beta} = \begin{pmatrix} \hat{S}_x & \hat{S}_y & \hat{S}_z \end{pmatrix} \begin{pmatrix} D_{xx} & D_{xy} & D_{xz} \\ D_{yx} & D_{yy} & D_{yz} \\ D_{zx} & D_{zy} & D_{zz} \end{pmatrix} \begin{pmatrix} \hat{S}_x \\ \hat{S}_y \\ \hat{S}_z \end{pmatrix} \\
 &= \left(\hat{S} \right)^T (D) \left(\hat{S} \right), \quad (5.26)
 \end{aligned}$$

$$D_{\alpha\beta} \equiv \sum_{\mu} \frac{\lambda^2 \langle g | \hat{L}_{\alpha} | \mu \rangle \langle \mu | \hat{L}_{\beta} | g \rangle}{\varepsilon - \varepsilon_{\mu}} = D_{\beta\alpha}^*. \quad (5.27)$$

In the same way we get

$$\hat{H}_{s3} = \sum_{\alpha, \beta, \gamma}^{x,y,z} D_{\alpha\beta\gamma} \hat{S}_{\alpha} \hat{S}_{\beta} \hat{S}_{\gamma}, \quad (5.28)$$

$$D_{\alpha\beta\gamma} \equiv \sum_{\mu, \nu} \frac{\lambda^3 \langle g | \hat{L}_{\alpha} | \mu \rangle \langle \mu | \hat{L}_{\beta} | \nu \rangle \langle \nu | \hat{L}_{\gamma} | g \rangle}{(\varepsilon - \varepsilon_{\mu})(\varepsilon - \varepsilon_{\nu})}, \quad (5.29)$$

$$\hat{H}_{s4} = \sum_{\alpha, \beta, \gamma, \delta}^{x,y,z} D_{\alpha\beta\gamma\delta} \hat{S}_{\alpha} \hat{S}_{\beta} \hat{S}_{\gamma} \hat{S}_{\delta}, \quad (5.30)$$

$$D_{\alpha\beta\gamma\delta} = \sum_{\mu, \nu, \rho} \frac{\lambda^4 \langle g | \hat{L}_{\alpha} | \mu \rangle \langle \mu | \hat{L}_{\beta} | \nu \rangle \langle \nu | \hat{L}_{\gamma} | \rho \rangle \langle \rho | \hat{L}_{\delta} | g \rangle}{(\varepsilon - \varepsilon_{\mu})(\varepsilon - \varepsilon_{\nu})(\varepsilon - \varepsilon_{\rho})} = D_{\delta\gamma\beta\alpha}^*. \quad (5.31)$$

$\hat{H}_s = \sum_i^{2,3,\dots} \hat{H}_{si}$ is called spin Hamiltonian.

Some symmetries simplify the expression of the spin Hamiltonian by eliminating many terms as below.

- i. Under the time reversal operation, the sign of $\hat{S}$ changes while $\lambda \hat{L} \cdot \hat{S}$ remains unchanged. So for parameterized $\{D_{\alpha\beta\dots}\} \hat{H}_{s, i=\text{odd}} = 0$.
- ii. Being Hermitian, (D) can be diagonalized in an appropriated coordinate system (A4.2.4), and $\hat{H}_{s2}$ in the coordinate system simplifies to

$$(\hat{S})^T (D) (\hat{S}) = D_{xx} \hat{S}_x^2 + D_{yy} \hat{S}_y^2 + D_{zz} \hat{S}_z^2. \quad (5.32)$$

The spin Hamiltonians in the CEF of trigonal, tetragonal, and hexagonal symmetry in the coordinate system of z -axis along the symmetry axis of rotation simplifies to

$$\hat{H}_{s2} + \hat{H}_{s4} = A \hat{S}_z^2 + B \hat{S}_z^4. \quad (5.33)$$

For the cubic symmetrical CEF $D_{xx} = D_{yy} = D_{zz} \equiv D$, so

$$\hat{H}_{s2} = DS(S+1) = \text{const.}, \quad (5.34)$$

and the second-order perturbation term does not split the energy level. The forth perturbation Hamiltonian simplifies to

$$\hat{H}_{s4} = C(\hat{S}_x^4 + \hat{S}_y^4 + \hat{S}_z^4). \quad (5.35)$$

② Total spin Hamiltonian.

The ion in general case is also in the effective field composed of molecular field and applied magnetic field

$$\vec{H}_{\text{ef}} \equiv \vec{H}_{\text{ml}} + \vec{H}. \quad (5.36)$$

Total perturbation $\hat{H}'$ is the sum of the potential energy of the magnetic moment in the effective field and spin-orbit interaction:

$$\hat{H}' = \mu_B \vec{H}_{\text{ef}} \cdot (\hat{L} + 2\hat{S}) + \lambda \hat{L} \cdot \hat{S}. \quad (2.91) \quad (5.37)$$

Repeating the analytic procedure for the spin-orbit interaction in ① we get the first- and second-order perturbation matrix elements as

$$\mu_B \vec{H}_{\text{ef}} \cdot \langle S_l | 2\hat{S} | S_k \rangle, \quad (5.38)$$

and

$$\begin{aligned}
& \sum_{\mu} \sum_m \frac{\langle g, S_l | \hat{H}' | \mu, S_m \rangle \langle \mu, S_m | \hat{H}' | g, S_k \rangle}{\varepsilon - \varepsilon_{\mu}} \\
&= \sum_{\mu} \sum_m \frac{\langle g | \hat{L} | \mu \rangle \cdot \langle S_l | \mu_B \vec{H}_{\text{ef}} + \lambda \hat{S} | S_m \rangle \langle \mu | \hat{L} | g \rangle \cdot \langle S_m | \mu_B \vec{H}_{\text{ef}} + \lambda \hat{S} | S_k \rangle}{\varepsilon - \varepsilon_{\mu}} \\
& \quad \left(\langle g, S_l | 2\mu_B \hat{S} \cdot \vec{H}_{\text{ef}} | \mu, S_m \rangle \propto \langle g | \mu \rangle = 0 \right) \\
&= \sum_{\mu} \sum_m \frac{\sum_{\alpha, \beta}^{x, y, z} \langle g | \hat{L}_{\alpha} | \mu \rangle \langle S_l | \mu_B H_{\text{ef}\alpha} + \lambda \hat{S}_{\alpha} | S_m \rangle \langle \mu | \hat{L}_{\beta} | g \rangle \langle S_m | \mu_B H_{\text{ef}\beta} + \lambda \hat{S}_{\beta} | S_k \rangle}{\varepsilon - \varepsilon_{\mu}} \\
&= \sum_{\alpha, \beta}^{x, y, z} \left\langle S_l \left| \frac{D_{\alpha\beta}}{\lambda^2} \left(\mu_B H_{\text{ef}\alpha} + \lambda \hat{S}_{\alpha} \right) \left(\mu_B H_{\text{ef}\beta} + \lambda \hat{S}_{\beta} \right) \right| S_k \right\rangle \\
&= \left\langle S_l \left| 2\mu_B (H_{\text{ef}})^T \frac{(D)}{\lambda} (\hat{S}) + (\hat{S})^T (D) (\hat{S}) \right| S_k \right\rangle. \tag{5.39}
\end{aligned}$$

The total spin Hamiltonian is the sum of those of (5.38) and (5.39)

$$\hat{H}_s = \mu_B (H_{\text{ef}})^T (g) (\hat{S}) + (\hat{S})^T (D) (\hat{S}), \tag{5.40}$$

$$(g) \equiv 2 \left[1 + \frac{(D)}{\lambda} \right]. \tag{5.41}$$

The first term in the right of (5.40) is the potential energy of the magnetic polarization moment— $\mu_B (g) (\hat{S})$ in the effective field (H_{ef}). Here (g) is the g factor tensor in the CEF, which includes not only the $g = 2$ factor of the electron spin of isolated ion but also the tensor $2(D)/\lambda$. The additional magnetic polarization moment— $2\mu_B (D) (\hat{S})/\lambda$ is the residual orbital magnetic polarization moment produced by the mixing of the excited orbitals into the ground state. (D) being tensor it is anisotropic.

③ Magnetocrystalline anisotropy of the 3d ion.

When $\vec{H} = 0$, we get a set of spin eigenstates $\{|i\rangle\}$ and eigenenergy $\{\varepsilon_i\}$ through solving the perturbation equation (5.23) in which $\hat{H}'$ is given by (5.37) and $\vec{H}_{\text{ml}}$ is in the direction of $(\theta_{\text{ml}}, \phi_{\text{ml}})$. The magnetic polarization moment is

$$\vec{p}_J = (p_J) = - \frac{\mu_B \sum_i (g) \langle i | (\hat{S}) | i \rangle \exp \frac{-\varepsilon_i}{k_B T}}{Z}, \tag{5.42}$$

$$Z = \sum_i \exp \frac{-\varepsilon_i}{k_B T}. \tag{5.43}$$

The magnetocrystalline anisotropy energy of the ion is

$$f_K(\theta_{\text{ml}}, \phi_{\text{ml}}, T) = -k_B T \ln Z. \quad (5.44)$$

By calculating $f_K(\theta_{\text{ml}}, \phi_{\text{ml}}, T)$ for some different $(\theta_{\text{ml}}, \phi_{\text{ml}})$ crystal axis directions we can get the magnetocrystalline anisotropy constants for the ion.

5.2.3.2 The Case of Ground Energy Level in CEF is Degenerate in Orbital State

The analysis in the case of the ground energy level is degenerate in orbital state is complicated. Consider $\text{Co}^{+2}(3d^7)$ ion in the spinel ferrite $\text{CoO} \cdot \text{Fe}_2\text{O}_3$ [8] as an example. Only the idea and the result will be presented. Co^{+2} occupies the octahedral site (Fig. 3.12). In the cubic symmetric CEF produced by the nearest six adjacent O^{2-} ions (Fig. 3.25), the ground term ^4F energy level splits into three energy levels (Table a4.1) with the ground level threefold degenerate in orbital state. Under the trigonal symmetric CEF interaction produced by the next nearest six metal ions (Fig. 3.25) this ground energy level splits into twofold degenerate in orbital state ground level and non-degenerate excited state level (Table a4.1). The effects of the excited state will be neglected below. The two orbitals of the ground states are

$$\Phi_1 = \sqrt{\frac{5}{6}}|\alpha, 3, -2\rangle - \sqrt{\frac{1}{6}}|\alpha, 3, 1\rangle, \\ (|\alpha, L, M_L\rangle \text{ is the orbital expressed in the } \langle 100 \rangle \text{ coordinate system}) \quad (5.45)$$

$$\Phi_{-1} = -\sqrt{\frac{5}{6}}|\alpha, 3, 2\rangle - \sqrt{\frac{1}{6}}|\alpha, 3, -1\rangle. \quad (5.46)$$

All of the matrix elements of $\hat{L}_X$ and $\hat{L}_Y$ ($(X, Y, Z) = ([\bar{1}\bar{1}2], [1\bar{1}0], [111])$) (Fig. 3.25) with respect to Φ_1 and Φ_{-1} are zero, and the matrix of $\hat{L}_Z$ is

$$\begin{pmatrix} \langle \Phi_1 | \hat{L}_Z | \Phi_1 \rangle & \langle \Phi_1 | \hat{L}_Z | \Phi_{-1} \rangle \\ \langle \Phi_{-1} | \hat{L}_Z | \Phi_1 \rangle & \langle \Phi_{-1} | \hat{L}_Z | \Phi_{-1} \rangle \end{pmatrix} = \begin{pmatrix} -\frac{3}{2} & 0 \\ 0 & \frac{3}{2} \end{pmatrix}. \quad (5.47)$$

The orbital angular momentum is not completely quenched. The matrix of the spin-orbit interaction with respect to Φ_1 and Φ_{-1} is

$$\frac{3}{2} \begin{pmatrix} -\lambda \hat{S}_Z & 0 \\ 0 & \lambda \hat{S}_Z \end{pmatrix}. \quad (5.48)$$

The spin quantum number of Co^{+2} is $S = 3/2$, so each of Φ_1 and Φ_{-1} is fourfold degenerate in spin. Taking the sum of exchange interaction $2\mu_B \vec{H}_{\text{ex}} \cdot \hat{S}$ and spin-orbit interaction $\lambda \hat{L} \cdot \hat{S}$ as perturbation, solve the perturbation secular equation

$$|\langle \Phi_p, S_k | 2\mu_B \vec{H}_{\text{ex}} \cdot \hat{S} + \lambda \hat{L} \cdot \hat{S} | \Phi_q, S_l \rangle - \varepsilon \delta(p, q) \delta(S_k, S_l) | = 0. \\ (p, q = \pm 1; k, l = \pm \frac{1}{2}, \pm \frac{3}{2}) \quad (5.49)$$

The spin-orbit eigenstates and the perturbation eigenenergies are $|\Phi_{\pm 1}, S = 3/2, M_S\rangle$ and

$$\varepsilon = \left[2\mu_B H_{\text{ex}} \mp \frac{3}{2} \lambda \cos \theta_{\text{ex}} + \frac{9}{4} \frac{(\lambda \sin \theta_{\text{ex}})^2}{4\mu_B H_{\text{ex}}} \right] M_S. \\ \left(|\lambda|/\mu_B H_{\text{ex}} \ll 1, M_S = \pm \frac{1}{2}, \pm \frac{3}{2} \right) \quad (5.50)$$

Here θ_{ex} is the angle between $\vec{H}_{\text{ex}}$ and $[111]$ direction. The degeneration of each orbital state is removed completely. Equation (5.50) shows that the $[111]$ axis is the easy axis. In brief summary, the orbital angular momenta of $\Phi_{\pm 1}$ are fixed along the $[111]$ axis, and the energy of the ion is minimum when the spin is arranged also along the $[111]$ axis direction.

The probability of the Co^{+2} occupation on the $[111]$, $[\bar{1}11]$, $[1\bar{1}1]$, and $[\bar{1}\bar{1}1]$ axes is the same, so the magnetocrystalline anisotropy energy density is

$$F_K(\theta, \phi) = -\frac{N}{4} k_B T \sum_j^{1, \dots, 4} \ln Z_j, \\ ((\theta, \phi): \text{direction of } \vec{M}_S; N: \text{Co}^{+2} \text{ number in a unit volume}) \quad (5.51)$$

$$Z_j = \sum_i \exp \frac{-\varepsilon_{ji}(\theta, \phi)}{k_B T}. \quad (\varepsilon_{ji}: i^{\text{th}} \text{ eigenenergy on the } j^{\text{th}} \text{ axis position}) \quad (5.52)$$

5.2.3.3 Physical Picture of Magnetocrystalline Anisotropy for 3d Ions

Summarizing above arguments in Sects. 5.2.3.1 and 5.2.3.2, we get the following physical picture of the magnetocrystalline anisotropy for 3d ions. The electronic cloud and the orbital angular momentum of the ion are fixed by the CEF. In the absence of magnetic field the spin direction is fixed in an easy direction to make the spin-orbit interaction energy minimum. If a field is applied, the spin magnetic moment rotates toward the field direction, which causes increase in the spin-orbit

interaction. The orbital angular momentum is also affected by the applied magnetic field and spin rotation through the spin–orbit interaction, but its change is limited because of much stronger CEF interaction. The change in the spin–orbit interaction constitutes major part of the magnetocrystalline anisotropy energy of the ion. If the orbital ground state is not degenerate, the orbital angular momentum is of residual and is much smaller than the case of degenerate, thus the spin–orbit interaction and hence the magnetocrystalline anisotropy energy is much smaller. The value of $|K_1|$ for $\text{NiO} \cdot \text{Fe}_2\text{O}_3$ is roughly 1/40 folds of K_1 for $\text{CoO} \cdot \text{Fe}_2\text{O}_3$ (Table 5.1). The large difference originates from the fact that by occupying the same octahedral site, the ground energy level of the orbital state for $\text{Ni}^{+2}(5d^8)$ is nondegenerate but $\text{Co}^{+2}(5d^7)$ is degenerate. The orbital angular momentum of $\text{Fe}^{+3}(5d^5)$ being zero the magnetocrystalline anisotropy is very small.

5.2.4 Single-Ion Model for 4f Ion

5.2.4.1 Magnetocrystalline Anisotropy at 0 K

When the exchange interaction is much stronger than the CEF interaction, the ion is at the ground state of $|4f^n, L, S, J, -J\rangle$. The magnetocrystalline anisotropy energy is the average of the CEF Hamiltonian with respect to this state $\langle 4f^n, L, S, J, -J | \hat{H}_{\text{CEF}} | 4f^n, L, S, J, -J \rangle$.

The CEF Hamiltonian expressed in the crystal coordinate system are known (Sect. 3.6.2). The state $|4f^n, L, S, J, -J\rangle$ is given in the quantization axis coordinate system. To calculate the average, the CEF Hamiltonian expressed in the crystal coordinate system is needed to transform to that in the quantization axis coordinate system.

Take the magnetocrystalline anisotropy energy arising from the most important CEF Hamiltonian term $\hat{H}_{\text{CF20}} = A_{20} \langle r^2 \rangle \sum_i^{1,2,\dots,n} Y_{20}[\theta_c(i), \phi_c(i)]$ for tetragonal or hexagonal symmetry sites ((3.89)–(3.90)) as an example. Let the axis of the fourfold or sixfold rotation symmetry the z axis of the crystal coordinate system, (Θ, Φ) the zenith and azimuth angles of the quantum axis (axis of $\hat{J}_z$) in the crystal coordinate system, and (θ_c, ϕ_c) and (θ_q, ϕ_q) the angles of the position vector of the 4f electron in the crystal axis coordinate system and in the quantization axis coordinate system, respectively.

$$Y_{\lambda\kappa}(\theta_c, \phi_c) = \sum_{\kappa'}^{-\lambda, -\lambda+1, \dots, \lambda} \langle Y_{\lambda\kappa'}(\theta_q, \phi_q) | Y_{\lambda\kappa}(\theta_c, \phi_c) \rangle Y_{\lambda\kappa'}(\theta_q, \phi_q). \quad (5.53)$$

$$\begin{aligned}
& \langle 4f^n, L, S, J, -J | Y_{\lambda\kappa}(\theta_c, \phi_c) | 4f^n, L, S, J, -J \rangle \\
&= \langle Y_{\lambda 0}(\theta_q, 0) | Y_{\lambda\kappa}(\theta_c, \phi_c) \rangle \langle 4f^n, L, S, J, -J | Y_{\lambda 0}(\theta_q, \phi_q) | 4f^n, L, S, J, -J \rangle, \\
& (\langle 4f^n, L, S, J, -J | Y_{\lambda, \kappa \neq 0} | 4f^n, L, S, J, -J \rangle = 0, \text{A4.6, (a4.35), A4.8.1}) \quad (5.54)
\end{aligned}$$

where

$$\begin{aligned}
& \langle Y_{\lambda 0}(\theta_q, 0) | Y_{\lambda\kappa}(\theta_c, \phi_c) \rangle \\
&= \sqrt{\frac{4\pi}{2\lambda+1}} \left\langle \sum_{\kappa'}^{-\lambda, -\lambda+1, \dots, \lambda} Y_{\lambda\kappa'}^*(\Theta, \Phi) Y_{\lambda\kappa'}(\theta_c, \phi_c) \right| Y_{\lambda\kappa}(\theta_c, \phi_c) \rangle \quad (2.23) \\
&= \sqrt{\frac{4\pi}{2\lambda+1}} Y_{\lambda\kappa}(\Theta, \Phi). \quad (5.55)
\end{aligned}$$

The magnetocrystalline anisotropy energy of an ion is

$$\begin{aligned}
f_K(\Theta, \Phi) &= A_{20} \langle r^2 \rangle \left\langle 4f^n, L, S, J, -J \right| \sum_i^{1,2,\dots,n} Y_{20}[\theta_c(i), \phi_c(i)] \left| 4f^n, L, S, J, -J \right\rangle \\
&= A_{20} \langle r^2 \rangle \langle Y_{20}(\theta_q, 0) | Y_{20}(\theta_c, 0) \rangle \\
&\quad \times \sum_i^{1,2,\dots,n} \left\langle 4f^n, L, S, J, -J \right| \sqrt{\frac{5}{4\pi}} U_0^2[\theta_q(i), \phi_q(i)] \left| 4f^n, L, S, J, -J \right\rangle \\
&\quad ((2.24), (5.54)) \\
&= A_{20} \langle r^2 \rangle \sqrt{\frac{4\pi}{5}} Y_{20}(\Theta, \Phi) \langle J, -J | \sqrt{\frac{5}{4\pi}} \tilde{O}_{20} | J, -J \rangle \alpha_J \\
&\quad (\tilde{O}_{20}: \text{Racah operator equivalent,} \\
&\quad \alpha_J: \text{second-order Stevens coefficient, (5.55), (a4.40)–(a4.41)}) \\
&= -A_{20} \langle r^2 \rangle \alpha_J \frac{3}{4} \sqrt{\frac{5}{\pi}} J \left(J - \frac{1}{2} \right) \sin^2 \Theta. \quad (\text{Table a4.2}) \quad (5.56)
\end{aligned}$$

Equation (5.56) shows that $\hat{H}_{\text{CF20}}$ produces uniaxial anisotropy of magnetocrystalline anisotropy constant

$$K_1 = -A_{20} \langle r^2 \rangle \alpha_J \frac{3}{4} \sqrt{\frac{5}{\pi}} J \left(J - \frac{1}{2} \right). \quad (\text{per ion}) \quad (5.57)$$

K_1 is related with both of the properties of the ion including $\langle r^2 \rangle$ of the 4f subshell, α_J , and J , and the environmental parameter A_{20} . With increase of atomic number the value of $A_{20} \langle r^2 \rangle$ for the R ion in $\text{R}_2\text{Fe}_{14}\text{B}$ (R: rare earth), for instance, decreases moderately from ~ 440 K for $\text{Tb}^{+3}(4f^8)$ to ~ 350 K for $\text{Tm}^{+3}(4f^{12})$ [9]. In contrast, the value of $\alpha_J J(J - 1/2)$ varies strikingly and irregularly (Table 5.2).

Table 5.2 The values of J , $J(J - 1/2)$, α_J , and $\alpha_J J(J - 1/2)$ for R^{+3} ions

R^{+3}	J	$J(J - 1/2)$	$\alpha_J \times 10^3$ [10]	$J(J - 1/2)\alpha_J \times 10^3$
$Pr^{+3}(4f^2)$	4	14	-21.0	-294
$Nd^{+3}(4f^3)$	4.5	18	-6.4	-116
$Sm^{+3}(4f^5)$	2.5	5	41.3	206
$Tb^{+3}(4f^8)$	6	33	-10.1	-333
$Dy^{+3}(4f^9)$	7.5	52.5	-6.3	-331
$Ho^{+3}(4f^{10})$	8	60	-2.22	-133
$Er^{+3}(4f^{11})$	7.5	52.5	2.54	133
$Tm^{+3}(4f^{12})$	6	33	10.1	333
$Yb^{+3}(4f^{13})$	3.5	10.5	31.7	334

According to (5.57), the sign of $A_{20}\alpha_J$ decides whether the c axis is easy or hard axis. The easy axis of Nd^{+3} in $R_2Fe_{14}B$ is c axis, so the easy axes of Pr^{+3} , Tb^{+3} , Dy^{+3} , and Ho^{+3} of same α_J sign are also c axis. The absolute values of $J(J - 1/2)\alpha_J$ being among the largest and roughly threefolds of Nd^{+3} , the values of K_1 of Tb^{+3} and Dy^{+3} are the largest and are about threefolds of Nd^{+3} . On the contrary Sm^{+3} , Er^{+3} , Tm^{+3} , and Yb^{+3} of opposite α_J sign the c axis is hard axis. The anisotropies of Tm^{+3} and Yb^{+3} are the largest followed by Sm^{+3} .

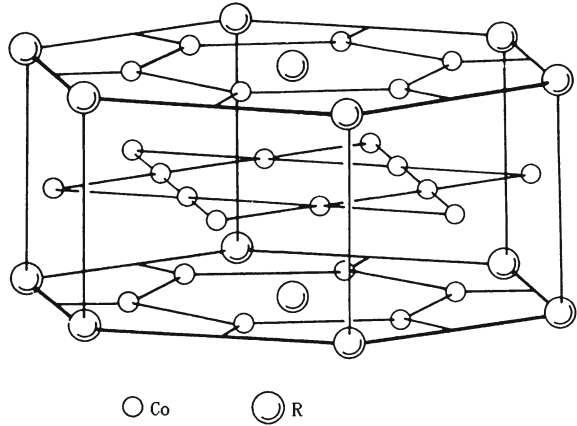
Naturally, the higher order terms of CEF Hamiltonian also affect the anisotropy. But they play secondary role such as the $\sum_i^{1,2,\dots,n} \sum_\lambda^{4,6} \langle r^\lambda \rangle A_{\lambda 0} Y_{\lambda 0}(i)$ term deviates the easy axis of Nd^{+3} ions in $Nd_2Fe_{14}B$ from the c axis to easy cone [11]. The above analyses are in coincidence with experiment.

In brief summary the magnetocrystalline anisotropy of 4f ions originates from the CEF and exchange interactions. The CEF fixes the electronic cloud. The spin-orbit interaction being much larger than the CEF interaction, the magnetization rotation induces the rotation of the electronic cloud. The increased CEF interaction energy constitutes the major part of the magnetocrystalline anisotropy energy.

5.2.4.2 Magnetocrystalline Anisotropy of RCO_5 (R: rare earth) as a Function of Temperature

In $SmNi_5$ and $LaCo_5$ both Ni and La being nonmagnetic the only exchange interaction is of Sm-Sm in $SmNi_5$ and Co-Co in $LaCo_5$. The Curie temperature $T_C = 25$ and 850 K of $SmNi_5$ and $LaCo_5$, therefore, correspond to T_R and T_T in (3.33) and (3.34) of Néel's molecular field theory, which represents the strengths of Sm-Sm and Co-Co exchange interactions. $T_C = 1,000$ K of $SmCo_5$ corresponds to T_N in (3.37). $T_{TR} = 380$ K, which represents the strength of Sm-Co exchange interaction, is obtained by inserting the above parameters into (3.37). The results demonstrate that the R-R exchange interactions are negligibly smaller than the R-Co and Co-Co exchange interactions and can be neglected.

Fig. 5.3 Crystal structure of RCo₅ [6]



The R ion site has hexagonal symmetry (Fig. 5.3). The Co-sublattice has large magnetocrystalline anisotropy constant $K_1^{\text{Co}} > 0$ (per molecular f.u.) making YCo₅ (Y: non-magnetic) and LaCo₅ uniaxial in the whole temperature range below T_C .

Consider the ground multiplet of a R^{+3} ion under the perturbation of the spin-orbit, CEF, and R-Co exchange interactions

$$\begin{aligned} \hat{H}' = & \lambda \hat{L} \cdot \hat{S} + \sum_i^{1,2,\dots,n} \left\{ \sum_{\lambda}^{2,4,6} \langle r^{\lambda} \rangle A_{\lambda}^0 U_{\lambda}^{\lambda}(i) + \langle r^6 \rangle A_6^6 [U_6^6(i) + U_{-6}^6(i)] \right\} \\ & + 2\mu_B \hat{S} \cdot \vec{H}_{\text{ex}}, \end{aligned} \quad (3.90) \quad (5.58)$$

in which both the exchange field $\vec{H}_{\text{ex}}$ and the magnetic polarization of the Co-sublattice per f.u. $\vec{J}_{\text{Co}}$ are anisotropic as

$$\vec{H}_{\text{ex}}(\theta_{\text{Co}}, T) = \vec{H}_{\text{ex}}(T)[1 - p(T) \sin^2 \theta_{\text{Co}}], \quad (5.59)$$

$$\vec{J}_{\text{Co}}(\theta_{\text{Co}}, T) = \vec{J}_{\text{Co}}(T)[1 - p'(T) \sin^2 \theta_{\text{Co}}], \quad (5.60)$$

where θ_{Co} is the tilt angle of $\vec{J}_{\text{Co}}$ from the c axis, and $p(0) = 0.02$ [12] and $p'(0) = 0.037$ [13] have been measured for GdCo₅ and YCo₅, respectively. The values of $\langle r^n \rangle$ are known for all R^{+3} ions. Suppose $\{A_{\lambda}^{\kappa}\}$ is independent of temperature, $\vec{H}_{\text{ex}}$ is proportional and antiparallel to $\vec{J}_{\text{Co}}$, the values of $J_{\text{Co}}(T/T_C)/J_{\text{Co}}(0)$ and $p'(T)$ measured for YCo₅ are the same for all RCo₅, and $p(T)/p(0) = p'(T)/p'(0)$.

For a given $\vec{J}_{\text{Co}}$ direction, the sets of eigenfunctions $\{|i\rangle\}$ and eigenenergies $\{\varepsilon_i\}$ ($i = 1, 2, \dots, \sum_J (2J + 1)$) are obtained by solving the perturbation secular equation ((a6.8)–(a6.9))

$$|\langle 4f^n, L, S, J, M_J | \hat{H}' | 4f^n, L, S, J', M_{J'} \rangle - \varepsilon \langle J, M_J | J', M_{J'} \rangle| = 0. \quad (5.61)$$

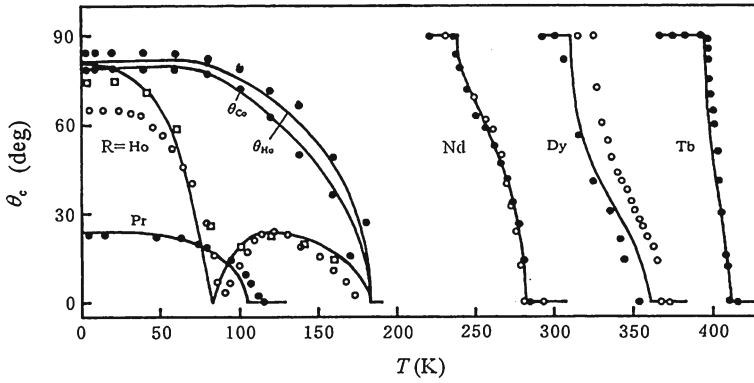


Fig. 5.4 Temperature dependences of θ_c for RCo_5 ($\text{R}=\text{Pr}, \text{Nd}, \text{Tb}, \text{Dy}$ and Ho) and those of θ_{Co} and θ_{Ho} for HoCo_5 . Symbols experiments; solid lines calculations

The $\{J, J'\}$ space is of the ground multiplet for heavy R ions, of the ground and the first excited multiplet for Pr and Nd ion with $\lambda = 610$ and 536 K, respectively, and of the ground and the two lowest excited multiplets ($J, J' = 5/2, 7/2, 9/2$) for Sm ion with $\lambda = 410$ K (Fig. 2.3).

The free energy of RCo_5 per f.u. is

$$F_K(T, \theta_{\text{Co}}) = -k_B T \ln Z + K_1^{\text{Co}}(T) \sin^2 \theta_{\text{Co}}, \quad (5.62)$$

where Z is the distribution function

$$Z = \sum_i \exp\left(-\frac{\varepsilon_i}{k_B T}\right). \quad (5.63)$$

The equilibrium direction of $\vec{H}_{\text{ex}}$ is determined from minimization of F_K . The magnetic polarization moment of the R^{+3} ion is

$$\vec{J}_R = \frac{-\mu_B \sum_i \langle i | 2\hat{S} + \hat{L} | i \rangle \exp\left(-\frac{\varepsilon_i}{k_B T}\right)}{Z} \quad (5.64)$$

and that of the compound is

$$\vec{J} = \vec{J}_R + \vec{J}_{\text{Co}}. \quad (5.65)$$

The direction of $\vec{J}$ is the easy direction. Figure 5.4 shows the temperature dependences of the cone angles θ_c of $\vec{J}$ for the compounds which have spin reorientation transformations and those of the cone angles θ_{Co} and θ_{Ho} of $\vec{J}_{\text{Co}}$ and $\vec{J}_{\text{Ho}}$ for HoCo_5 [14]. The compounds of $\text{R} = \text{Ce}, \text{Sm}, \text{Gd}$, and Er are axial in the whole temperature range. Figure 5.5 demonstrates the temperature dependence of K_1 for SmCo_5 [15].

Table 5.3 Fitted values of $2\mu_B H_{\text{ex}}$, A_{λ}^{κ} , J_{Co} , and K_1^{Co} for RCO_5 [14]

R	$2\mu_B H_{\text{ex}}$	A_2^0	A_4^0 (K)	A_6^0	A_6^6	J_{Co} ($\mu_B/\text{f.u.}$)	K_1^{Co} (K/f.u.)
Pr	1,300	25	−75	250	−600	7.7	45
Nd	750	−1,020	0	115	150	7.7	45
Sm	440	−330	−50	0	0	8.33	45
Tb	265	−340	−240	0	0	8.75	44
Dy	235	−425	−50	0	0	8.92	42
Ho	220	−615	−260	−30	0	9.24	37

Fig. 5.5 K_1 of SmCo_5 versus temperature. Dot experiment; full curve calculation

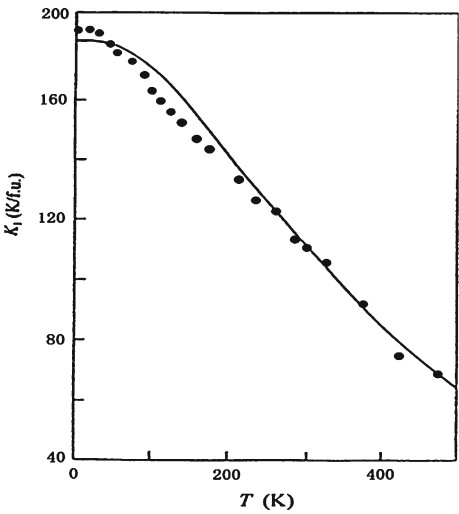
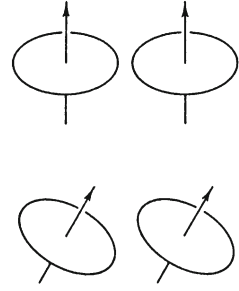


Table 5.3 lists the values of the parameters $2\mu_B H_{\text{ex}}$, A_{λ}^{κ} , J_{Co} , and K_1^{Co} used in the calculations. They were obtained by fitting the calculations with experimental curves of spontaneous magnetization vs. temperature, magnetization curves along major crystal axes directions, and the experimental curves in Figs. 5.4 and 5.5.

5.2.5 Two-Ion Model

The physical picture of this model is as follows. When the spins rotate, the electron clouds of the neighboring two ions also rotate under the action of the spin–orbit interaction thus changing the overlap of the electron clouds (Fig. 5.6) and hence the change in the electric Coulomb interaction between the ions. Van Vleck (1937) proposed that the expression of the interaction has the form of magnetic moment interaction (5.22):

Fig. 5.6 The overlap of the electron cloud changes with the spin direction



$$\hat{f}_K = C \left[\hat{S}_1 \cdot \hat{S}_2 - 3 \frac{(\hat{S}_1 \cdot \vec{r})(\hat{S}_2 \cdot \vec{r})}{r^2} \right], \quad (5.66)$$

where C is a coefficient. The interaction is called pseudo-magnetic moment interaction. The first term in the right has the form of isotropic exchange interaction (4.17). The second term is also proportional to spins but is anisotropic, so $\hat{f}_K$ is also called anisotropic exchange interaction. In fact, the coefficient 3 of the last term in the bracket should be replaced by a coefficient the value of which depends on the two ions (5.59).

5.3 Shape Anisotropy

5.3.1 Demagnetizing Field and Demagnetizing Energy

The magnetic field within a magnetic body produced by the magnetic moments of the body itself is called demagnetizing field. In general, demagnetizing field vector varies in value and direction with position even if the object is magnetized uniformly. The magnetostatic energy is called the demagnetizing energy of the object.

5.3.2 Demagnetizing Factor and Demagnetizing Energy of an Ellipsoidal Magnet and Shape Anisotropy

If a magnetic body is a uniformly magnetized ellipsoid, the demagnetizing field vector $\vec{H}_d$ is uniform and is linearly dependent on the components of magnetization vector $\vec{M}$:

$$(H_d) = -(N)(M) = \begin{pmatrix} H_{dx} \\ H_{dy} \\ H_{dz} \end{pmatrix} = - \begin{pmatrix} N_{xx} & N_{xy} & N_{xz} \\ N_{yx} & N_{yy} & N_{yz} \\ N_{zx} & N_{zy} & N_{zz} \end{pmatrix} \begin{pmatrix} M_x \\ M_y \\ M_z \end{pmatrix}. \quad (5.67)$$

(N) is called demagnetizing factor tensor.

(N) is diagonalized in the principal axes coordinate system of the ellipsoid (Note 1 of this section). In the following we will use this principal axes coordinate. Let d_α ($\alpha = x, y$) denote the equatorial diameters, d_z the polar diameter, and N_α ($\alpha = x, y, z$) the demagnetizing factors along the principal axes, then (5.67) simplifies to

$$\vec{H}_d = - \sum_{\alpha}^{x,y,z} N_\alpha M_\alpha \vec{e}_\alpha. \quad (\vec{e}_\alpha: \text{unit vector in the } \alpha \text{ direction}) \quad (5.68)$$

N_α satisfies the relation of

$$\sum_{\alpha}^{x,y,z} N_\alpha = 1. \quad (5.69)$$

The demagnetizing energy density is (1.82)

$$F_d = \frac{\mu_0}{2} \sum_{\alpha}^{x,y,z} N_\alpha M_\alpha^2. \quad (5.70)$$

If the ellipsoid is spheroid ($d_x = d_y$), the demagnetizing factors along the long axis directions are given by

$$N_z = \frac{1}{k^2 - 1} \left[\frac{k}{\sqrt{k^2 - 1}} \ln(k + \sqrt{k^2 - 1}) - 1 \right], \quad \left(k \equiv \frac{d_z}{d_x} > 1 \right) \quad (5.71)$$

$$N_\perp \equiv N_x = N_y = \frac{1}{2} \left[\frac{k^2}{(k^2 - 1)^{3/2}} \sin^{-1} \frac{\sqrt{k^2 - 1}}{k} - \frac{1}{k^2 - 1} \right]. \quad \left(k \equiv \frac{d_x}{d_z} > 1 \right) \quad (5.72)$$

The demagnetizing energy density as a function of the angle θ between $\vec{M}$ and the z axis is

$$F_d = \frac{\mu_0}{2} (N_\perp \sin^2 \theta + N_z \cos^2 \theta) M^2 = \frac{\mu_0 M^2}{2} N_z + \frac{\mu_0 M^2}{2} (N_\perp - N_z) \sin^2 \theta, \quad (5.73)$$

which is anisotropic.

Note 1

The x component of the demagnetizing field produced by the y component of the magnetic moment $M_y v$ (v : volume of the magnetic object) is

$$-N_{xy}M_y = \frac{3M_y}{4\pi} \int \frac{(y-y')(x-x')}{|\vec{r}-\vec{r}'|^5} dv'. \quad ((1.46), (5.67)) \quad (5.74)$$

The y component of the demagnetizing field produced by the component $M_x v$ at the same position is

$$-N_{yx}M_x = \frac{3M_x}{4\pi} \int \frac{(x-x')(y-y')}{|\vec{r}-\vec{r}'|^5} dv'. \quad (5.75)$$

Therefore,

$$N_{xy} = N_{yx} = -\frac{3}{4\pi} \int \frac{(x-x')(y-y')}{|\vec{r}-\vec{r}'|^5} dv', \quad (5.76)$$

that is, (N) is an Hermitian and hence can be diagonalized in an appropriate coordinate system (A4.2.4). From the geometrical symmetry we get that the system is the principal axes coordinate system of the ellipsoid.

5.4 Induced Magnetic Anisotropy

Induced magnetic anisotropy is often tersely called induced anisotropy. There are several kinds of induced anisotropy. The followings are typical examples.

5.4.1 Anisotropy of Co Metal Induced by Cooling in a Magnetic Field

The crystal structure of Co metal is fcc and hcp (Fig. 3.11) above and below 410°C. The magnetocrystalline anisotropy of the hcp Co is easy plane between 410 and 310°C, easy cone between 310 and 260°C, and easy axis below 260°C.

When a polycrystalline Co is cooled in a magnetic field $\vec{H}_t$ from a high temperature to R.T., an easy plane anisotropy of hard axis parallel to $\vec{H}_t$ is induced. The anisotropy energy is $F_a = K_a \sin^2 \theta$ with $K_a \sim -5 \times 10^4 \text{ J/m}^3$, where θ is the angle between the magnetization vector $\vec{M}$ and $\vec{H}_t$ [16].

The crystal texture of preferential alignment of the c axis about the plane normal to $\vec{H}_t$ is formed through the treatment giving rise to the induced magnetic anisotropy. During the cooling $\vec{M}$ aligns parallel to $\vec{H}_t$. To decrease the magnetocrystalline anisotropy energy, the hcp grains nucleate by making the easy c plane about the $\vec{H}_t$ direction and hence the hard c axis direction about the plane normal to $\vec{H}_t$ direction. At R.T. the c axis becomes easy axis and hence $\vec{H}_t$ direction becomes hard direction [17].

Fig. 5.7 Hysteresis loops of Fe-65%Ni alloy after cooled in the absence of magnetic field (1) and in a magnetic field ($\vec{H}/\vec{H}_t$) (2) [4]

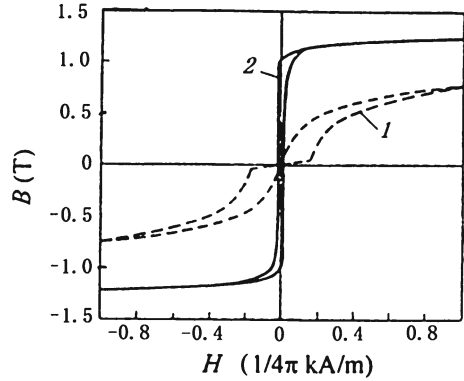
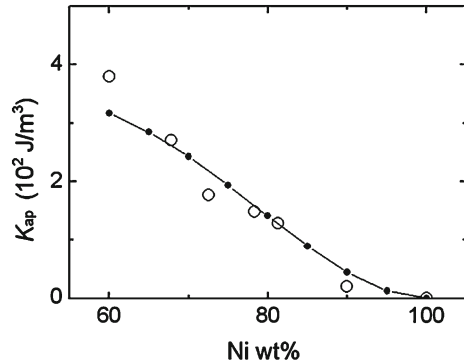


Fig. 5.8 K_{ap} versus Ni content for Fe-Ni alloys. $\circ$ experiment [18, 19]; $\bullet$ $K_{ap} = 55C_{Ni}^2C_{Fe}^2$ ($C_{Ni} = N_{Ni}/N$)



5.4.2 Atomic Pair Ordering Anisotropy

When a polycrystalline Fe-Ni, Ni-Co, or Fe-Co alloy of cubic crystal structure is cooled in a magnetic field $\vec{H}_t$ from a high temperature to R.T. or annealed in a magnetic field $\vec{H}_t$ at a temperature below Curie temperature and then quickly cooled to R.T., a uniaxial anisotropy of easy axis in the $\vec{H}_t$ direction is induced, and the hysteresis loop varies strikingly (Fig. 5.7). Figure 5.8 shows the anisotropy constant K_{ap} as a function of Ni content for Fe-Ni alloys.

The mechanism of the anisotropy is as below [19]. Assume a cubic crystal composed of magnetic atoms A and B. The alloy is a substitution solid solution. The content of B is so small that it can be considered that any atomic pair ab (= AA, AB or BB) is surrounded by adjacent atoms of A. The energy of the pair on the crystal i -axis is

$$l_{ab} \left(\cos^2 \theta_i - \frac{1}{3} \right), \quad (5.77)$$

where θ_i is the angle between $\vec{M}$ and i -axis (5.66). Let N_A and N_B denote the number of atom A and B, $N = N_A + N_B$, N_{AAi} , N_{ABi} , and N_{BBi} the number of AA, AB, and BB pairs on the i -axis all in a unit volume, and $\{\alpha_j\}$, $\{\beta_j\}$, and $\{\gamma_{ji}\}$ ($j = x, y, z$) the direction cosines of $\vec{M}$, $\vec{H}_t$, and i -axis. It holds

$$2N_{AAi} + N_{ABi} = 2N_A, \quad 2N_{BBi} + N_{ABi} = 2N_B, \quad (i = 1, 2, \dots, n) \quad (5.78)$$

and the anisotropy energy density is

$$\begin{aligned} F_{\text{ap}} &= \sum_i^{1,2,\dots,n} (N_{AAi}l_{AA} + N_{BBi}l_{BB} + N_{ABi}l_{AB}) \cos^2 \theta_i \\ &= l_0 \sum_i^{1,2,\dots,n} N_{BBi} \left(\sum_j^{x,y,z} \alpha_j \gamma_{ji} \right)^2, \end{aligned} \quad (5.79)$$

$$l_0 \equiv l_{AA} + l_{BB} - 2l_{AB}. \quad (5.80)$$

When the alloy is annealed at temperature T_t below Curie temperature in $\vec{H}_t$ for long enough time, the atomic pair distribution reaches equilibrium and N_{BBi} becomes

$$\begin{aligned} N_{BBi} &= N_{BB} \frac{\exp \left[-\frac{l_0(T_t) \cos^2 \theta_i}{k_B T_t} \right]}{\sum_i^{1,2,\dots,n} \exp \left[-\frac{l_0(T_t) \cos^2 \theta_i}{k_B T_t} \right]} \approx \frac{N_{BB}}{n} \left[1 - \frac{l_0(T_t)}{k_B T_t} \left(\sum_j^{x,y,z} \beta_j \gamma_{ji} \right)^2 \right], \\ &\quad \left(l_0(T_t) \ll k_B T_t, N_{BB} = \sum_i^{1,2,\dots,n} N_{BBi} \right) \end{aligned} \quad (5.81)$$

which differs for different i axes. The distribution preserves after cooling to a temperature T quickly. Inserting (5.81) into the last expression of (5.79), we get the expression of anisotropy energy at T as

$$\begin{aligned} F_{\text{ap}}(T) &= l_0(T) \sum_i^{1,2,\dots,n} \frac{N_{BB}}{n} \left[1 - \frac{l_0(T_t)}{k_B T_t} \left(\sum_j^{x,y,z} \beta_j \gamma_{ji} \right)^2 \right] \left(\sum_j^{x,y,z} \alpha_j \gamma_{ji} \right)^2 \\ &= \frac{N_{BB} l_0(T)}{n} \sum_i^{1,2,\dots,n} \left[\left(\sum_j^{x,y,z} \alpha_j \gamma_{ji} \right)^2 - \frac{l_0(T_t)}{k_B T_t} \left(\sum_j^{x,y,z} \beta_j \gamma_{ji} \right)^2 \left(\sum_j^{x,y,z} \alpha_j \gamma_{ji} \right)^2 \right] \\ &= -\frac{N_{BB} l_0(T) l_0(T_t)}{k_B T_t} \left(k_1 \sum_j^{x,y,z} \alpha_j^2 \beta_j^2 + k_2 \sum_{j,l}^{xy,yz,zx} \alpha_j \alpha_l \beta_j \beta_l \right), \quad (\text{Note 1 of this section}) \\ &\quad \left(\sum_i^{1,2,\dots,n} \left(\sum_j^{x,y,z} \alpha_j \gamma_{ji} \right)^2 = \text{const.} \right) \end{aligned} \quad (5.82)$$

Table 5.4 The values of k_1 and k_2 for different crystal structures

Crystal structure	k_1	k_2
Simple cubic	1/3	0
bcc	0	4/9
fcc	1/12	4/12
Isotropic	2/15	4/15

$$k_1 \equiv \frac{1}{n} \sum_i^{1,2,\dots,n} (\gamma_{xi}^4 - \gamma_{xi}^2 \gamma_{yi}^2), \quad (5.83)$$

$$k_2 \equiv \frac{4}{n} \sum_i^{1,2,\dots,n} \gamma_{xi}^2 \gamma_{yi}^2. \quad (5.84)$$

Such anisotropy originating from the anisotropy of atomic pair ordering is called atomic pair ordering anisotropy. The values of k_1 and k_2 for different crystal structures are given in Table 5.4 (Note 2 of this section). $N_{BB} \propto C_B^2$. If C_B is not very small, the intra-pair interaction is affected by the distribution of adjacent neighbor atoms of A and B around the pair and N_{BB} in (5.82) is replaced by $NnC_A^2 C_B^2/4$ [20, 21]. The anisotropy energy of isotropic materials (polycrystals) in this case is

$$F_{ap}(T) = -\frac{NnC_A^2 C_B^2 l_0(T) l_0(T_t)}{15k_B T_t} \cos^2 \theta, \quad (5.85)$$

where θ is the angle between $\vec{M}$ and $\vec{H}_t$ [19]. This is the uniaxial anisotropy with the easy axis in the $\vec{H}_t$ direction. Since l_0 is proportional to the square of the atomic spin ((5.66), (5.77)) and the spin is proportional to the saturation magnetization, (5.85) can also be expressed as

$$F_{ap}(T) = G \frac{C_A^2 (1 - C_A)^2 J_s^2(T) J_s^2(T_t)}{T_t} \sin^2 \theta. \quad (G: \text{const.}) \quad (5.86)$$

The atomic ordering anisotropy also develops in the cold rolled Fe-50Ni alloy but two orders larger in magnitude than those induced by the thermal treatment. Apparently the slipping processes promote the formation of the atomic pair ordering [19].

5.4.3 Shape Anisotropy of Magnetic Film Deposited by Oblique Incidence

If a Fe-83%Ni alloy film is vapor deposited by oblique incidence in the absence of magnetic field, a uniaxial anisotropy is induced within the film plane. With increase

Fig. 5.9 Grains of oblique incidence vacuum deposited Fe-83%Ni alloy film ($\theta = 85^\circ$). The large shadow behind a large black impurity shows the direction of the vapor deposition [22]



of incidence angle with the normal of the film θ , the anisotropy field increases, reaches a maximum of $\sim 3 \times 10^{-2}$ T at $\theta \sim 55^\circ$, decreases monotonically, becomes negative above $\sim 70^\circ$, and becomes $\sim -7 \times 10^{-2}$ T at $\sim 80^\circ$. Here positive means the easy axis is normal to the incidence plane and the negative in the incidence plane.

The grain is spheroid with the long axis in the incident plane, and the length of the long axis increases with increase of θ . Caused by the shadow effect, a large void space is formed behind the grains. The grain chains in the direction normal to the incidence plane are also formed (Fig. 5.9). When θ is small, the shape anisotropy of the grain chains plays the major role and the easy axis of the film is normal to the incident plane. When θ becomes very large, the shape anisotropy of each grain becomes the major factor for the anisotropy and the easy axis becomes in the incident plane.

The oblique incident effect is universal and is not affected by the method of preparation and composition of the film.

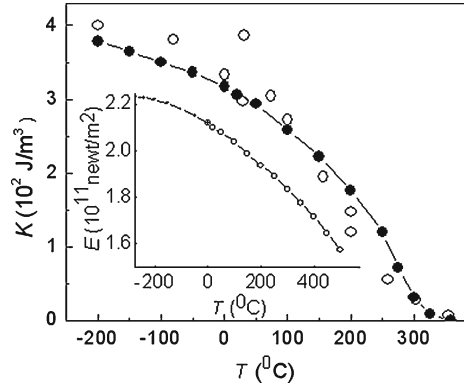
5.4.4 Magnetization-Induced Anisotropy of Thin Film

A polycrystalline magnetic film consists of grains and void network surrounding the grains. When a magnetic film is deposited by normal incidence in a magnetic field $\vec{H}_t$ parallel to the film plane or annealed in $\vec{H}_t$ after deposition in the absence of magnetic field, a uniaxial anisotropy of easy axis in the $\vec{H}_t$ direction is induced in the film plane. The value of the anisotropy constant mainly depends on the film composition, the substrate temperature during the deposition or annealing T_t and the temperature of measurement T .

The anisotropy originates primarily from three mechanisms [23]:

- ① Atomic pair ordering anisotropy;

Fig. 5.10 K versus T for Ni film annealed at 400°C. $\circ$ experiment; $\bullet$ calculation ($T_\lambda = 250^\circ\text{C}$); inset E versus T



- ② Shape anisotropy. The grain of the film is columnar grown in the normal direction of the film or spheroidal. The columnar grain has the elliptical section with the long axis in the field direction to decrease the demagnetizing energy. The long axis of the spheroidal grain is also along the field direction for the same reason. The shape anisotropy and the isotropic distribution of the grain centers on the film plane result in a fairly large shape anisotropy of the film;
- ③ Anisotropic elastic energy. The film is rigidly coupled with the substrate below a critical temperature T_λ . The magnetostriction strain being fixed by the coupling, there appears the elastic energy depending on the $\vec{M}$ direction.

Let K_{ap} , K_s , and K_λ denote the anisotropy constants of the above three anisotropies, E the Young's module, η the Poisson ratio, d the grain size in the film plane, and γ the average grain surface energy density (surface tensile). The anisotropy constants are (Note 3 of this section)

$$K_{\text{ap}}(T) = K_{\text{apu}} \frac{J_s^2(T) J_s^2(T_t)}{J_s^2(\text{R.T.}) J_s^2(T_u)} \frac{T_u}{T_t}, \quad (K_{\text{apu}} \equiv K_{\text{ap}}(T = \text{R.T.}; T_t = T_u)) \quad (5.87)$$

$$K_s(T) = \frac{J_s^2(T) J_s^2(T_t) d}{C \mu_0^2 \gamma}, \quad (C = 80 \text{ or } 152 \text{ for spheroidal or columnar grain film}) \quad (5.88)$$

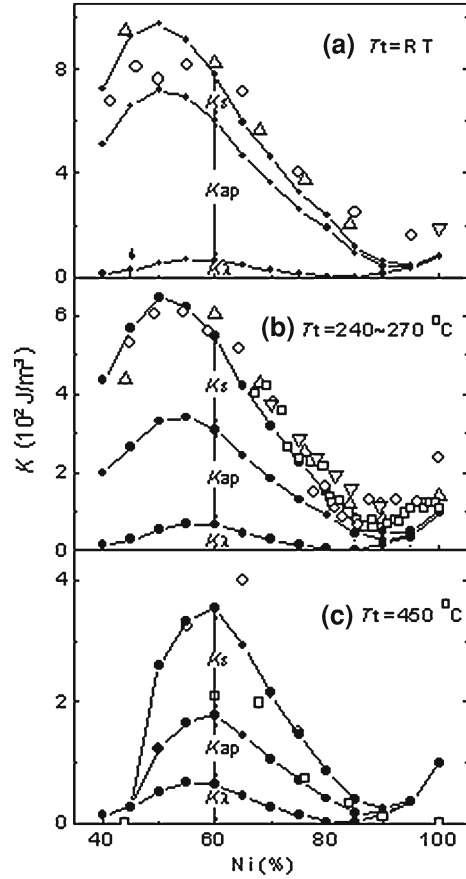
$$K_\lambda(T) = \frac{9\lambda_s(T_0)\lambda_s(T)E(T)}{4(1+\eta)}, \quad (T_0 = T \text{ if } T > T_\lambda; = T_\lambda \text{ if } T < T_\lambda) \quad (5.89)$$

and the anisotropy constant of the film is the linear sum of them:

$$K = K_{\text{ap}} + K_s + K_\lambda. \quad (5.90)$$

Figures 5.10 and 5.11 demonstrate the comparison of the calculations with experiments. Figure 5.10 shows the temperature dependence of K for a Ni film, and Fig. 5.11 the Ni content dependences of K_{ap} , K_s , K_λ , and K at R.T. for Fe-Ni alloy films [23].

Fig. 5.11 Anisotropy constants of Fe-Ni film versus Ni content. Open symbols experiment; ● calculation ($C = 152$, $T_u = 150^\circ\text{C}$, $T_0 = 300^\circ\text{C}$, $T_t, d =$ (a) 20°C , 20 nm; (b) 250°C , 30 nm; (c) 450°C , 40 nm)



5.4.5 Magnetic Anisotropy of Alnico Induced by Tempering in a Magnetic Field

Alnico is an important series of permanent magnets. The alloy is single bcc α phase above $1,200^\circ\text{C}$, which is preserved after rapid cooling. During tempering in the temperature range $550\text{--}650^\circ\text{C}$, a high Fe-Co content and large M_s bcc α_1 phase coherently precipitates in a regular manner. The α_1 grain shape is rod-like with dimension $\sim 20 \times 20 \times 80$ nm, the rods are arranged in the $\langle 100 \rangle$ axis directions, and the adjacent rods are separated by ~ 10 nm distance by the Al-rich and Fe-Co-poor matrix α_2 phase network. The probability of distribution of the bar direction is the same along $[100]$, $[010]$, and $[001]$ directions.

If a magnetic field is applied during the precipitation, the α_1 phase bar grows preferentially along the $\langle 100 \rangle$ axis nearest to the field direction to decrease the shape anisotropy energy (Fig. 5.12). As a result large shape anisotropy is formed. The

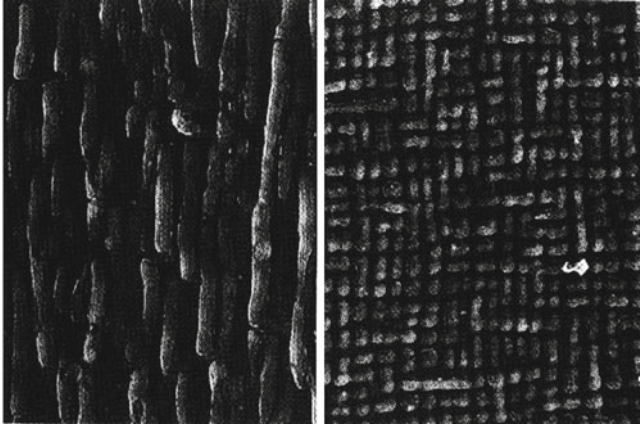


Fig. 5.12 $\alpha_1 + \alpha_2$ micrograph of Alnico 8 thermal treated in a magnetic field [24]. Left $\vec{H}_t$ up and down direction on the picture; right $\vec{H}_t \perp$ picture

anisotropy energy density of the magnet of ideally aligned grains is

$$F_d = \frac{\mu_0(\Delta M_s)^2 P(1-P)}{2} N_{//} + \frac{\mu_0(\Delta M_s)^2 P(1-P)}{2} (N_{\perp} - N_{//}) \sin^2 \theta, \quad (5.91)$$

where θ is the angle between $\vec{M}$ and the long axis of the precipitated bar (easy axis), $N_{\perp}$ and $N_{//}$ the demagnetizing factor of the isolate bar in the direction of the short axis and long axis, respectively, ΔM_s the difference of saturation magnetization of the α_1 and α_2 phase, and P the relative volume of the α_1 phase (Note 4 of this section).

The energy product of Co-rich magnet of high T_C being increased remarkably through the thermal treatment in a magnetic field, the treatment is in wide use (Sect. 10.3.3).

5.4.6 Unidirectional Anisotropy of Co-CoO Particles Induced by Cooling in a Magnetic Field

When an aggregate of ~ 20 nm size Co particles of oxidized surface is cooled from R.T. to 77 K in a magnetic field $\vec{H}_t$, a unidirectional anisotropy with the easy direction in the field direction is induced [25]. The anisotropy energy is

$$F_u = -K_u \cos \theta, \quad K_u \sim 10^5 \text{ (J/m}^3\text{)}, \quad (5.92)$$

where θ is the angle between $\vec{M}$ and $\vec{H}_t$. In contrast to the uniaxial easy axis anisotropy, $\theta = \pi$ for the unidirectional anisotropy is the hard direction. Figure 5.13a demonstrates the hysteresis loops at 77 K after cooled in $\vec{H}_t$ and in the absences of $\vec{H}_t$.

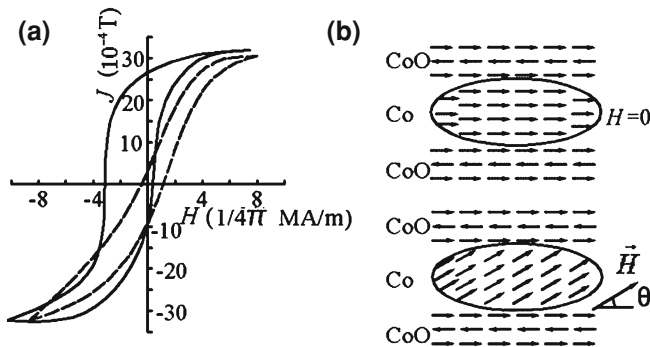


Fig. 5.13 **a** Hysteresis loops of Co particles of oxidized surfaces after cooled to 77 K in the absence of magnetic field (*dashed loop*) and in a magnetic field (*full loop*); **b** Co-CoO magnetic moments distribution in a magnetic field $\vec{H}$ after cooled to 77 K in a magnetic field [25]

After cooled in $\vec{H}_t$ the hysteresis loop is shifted along the abscissa and lost the symmetry of inversion with respect to the origin.

CoO in the surface-oxidized layers is anti-ferromagnetic with $T_N = 291$ K. During cooling in $\vec{H}_t$, $\vec{M}$ of metal Co inside the particle aligns in $\vec{H}_t$ direction and the magnetic moments of CoO are arranged to make the Co-CoO exchange interaction energy minimum. After cooled to 77 K, the magnetic moments directions of CoO are fixed by very large magnetocrystalline anisotropy of itself. If a field is applied at this temperature in a direction different from the easy direction, $\vec{M}$ of metal Co rotates toward the applied field direction but the magnetic moment directions of CoO remain unchanged (Fig. 5.13 b) giving rise to the increase in the exchange interaction energy between the Co and CoO. This kind of anisotropy is called exchange anisotropy. The exchange anisotropy has been observed on the ferromagnetic-antiferromagnetic boundary for a variety of media [26].

5.4.7 Magnetic Anisotropy of Amorphous Gd-Co Thin Film Easy Axis Normal to the Film Plane

In the amorphous Gd-Co alloy the atoms are randomly distributed so that the alloy can be considered isotropic. The magnetic moments of Co are ferromagnetically coupled through the strong Co-Co exchange interaction. The magnetic moments of Gd are coupled antiparallel with Co under the smaller Gd-Co exchange interaction making the Gd-Co alloy ferrimagnetic. The 4f layer being half occupied, the orbital angular momentum of $Gd^{+3}(4f^7)$ is zero and the CEF does not affect the direction of the magnetic moment direction of Gd. The shape anisotropy energy of the isotropic alloy film is (5.73)

$$F_d = \frac{\mu_0 M_s^2}{2} \cos^2 \theta, \quad (N_\perp = 0, N_z = 1) \quad (5.93)$$

where θ is the angle between $\vec{M}$ and normal of the film. The normal is hard axis and $\vec{M}$ stabilizes in the film plane.

The amorphous Gd-Co film is prepared by sputtering in the Ar atmosphere on the low temperature substrate. The film consists of microcolumns of tens nm diameter surrounded by Ar and gap network of several nm thickness. The column is grown normal to the film plane.

Normally the film plane is the easy plane, but the normal of the plane becomes easy axis for some composition film after appropriate oxidization [27]. The phenomenon can be explained as below [28]. At 0 K, the atomic moment $7 \mu_B$ of Gd is much larger than $\sim 1.7 \mu_B$ of Co. With increase of temperature the magnetic moment of Gd decreases faster than Co because of smaller Gd-Co exchange interaction than Co-Co. Consider a Gd-Co alloy film of compensation temperature (Sect. 3.4.2.2) slightly higher than R.T.. During the oxidation process, the Gd ions in the surface layer of the microcolumn oxidize preferentially thus decreasing the metal Gd content in the surface layer. The decrease of metal Gd content results in the decrease of the compensation temperature of the surface layers below R.T., such as the compensation temperature of $\text{Gd}_{14}\text{Co}_{70.6}\text{Mo}_{15.4}$ is 350 K and that of $\text{Gd}_{11}\text{Co}_{73.6}\text{Mo}_{15.4}$ is 160 K, thus reversing the magnetization direction of the surface layer opposite to the direction within the column. If the film is magnetized normal to the film plane, the magnetic surface charges of different signs distribute densely alternately on the film surfaces thus strikingly decreasing the demagnetizing energy in contrast to that the demagnetizing energy increases also very much if the film is magnetized in the film plane.

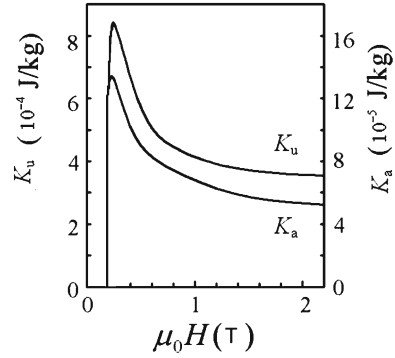
5.4.8 Magnetic Field-Induced Anisotropy of Cu-2%Mn Spin-Glass

Cu-2%Mn alloy has no net magnetization and is isotropic if it is cooled to 4.2 K in the absence of magnetic field. If a magnetic field $\vec{H}$ larger than a critical value is applied at 4.2 K, a unidirectional anisotropy superposed by a small uniaxial anisotropy is induced,

$$F_{ua} = -K_u \cos \theta + K_a \sin^2 \theta, \quad (K_u, K_a > 0) \quad (5.94)$$

where θ is the angle between $\vec{M}$ and $\vec{H}$. Figure 5.14 shows H dependences of K_u and K_a for $\text{Cu}_{97.9}\text{Mn}_{2.1}$. The values of K_u and K_a were obtained from the torque curves measured by rotating $\vec{H}$. K_u and K_a change little with the number of the rotation [29].

Fig. 5.14 K_u and K_a versus $\mu_0 H$ for $\text{Cu}_{97.9}\text{Mn}_{2.1}$ alloy cooled to 4.2 K in the absence of magnetic field



Note 1

$$\begin{aligned}
 & \sum_i (\alpha_x \gamma_{xi} + \alpha_y \gamma_{yi} + \alpha_z \gamma_{zi})^2 (\beta_x \gamma_{xi} + \beta_y \gamma_{yi} + \beta_z \gamma_{zi})^2 \\
 &= (\alpha_x^2 \beta_x^2 + \alpha_y^2 \beta_y^2 + \alpha_z^2 \beta_z^2) \sum_i \gamma_{xi}^4 \\
 & \quad + (\alpha_x^2 \beta_y^2 + \alpha_x^2 \beta_z^2 + \alpha_y^2 \beta_x^2 + \alpha_y^2 \beta_z^2 + \alpha_z^2 \beta_x^2 + \alpha_z^2 \beta_y^2) \sum_i \gamma_{xi}^2 \gamma_{yi}^2 \\
 & \quad + 4(\alpha_x \alpha_y \beta_x \beta_y + \alpha_y \alpha_z \beta_y \beta_z + \alpha_z \alpha_x \beta_z \beta_x) \sum_i \gamma_{xi}^2 \gamma_{yi}^2 \\
 &= (\alpha_x^2 \beta_x^2 + \alpha_y^2 \beta_y^2 + \alpha_z^2 \beta_z^2) \left(\sum_i \gamma_{xi}^4 - \sum_i \gamma_{xi}^2 \gamma_{yi}^2 \right) + \sum_i \gamma_{xi}^2 \gamma_{yi}^2 \\
 & \quad + 4(\alpha_x \alpha_y \beta_x \beta_y + \alpha_y \alpha_z \beta_y \beta_z + \alpha_z \alpha_x \beta_z \beta_x) \sum_i \gamma_{xi}^2 \gamma_{yi}^2 \\
 & \quad \left(\sum_i \gamma_{xi}^4 = \sum_i \gamma_{yi}^4 = \sum_i \gamma_{zi}^4, \sum_i \gamma_{xi}^2 \gamma_{yi}^2 = \sum_i \gamma_{yi}^2 \gamma_{zi}^2 = \sum_i \gamma_{zi}^2 \gamma_{xi}^2, \right. \\
 & \quad \left. \text{terms like } \alpha_x \alpha_y \beta_x \beta_z \sum_i \gamma_{xi}^2 \gamma_{yi} \gamma_{zi} \text{ are zero} \right) \quad (5.95)
 \end{aligned}$$

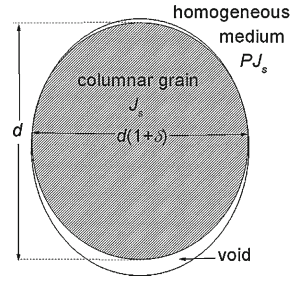
Note 2

Example 1 In the fcc crystal $n = 6$ and the i axes are $[110]$, $[1\bar{1}0]$, $[011]$, $[01\bar{1}]$, $[101]$, and $[10\bar{1}]$.

$$k_2 \equiv \frac{4}{6} \sum_i \gamma_{xi}^2 \gamma_{yi}^2 = \frac{4}{6} \left(\gamma_{x[110]}^2 \gamma_{y[110]}^2 + \gamma_{x[1\bar{1}0]}^2 \gamma_{y[1\bar{1}0]}^2 \right) = \frac{4}{6} \left(\frac{1}{2 \times 2} + \frac{1}{2 \times 2} \right) = \frac{4}{12}. \quad (5.96)$$

Example 2 The value of k_2 for isotropic material is

Fig. 5.15 Average environment of a columnar grain



$$k_2 \equiv \frac{4}{6} \sum_i \gamma_{xi}^2 \gamma_{yi}^2 = 4 \frac{\int_0^{\frac{\pi}{2}} \int_0^{\frac{\pi}{2}} \sin^4 \theta \cos^2 \phi \sin^2 \phi \sin \theta d\theta d\phi}{\int_0^{\frac{\pi}{2}} \int_0^{\frac{\pi}{2}} \sin \theta d\theta d\phi} = \frac{4}{15}. \quad (5.97)$$

Note 3

- (1) K_{ap} . Equation (5.87) is obtained directly from (5.86) and can be used if K_{apu} is known. The relation holds when the atomic pair ordering reached equilibrium at temperature T_l and the distribution is preserved at temperature T . The experimental data given in Fig. 5.8 are the maximum values among the experimental values obtained after cooling from 600°C to R.T. by different speeds for different Ni content alloys. Suppose the experimental data represent K_{apu} as a function of Ni content for the Fe-Ni films. T_u is a fitting parameter and $T_u = 150^\circ\text{C}$ is obtained from best fit of the calculations with experiments.
- (2) K_s . Take the columnar grain film as an example. Let $d(1 + \delta)$ and d denote the length of the long and short axis of the elliptical cross-section, respectively, and P the volume fraction of the grains. Suppose the film thickness is much larger than d and $\delta \ll 1$. The area of the elliptical cross-section and the length of its periphery are

$$S = \frac{\pi d^2}{4} (1 + \delta), \quad (5.98)$$

$$L \approx \pi d \left(1 + \frac{1}{2} \delta + \frac{7}{16} \delta^2 \right) = 2\sqrt{\pi S} \left(1 + \frac{19}{16} \delta^2 \right). \quad (5.99)$$

The demagnetizing factors of the isolated elliptical column along the long and short axes of the cross-section are

$$N_{//} = \frac{1}{2} - \frac{1}{4} \delta, \quad N_{\perp} = \frac{1}{2} + \frac{1}{4} \delta. \quad (5.100)$$

The distribution of the centers of the columnar grains in the film plane is isotropic. On the average, therefore, each column is in the void cylinder of sectional area S/P , and the void is in the homogeneous film of average magnetic polarization $J_s P$ (Fig. 5.15). From minimum condition of the sum of the demagnetizing

energy and surface energy under the fixed value of S

$$\frac{\partial}{\partial \delta} \left[\frac{J_s^2(T_t)}{2\mu_0} N_{//} S - \frac{P J_s^2(T_t)}{4\mu_0} S + \gamma L \right] = -\frac{J_s^2(T_t) S}{2\mu_0} \frac{1}{4} + \sqrt{\pi S} \frac{19}{4} \gamma \delta = 0 \quad (5.101)$$

we get

$$\delta(T_t) = \frac{J_s^2(T_t) d}{76\mu_0 \gamma}. \quad (5.102)$$

The first term in the bracket of the first expression of (5.101) is the intragrain magnetic moment interaction energy, i.e., the demagnetizing energy of the isolated grain, and the second term the intergrain magnetic moment interaction energy. The latter is irrelevant to δ and hence does not affect the value of δ . δ is very small indeed such as 5×10^{-5} for $J_s = 1 \text{ T}$, $d = 10 \text{ nm}$, and $\gamma = 2 \text{ J/m}^2$. The anisotropy constant of the shape anisotropy is

$$K_s(T) = \frac{J_s^2(T)}{2\mu_0} (N_{\perp} - N_{//}) = \frac{J_s^2(T) J_s^2(T_t) d}{152\mu_0^2 \gamma}. \quad (5.103)$$

The surface energy of Ni is 2.6 J/m^2 . A part of the grain is contacting with the adjacent grains and the grain boundary energy is much smaller than the surface energy, so in the calculations the average surface energy density of $\gamma = 2 \text{ J/m}^2$ was used. d is a fitting parameter.

- (3) K_{λ} . When a tensile stress σ_{xx} is exerted on an isotropic medium, the strains are $E A_{xx}$ in the stress direction and $-\eta A_{xx}$ in the directions normal to the stress direction. Thus the relation between the strains and stresses in the film plane parallel to the xy plane is

$$\begin{pmatrix} A_{xx} \\ A_{yy} \end{pmatrix} = \frac{1}{E} \begin{pmatrix} 1 & -\eta \\ -\eta & 1 \end{pmatrix} \begin{pmatrix} \sigma_{xx} \\ \sigma_{yy} \end{pmatrix}, \quad (5.104)$$

and the elastic energy is

$$F_{\lambda} = \int_0^{a_{xx}} \sigma_{xx} dA_{xx} + \int_0^{a_{yy}} \sigma_{yy} dA_{yy} = \frac{E}{2(1-\eta^2)} (A_{xx}^2 + 2\eta A_{xx} A_{yy} + A_{yy}^2). \quad (5.105)$$

Let the x axis be parallel to $\vec{H}_t$, the angle between $\vec{J}_s$ and $\vec{H}_t$ is θ , and A_p represent the sum of intrinsic strain and the strain caused by different thermal contractions of the film and the substrate in respect to demagnetized state at the temperature T_{λ} . At temperature $T (< T_{\lambda})$

$$\begin{aligned}
A_{xx} &= A_p + \lambda_s(T_\lambda) - (3/2)\lambda_s(T)(\cos^2 \theta - 1/3), \\
A_{yy} &= A_p - (1/2)\lambda_s(T_\lambda) - (3/2)\lambda_s(T)(\sin^2 \theta - 1/3), \\
K_\lambda &= F_\lambda\left(\theta = \frac{\pi}{2}\right) - F_\lambda(\theta = 0) = \frac{9\lambda_s(T)\lambda_s(T_\lambda)E}{4(1+\eta)}. \quad (5.106)
\end{aligned}$$

The value of E as a function of T is from the experimental data given in the inset of Fig. 5.10 and the value of η is 0.3 all of them are the values for Ni. The values of E , η , and γ vary little with the Ni content of Fe-Ni alloy, and above values are used for the all alloys.

T_λ is a fitting parameter and the value of 250–300°C was obtained from best fits.

Note 4

The magnetization vectors of the α_1 and α_2 phases are parallel, and the magnetic surface charge densities on the boundaries of the two phases are proportional to ΔM_s . The magnetostatic energy of the system is the same with the energy of same geometry system but magnetization of the precipitate phase α_1 is ΔM_s and that of the matrix phase α_2 is zero. The energy is composed of the intragrain and intergrain magnetic charge interactions.

The intragrain interaction per unit volume is

$$\frac{\mu_0(\Delta M_s)^2 P}{2} N_{//} + \frac{\mu_0(\Delta M_s)^2 P}{2} (N_\perp - N_{//}) \sin^2 \theta. \quad ((5.73)) \quad (5.107)$$

In average each precipitate grain is embedded in a homogeneous medium of magnetization $\Delta M_s P$. Let $\Delta \vec{M}_s = \Delta M_s(\sin \theta \vec{e}_x + \cos \theta \vec{e}_z)$, then the magnetic field in the precipitate grain produced by the matrix medium is

$$(N_\perp \sin \theta \vec{e}_x + N_{//} \cos \theta \vec{e}_z) \Delta M_s P. \quad (5.108)$$

The intergrain interaction energy density is a half of the Zeeman energy of $\Delta M_s P$ in the above field:

$$\begin{aligned}
& -\frac{1}{2} [\mu_0 \Delta M_s P (\sin \theta \vec{e}_x + \cos \theta \vec{e}_z)] [(N_\perp \sin \theta \vec{e}_x + N_{//} \cos \theta \vec{e}_z) \Delta M_s P] \\
& = -\frac{\mu_0(\Delta M_s P)^2}{2} N_{//} - \frac{\mu_0(\Delta M_s P)^2}{2} (N_\perp - N_{//}) \sin^2 \theta. \quad (5.109)
\end{aligned}$$

Equation (5.91) is the sum of (5.107) and (5.109).

5.5 Random Anisotropy and Effective Anisotropy

The Fe-based and Co-based amorphous soft magnetic materials of very small coercivity are composed of the 3d magnetic elements of Fe, Co, and/or Ni and roughly 20 at.% IIIB–VA (B, Si, P et al.) or 10 at.% IIIB–VB (Y, Ti, Zr, Hf, Nb, Ta) elements.

Dozens of μm thick thin ribbons are prepared by spraying a high temperature alloy liquid onto a high speed rotating Cu disk surface. The liquid cools down by as fast as 10^5 K/s speed. The amorphous films are prepared by sputtering onto a low temperature substrate. In the amorphous materials atoms distribute randomly, and there is no grain boundary nor defect of dislocation.

The nanocrystalline magnetic materials of better soft magnetic properties are prepared by annealing some 3d-based amorphous materials at $\sim 550^\circ\text{C}$ for dozens of minutes precipitating tens nm dimension crystallites in the amorphous matrix. The grains are smaller than the critical size of single domain (Sect. 7.3.8) and are in the single domain state.

In contrast to the above 3d-based amorphous and nanocrystalline soft magnetic materials, (Tb, Dy)-Fe amorphous films have coercivity of as large as $\sim 3 \text{ T}$ at low temperatures.

The above magnetic properties can be explained by use of random anisotropy model.

5.5.1 Random Anisotropy of Amorphous Magnetic Materials

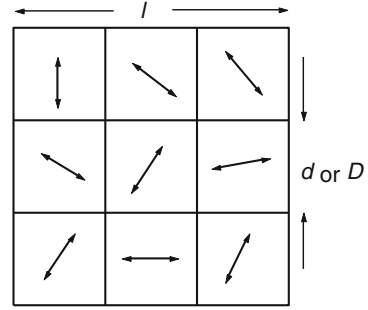
Under the CEF interactions the magnetic atom in amorphous materials has magnetic anisotropy, and the easy axis directions of different atoms distribute randomly. Such kind of anisotropy is called random anisotropy [30]. The magnetic atoms being exchange coupled with each other, the magnetic moment direction of each atom deviates more or less from the easy axis so that the moment directions are orderly arranged to some extent and the direction varies smoothly with position. Let K_1 denote the anisotropy constant and $\vec{e}_K(\vec{r})$ the unit vector of the easy direction. Local energy is composed of exchange and anisotropy energies and its density at position $\vec{r}$ is

$$F(\vec{r}) = A \sum_i^{x,y,z} [\nabla \alpha_i(\vec{r})]^2 - K_1 \frac{[\vec{M}(\vec{r}) \cdot \vec{e}_K(\vec{r})]^2}{M^2}, \quad ((4.113), (5.3), (5.4)) \quad (5.110)$$

The above case can be treated by using the following simplified model: partition the magnetic body into “structural correlation regions”. The dimension of the structural correlation region d is selected so that each region on the average contains one magnetic atom. Within a structural correlation region, the magnetic anisotropy is uniform, and $\vec{e}_K(\vec{r})$ changes discontinuously across the border of the regions (Fig. 5.16). Since the magnetic moments are exchange coupled, the variation of $\vec{M}(\vec{r})$ in a larger “magnetic correlation region” of dimension l varies not very large, and can be considered uniform $\vec{M}$ of the average of $\vec{M}(\vec{r})$ in the region. $\vec{M}$ changes discontinuously across the border of the magnetic correlation region.

The variation of magnetization direction of the magnetic body accompanies the change in the $\vec{M}$ direction and anisotropy energy of each magnetic correlation region.

Fig. 5.16 Random anisotropy model. *Double headed arrows* show the easy axis direction arrangement in each structural correlation region



According to the statistic fluctuation theory, the mean fluctuation amplitude of the anisotropy energy density F_K is inversely proportional to the square root of the number of independent anisotropies in the magnetic correlation region $N = (l/d)^3$:

$$F_K \sim \frac{K_1}{\sqrt{N}} = K_1 \left(\frac{d}{l} \right)^{\frac{3}{2}}. \quad (5.111)$$

The variation of $\vec{M}$ directions also accompanies the change of the exchange interaction energy of the region with the neighboring magnetic correlation regions. The change is roughly given by

$$F_{\text{ex}} \sim \frac{A}{l^2}. \quad (4.113) \quad (5.112)$$

The value of the magnetic correlation length l which gives rise to minimum change of the total energy is

$$l \sim \frac{16A^2}{9K_1^2 d^3}, \quad (5.113)$$

and corresponding change of the energy is

$$F \sim 0.1 \frac{K_1^4 d^6}{A^3}. \quad (5.114)$$

The model being fairly rough, the value of the coefficient is not important.

5.5.2 Effective Anisotropy of Amorphous Magnetic Materials

The above results are equivalent to the following more simple physical picture: the magnetic body consists of the magnetic correlation regions independent with each other [30]. In each magnetic correlation region the magnetization is uniform and the magnetic anisotropy constant is

$$K \sim 0.1 \frac{K_1^4 d^6}{A^3}. \quad (5.115)$$

The easy axis directions of different magnetic correlation regions are distributed randomly. Such anisotropy is called effective magnetic anisotropy or tersely effective anisotropy.

The orbital angular momentum being quenched, the values of K_1 for 3d ions are small, so the effective anisotropy $K (\propto K_1^4)$ of the 3d-based amorphous magnetic materials is very small. Correspondingly, the coercivity is also very small making them good soft magnetic materials. Tb and Dy ions of 4f transition element have intact orbital angular momentum and the values of $\alpha_J J(J - 1/2)$ are large (Table 5.2), so their K_1 are large (5.57). This is the reason why the 4f-Fe-based amorphous magnetic materials which encompass Tb or Dy have very large effective anisotropy $K (\propto K_1^4)$ and hence large coercivity (Sect. 10.2.1).

5.5.3 Effective Anisotropy of Nanocrystalline Materials

The materials of grain size 1–100 nm are called nanocrystal materials. Each crystallite is single domain, the size of the crystallite is D , the crystalline anisotropy constant is K_1 , and the easy axes are randomly distributed. These circumstances completely correspond to those of the preceding Sect. 5.5.2 for amorphous materials with the crystallite corresponding to the structural correlation region. By substituting d in Sect. 5.5.2 by D , we get the effective anisotropy constant [31]

$$K \sim 0.1 \frac{K_1^4 D^6}{A^3}. \quad (5.116)$$

With decrease of D , K decreases in proportion to D^6 which is confirmed by the experimental results of $H_c \propto D^6$ for nanocrystalline alloys ($H_c \propto K$, Sect. 10.2). If K_1 is small, we can get very small $K (\propto K_1^4)$ and hence very good soft magnetic property.

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Chapter 6

Magnetostrictive Effects

A change in magnetization accompanies small change in size and volume of the medium. A stress acting on a magnetic medium produces an additional anisotropic term in the thermal potential thus affecting the characteristics of the magnetization. This chapter will analyze these effects, and contains the sections of Magnetostriction and magneto-elastic energy; and Stress energy.

6.1 Magnetostriction and Magneto-Elastic Energy

6.1.1 Magnetostriction Phenomena

The relative change of dimension $\delta r/r = \lambda$ which accompanies the magnetization is called linear magnetostriction or tersely magnetostriction. When the magnetization saturates λ also saturates, and becomes zero when the spontaneous magnetization vanishes. Figure 6.1 demonstrates λ in the field direction as a function of magnetic field for polycrystalline Fe, Co, and Ni metals and 45Ni–Fe alloy along with the normalized magnetization curve for the alloy all at R.T.. Figure 6.2 demonstrates the temperature dependences of the magnetostriction coefficients (also called saturation magnetostrictions) λ_{100} and λ_{111} of single crystal Ni in the field direction applied in the [100] and [111] axes. Before the measurements the specimens were thermally demagnetized.

This section mainly analyzes the magnetostriction of cubic crystals. Magnetostriction is intimately related with elastic deformation. First review the essentials of elastic mechanics for cubic crystal.

Fig. 6.1 λ versus H for 45Ni–Fe 2, Fe 3, Co 4 and Ni 5, and B/B_s versus H for 45Ni–Fe 1 [1]

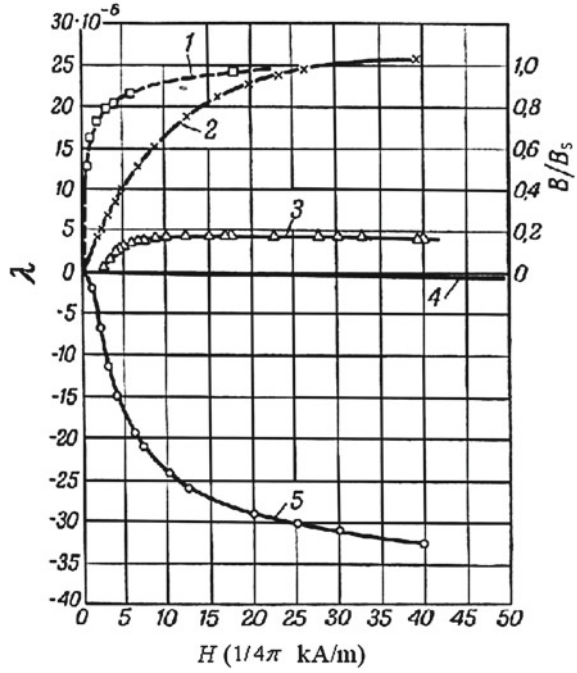
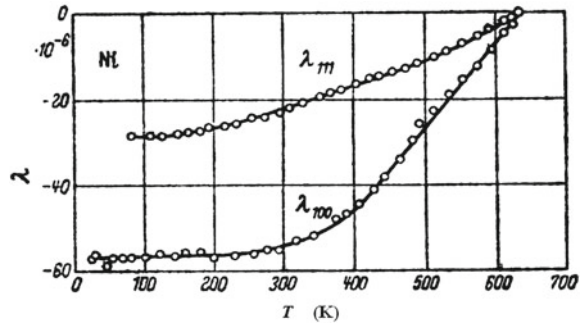


Fig. 6.2 λ_{100} and λ_{111} versus T for Ni [2]

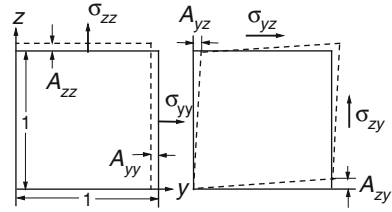


6.1.2 Elastic Mechanics for Cubic Crystal

6.1.2.1 Strain Tensor

In the following, it is prescribed that the crystal does not rotate and its origin is fixed. Let $\vec{r}_0(x_0, y_0, z_0)$ and $\vec{r}(x, y, z)$ denote the position vector of a point in the crystal before and after deformation. The elastic strain $\vec{r} - \vec{r}_0$ in the non-deformed $\langle 100 \rangle$ coordinate system is

Fig. 6.3 Meanings of A_{ij} and σ_{ij}



$$\vec{r} - \vec{r}_0 = (A) (r_0) = \begin{pmatrix} x - x_0 \\ y - y_0 \\ z - z_0 \end{pmatrix} = \begin{pmatrix} A_{xx} & A_{xy} & A_{xz} \\ A_{yx} & A_{yy} & A_{yz} \\ A_{zx} & A_{zy} & A_{zz} \end{pmatrix} \begin{pmatrix} x_0 \\ y_0 \\ z_0 \end{pmatrix}, \quad (6.1)$$

where (A) is the strain tensor. It can be seen from the above equation that $A_{zz} = \partial(z - z_0)/\partial z_0$ represents the relative elongation in the $[001]$ direction and $A_{yz} = \partial(y - y_0)/\partial z_0$ the tilt angle of the $[001]$ axis toward the $[010]$ direction (Fig. 6.3). Since the crystal does not rotate

$$A_{ji} = A_{ij}. \quad (6.2)$$

6.1.2.2 Stress Tensor

Let σ_{zz} and σ_{yz} represent the tensile stress in the $[001]$ direction and the shear stress in the $[010]$ direction, respectively, both applied on the unit (001) plane (Fig. 6.3). Since the crystal is in the equilibrium state

$$\sigma_{ji} = \sigma_{ij}. \quad (6.3)$$

6.1.2.3 Elastic Module Tensor

According to the Hook's law the elements of the symmetrical (A) and (σ) tensors are linearly related:

$$\begin{pmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \sigma_{zz} \\ \sigma_{xy} \\ \sigma_{yz} \\ \sigma_{zx} \end{pmatrix} = \begin{pmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{31} & C_{32} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{41} & C_{42} & C_{43} & C_{44} & C_{45} & C_{46} \\ C_{51} & C_{52} & C_{53} & C_{54} & C_{55} & C_{56} \\ C_{61} & C_{62} & C_{63} & C_{64} & C_{65} & C_{66} \end{pmatrix} \begin{pmatrix} A_{xx} \\ A_{yy} \\ A_{zz} \\ 2A_{xy} \\ 2A_{yz} \\ 2A_{zx} \end{pmatrix}, \quad (6.4)$$

where (C) is the elastic module tensor. The symmetry of the cubic crystal makes (C) symmetrical ($C_{ij} = C_{ji}$) by reducing the number of independent elements to three

of C_{11} , C_{12} , and C_{44} as

$$\begin{pmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \sigma_{zz} \\ \sigma_{xy} \\ \sigma_{yz} \\ \sigma_{zx} \end{pmatrix} = \begin{pmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{pmatrix} \begin{pmatrix} A_{xx} \\ A_{yy} \\ A_{zz} \\ 2A_{xy} \\ 2A_{yz} \\ 2A_{zx} \end{pmatrix}. \quad (\text{Note 1 of this section}) \quad (6.5)$$

6.1.2.4 Elastic Energy

The elastic energy is (Note 2 of this section)

$$\begin{aligned} F_{\text{el}}(A) &= \sum_i^{x,y,z} \int_0^{A_{ii}} \sigma_{ii} dA_{ii} + \sum_{ij}^{xy,yz,zx} \int_0^{A_{ij}} \sigma_{ij} (2dA_{ij}) \\ &= \frac{C_{11}}{2} \sum_i^{x,y,z} A_{ii}^2 + C_{12}(A_{xx}A_{yy} + A_{yy}A_{zz} + A_{zz}A_{xx}) \\ &\quad + 2C_{44}(A_{xy}^2 + A_{yz}^2 + A_{zx}^2) \\ &= \frac{C_1}{2} \left(\sum_i^{x,y,z} A_{ii} \right)^2 + C_2 \sum_i^{x,y,z} A_{ii}^2 + 2C_3 (A_{xy}^2 + A_{yz}^2 + A_{zx}^2), \end{aligned} \quad (6.6)$$

$$C_1 \equiv C_{12}, \quad C_2 \equiv \frac{C_{11} - C_{12}}{2}, \quad C_3 \equiv C_{44}. \quad (6.7)$$

Typical C_{ij} ($ij = 11, 12, 44$) values: $C_{11} = 2.41 \times 10^{11} \text{ J/m}^3$, $C_{12} = 1.46 \times 10^{11} \text{ J/m}^3$ and $C_{44} = 1.12 \times 10^{11} \text{ J/m}^3$ for Fe crystal at R.T..

6.1.3 Magneto-Elastic Energy

The magnetostriction phenomenon reveals that magnetocrystalline anisotropy energy F_K not only depends on the $\vec{M}$ direction $\alpha (\equiv \{\alpha_i\} (i = x, y, z)$: the direction cosines), but also on the strain tensor elements ($A \equiv \{A_{ij}\}$). F_K can be linearly decomposed into three parts: the term $F_K^0(\alpha)$ including only α , the magneto-elastic energy $F_{\text{ms}}(\alpha, A)$ including mixed terms of α and A , and the elastic energy $F_{\text{el}}(A)$ (6.6) including only A . From the symmetry of the cubic crystal it is easily deduced that the functional form of $F_K^0(\alpha)$ is the same with that of F_K (5.2). The linear expansion

of $F_{\text{ms}}(\alpha, A)$ with respect $\{A_{ij}\}$ is (Note 3 of this section)

$$F_{\text{ms}}(\alpha, A) = a_0 \sum_i^{x,y,z} A_{ii} + a_1 \sum_i^{x,y,z} \left(\alpha_i^2 - \frac{1}{3} \right) A_{ii} + 2a_2 \sum_{ij}^{xy,yz,zx} \alpha_i \alpha_j A_{ij} \\ + a_3 s \sum_i^{x,y,z} A_{ii} + a_4 \sum_i^{x,y,z} \left(\alpha_i^4 + \frac{2s}{3} - \frac{1}{3} \right) A_{ii} + \dots, \quad (a_i : \text{const.}) \quad (6.8)$$

$$s \equiv \alpha_x^2 \alpha_y^2 + \alpha_y^2 \alpha_z^2 + \alpha_z^2 \alpha_x^2. \quad (6.9)$$

6.1.4 Spontaneous Strain Tensor

By taking into account the effect of strain, the magnetocrystalline anisotropy energy is

$$F_K(\alpha, A) = F_K^0(\alpha) + F_{\text{ms}}(\alpha, A) + F_{\text{el}}(A). \quad (6.10)$$

From minimum condition of $F_K(\alpha, A)$ with respect to $\{A_{ij}\}$ for a given α

$$\frac{\partial F_K(\alpha, A)}{\partial A_{ij}} = \frac{\partial F_{\text{ms}}(\alpha, A)}{\partial A_{ij}} + \frac{\partial F_{\text{el}}(A)}{\partial A_{ij}} = 0 \quad (ij = xx, yy, zz, xy, yz, zx) \quad (6.11)$$

we get the spontaneous strain tensor elements $\{A_{ij}^0\}$ as a function of α as

$$A_{ii}^0 = -\frac{a_1}{2C_2} \left(\alpha_i^2 - \frac{1}{3} \right) - \frac{a_3 s}{3C_1 + 2C_2} \\ - \frac{a_4}{2C_2} \left(\alpha_i^4 + \frac{2s}{3} - \frac{1}{3} \right) + \dots, \quad (i = x, y, z) \\ A_{ij}^0 = -\frac{a_2}{2C_3} \alpha_i \alpha_j - \frac{a_5}{2C_3} \alpha_i \alpha_j \alpha_k^2 \dots \quad (ij = xy, yz, zx; \quad k \neq i \neq j) \quad (6.12)$$

Under spontaneous strains $\{A_{ij} = A_{ij}^0\}$ (6.10) becomes

$$F_K(\alpha) \equiv F_K(\alpha, A^0) = F_K^0(\alpha) + F_{\text{ms}}(\alpha, A^0) + F_{\text{el}}(A^0) \\ = (K_1^0 + \Delta K_1)(\alpha_x^2 \alpha_y^2 + \alpha_y^2 \alpha_z^2 + \alpha_z^2 \alpha_x^2) + (K_2^0 + \Delta K_2) \alpha_x^2 \alpha_y^2 \alpha_z^2 + \dots, \quad (6.13)$$

$$\Delta K_1 = \frac{a_1^2}{2C_2} - \frac{a_2^2}{2C_3} + \frac{2a_4}{3C_2} + \dots, \quad (6.14)$$

$$\Delta K_2 = -\frac{3a_1a_4}{C_2} - \frac{a_4^2}{C_2} + \dots \quad (6.15)$$

6.1.5 Phenomenological Expression of Magnetostriction for Cubic Crystal

Let $\delta\vec{r}$ represent the spontaneous magnetostrictive distortion at position $\vec{r} = \sum_i^{x,y,z} r_i \vec{e}_i$ ($\vec{e}_i$: unit vector in the i -axis direction) and $\beta_i = r_i/r$. The saturation magnetostriction in the $\vec{r}$ direction is

$$\begin{aligned} \lambda_{\beta\alpha} &= \frac{\delta\vec{r}}{r} \cdot \frac{\vec{r}}{r} = \frac{\sum_{i,j}^{x,y,z} A_{ij}^0 r_j \vec{e}_i}{r} \cdot \frac{\sum_i^{x,y,z} r_i \vec{e}_i}{r} = \sum_{i,j}^{x,y,z} A_{ij}^0 \beta_i \beta_j \\ &= b_1 \left(\sum_i^{x,y,z} \alpha_i^2 \beta_i^2 - \frac{1}{3} \right) + 2b_2 (\alpha_x \alpha_y \beta_x \beta_y + \alpha_y \alpha_z \beta_y \beta_z + \alpha_z \alpha_x \beta_z \beta_x) + \dots = \lambda_{\alpha\beta}, \end{aligned} \quad (6.16)$$

$$b_1 = -\frac{a_1}{2C_2}, \quad b_2 = -\frac{a_2}{2C_3}. \quad (a_0 = 0) \quad (6.17)$$

$\lambda_{\beta\alpha}$ of both $\vec{r}$ and $\vec{M}$ are in the [100] and [111] directions are

$$\lambda_{100} = \frac{2b_1}{3}, \quad \lambda_{111} = \frac{2b_2}{3}. \quad (6.18)$$

Exploiting the relations of (6.17) and (6.18), (6.12) can be expressed by using the coefficients λ_{100} and λ_{111} instead of $\{a_i\}$ as

$$A_{ii}^0 = \frac{3}{2} \lambda_{100} (\alpha_i^2 - \frac{1}{3}) + \dots, \quad A_{ij}^0 = \frac{3}{2} \lambda_{111} \alpha_i \alpha_j + \dots \quad (6.19)$$

Exploiting the relations of (6.16), (6.18) can also be expressed by using the coefficients λ_{100} and λ_{111} as

$$\lambda_{\alpha\beta} = \frac{3}{2} \lambda_{100} \left(\sum_i^{x,y,z} \alpha_i^2 \beta_i^2 - \frac{1}{3} \right) + 3 \lambda_{111} (\alpha_x \alpha_y \beta_x \beta_y + \alpha_y \alpha_z \beta_y \beta_z + \alpha_z \alpha_x \beta_z \beta_x) + \dots \quad (6.20)$$

Here the value of the constant term is selected to make the spontaneous distortion zero at the ideal demagnetized state. Take Ni metal as an example. There are four easy axes of [111], $[1\bar{1}1]$, $[11\bar{1}]$, and $[\bar{1}11]$. Therefore, at the ideal demagnetized state, there are eight kinds of domain of $\vec{M}$ in the easy directions of $\alpha_x = \pm 1/\sqrt{3}$,

$\alpha_y = \pm 1/\sqrt{3}$ and $\alpha_z = \pm 1/\sqrt{3}$ with same volume. It can be easily proved that the average of $\lambda_{\alpha\beta}$ expressed by (6.20) along the eight easy directions is zero.

If the magnetostriction is isotropic, i.e., $\lambda_{100} = \lambda_{111} = \lambda_s$, (6.20) simplifies to

$$\lambda_{\alpha\beta} = \frac{3}{2}\lambda_s \left(\cos^2 \theta - \frac{1}{3} \right) + \dots, \quad (6.21)$$

where θ is the angle between the directions of $\vec{M}$ and magnetostriction measurement.

By averaging (6.20) we get the magnetostriction of isotropic polycrystal of saturation magnetization as

$$\lambda = \frac{3}{2}\lambda_s \left(\cos^2 \theta - \frac{1}{3} \right) + \dots, \quad (6.22)$$

$$\lambda_s \equiv \frac{2}{5}\lambda_{100} + \frac{3}{5}\lambda_{111}. \quad (6.23)$$

When θ is 0 and $\pi/2$, λ equals to λ_s and $-\lambda_s/2$, respectively. Therefore through the measurement of the difference of dimensions of the object along these two directions we can get the value of λ_s and do not need to demagnetize thermally before the measurement.

6.1.6 Phenomenological Expressions of Magnetostriction for Hexagonal Crystal

Take the a , b , and c axis (Fig. 3.11) as x , y , and z axis, respectively. By using the similar method used in the previous Sect. 6.1.5 for the cubic crystals we get

$$\begin{aligned} \lambda_{\alpha\beta} = & \lambda_1 \alpha_z^2 \beta_z^2 + \lambda_2 \left(\alpha_x^2 \beta_x^2 + \alpha_y^2 \beta_y^2 \right) + \lambda_3 \left(\alpha_x^2 \beta_y^2 + \alpha_y^2 \beta_x^2 \right) \\ & + 2(\lambda_2 - \lambda_1) \alpha_x \alpha_y \beta_x \beta_y + 2\lambda_4 \alpha_z \beta_z (\alpha_x \beta_x + \alpha_y \beta_y) + \dots, \end{aligned} \quad (6.24)$$

or

$$\begin{aligned} \lambda_{\alpha\beta} = & \lambda_A [(\alpha_x \beta_x + \alpha_y \beta_y)^2 - (\alpha_x \beta_x + \alpha_y \beta_y) \alpha_z \beta_z] \\ & + \lambda_B \left[(1 - \alpha_z^2) (1 - \beta_z^2) - (\alpha_x \beta_x + \alpha_y \beta_y)^2 \right] \\ & + \lambda_C \left[(1 - \alpha_z^2) \beta_z^2 - (\alpha_x \beta_x + \alpha_y \beta_y) \alpha_z \beta_z \right] \\ & + 4\lambda_D (\alpha_x \beta_x + \alpha_y \beta_y) \alpha_z \beta_z + \dots \end{aligned} \quad (6.25)$$

Table 6.1 Values of magnetostriction coefficients for Fe (20 °C), Ni (20 °C), and Co(0 °C)

Metal (structure)	$\lambda_{100}/10^{-6}$	$\lambda_{111}/10^{-6}$	$\lambda_A/10^{-6}$	$\lambda_B/10^{-6}$	$\lambda_C/10^{-6}$	$\lambda_D/10^{-6}$
Fe(bcc) [3]	20.7	−21.2				
Ni(fcc) [3]	−45.9	−24.3				
Co(hcp) [4]			−50	−107	126	−105

Table 6.1 shows the values of magnetostriction coefficients for Fe, Ni, and Co metals.

6.1.7 Origin of Magnetostriction

The exchange interaction, CEF interaction, pseudo magnetic moment interaction, etc depend on the distance between the atoms. When $\vec{M}$ direction varies, these energies are affected. The total energy can be reduced through appropriate distortion but with the cost of increase in the elastic energy. The spontaneous magnetostriction deformation makes the total energy minimum.

Note 1

The symmetry of cubic crystal makes $\partial\sigma_{ii}/\partial A_{ii}$ for $ii = xx, yy$, and zz the same:

$$C_{11} = C_{22} = C_{33}, \quad (6.26)$$

$\partial\sigma_{ii}/\partial A_{jj}$ ($j \neq i$) for all i and j the same:

$$C_{12} = C_{13} = C_{21} = C_{23} = C_{31} = C_{32}, \quad (6.27)$$

$\partial\sigma_{ii}/\partial A_{ij}$ ($j \neq i$) for all i and j the same:

$$C_{14} = C_{16} = C_{24} = C_{25} = C_{35} = C_{36}, \quad (6.28)$$

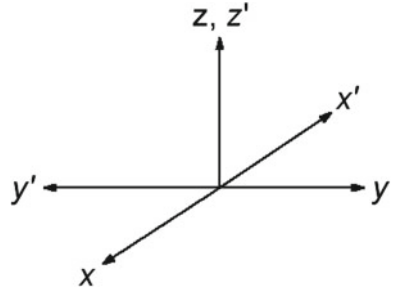
$\partial\sigma_{ii}/\partial A_{jk}$ ($j \neq k \neq i$) for different sequences of i, j and k the same:

$$C_{15} = C_{26} = C_{34}, \quad (6.29)$$

$\partial\sigma_{ij}/\partial A_{ii}$ and $\partial\sigma_{ij}/\partial A_{jj}$ ($j \neq i$) for all i and j the same:

$$C_{41} = C_{42} = C_{52} = C_{53} = C_{61} = C_{63}, \quad (6.30)$$

Fig. 6.4 xyz and $x'y'z'$ coordinate system



$\partial\sigma_{ij}/\partial A_{kk}$ ($k \neq i \neq j$) for different sequences of i, j and k the same:

$$C_{43} = C_{51} = C_{62}, \quad (6.31)$$

$\partial\sigma_{ij}/\partial A_{ij}$ ($j \neq i$) for $ij = xy, yz$ and zx the same:

$$C_{44} = C_{55} = C_{66}, \quad (6.32)$$

$\partial\sigma_{ij}/\partial A_{jk}$ ($k \neq i \neq j$) for $ij = xy, yz$ and zx the same:

$$C_{45} = C_{46} = C_{54} = C_{56} = C_{64} = C_{65}. \quad (6.33)$$

Thus the elastic module tensor in (6.4) can be expressed by the eight elements of $C_{11}, C_{12}, C_{14}, C_{15}, C_{41}, C_{43}, C_{44}$, and C_{45} as

$$\begin{pmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{31} & C_{32} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{41} & C_{42} & C_{43} & C_{44} & C_{45} & C_{46} \\ C_{51} & C_{52} & C_{53} & C_{54} & C_{55} & C_{56} \\ C_{61} & C_{62} & C_{63} & C_{64} & C_{65} & C_{66} \end{pmatrix} = \begin{pmatrix} C_{11} & C_{12} & C_{12} & C_{14} & C_{15} & C_{14} \\ C_{12} & C_{11} & C_{12} & C_{14} & C_{14} & C_{15} \\ C_{12} & C_{12} & C_{11} & C_{15} & C_{14} & C_{14} \\ C_{41} & C_{41} & C_{43} & C_{44} & C_{45} & C_{45} \\ C_{43} & C_{41} & C_{41} & C_{45} & C_{44} & C_{45} \\ C_{41} & C_{43} & C_{41} & C_{45} & C_{45} & C_{44} \end{pmatrix}. \quad (6.34)$$

By rotating the coordinate system about the $[001]$ axis by π , we get the coordinate system $x'y'z'$ (Fig. 6.4). The relations between the tensor stress and tensor strain elements $A_{i'j'}$ and $\sigma_{i'j'}$ ($i, j = x, y, z$) in the $x'y'z'$ coordinate with those of A_{ij} and σ_{ij} in the xyz coordinate are

$$\begin{aligned} A_{i'i'} &= A_{ii}, & \sigma_{i'i'} &= \sigma_{ii}, \\ A_{x'y'} &= A_{xy}, & \sigma_{x'y'} &= \sigma_{xy}, \\ A_{z'\alpha'} &= -A_{z\alpha}, & \sigma_{z'\alpha'} &= -\sigma_{z\alpha}, \quad (\alpha = x, y) \end{aligned} \quad (6.35)$$

while the elastic module tensor remains the same. Therefore the counterpart of (6.4) in the $x'y'z'$ coordinate system is

$$\begin{pmatrix} \sigma_{x'x'} \\ \sigma_{y'y'} \\ \sigma_{z'z'} \\ \sigma_{x'y'} \\ \sigma_{y'z'} \\ \sigma_{z'x'} \end{pmatrix} = \begin{pmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \sigma_{zz} \\ \sigma_{xy} \\ -\sigma_{yz} \\ -\sigma_{zx} \end{pmatrix} = \begin{pmatrix} C_{11} & C_{12} & C_{12} & C_{14} & C_{15} & C_{14} \\ C_{12} & C_{11} & C_{12} & C_{14} & C_{14} & C_{15} \\ C_{12} & C_{12} & C_{11} & C_{15} & C_{14} & C_{14} \\ C_{41} & C_{41} & C_{43} & C_{44} & C_{45} & C_{45} \\ C_{43} & C_{41} & C_{41} & C_{45} & C_{44} & C_{45} \\ C_{41} & C_{43} & C_{41} & C_{45} & C_{45} & C_{44} \end{pmatrix} \begin{pmatrix} A_{xx} \\ A_{yy} \\ A_{zz} \\ 2A_{xy} \\ -2A_{yz} \\ -2A_{zx} \end{pmatrix}. \quad (6.36)$$

Comparing (6.36) with (6.4) we get

$$C_{15} = C_{14} = C_{45} = C_{43} = C_{41} = 0. \quad (6.37)$$

Note 2

$$\begin{aligned} & \int_0^{A_{xx}} \sigma_{xx} dA_{xx} + \int_0^{A_{yy}} \sigma_{yy} dA_{yy} + \int_0^{A_{zz}} \sigma_{zz} dA_{zz} \\ &= \int_0^{A_{xx}} [C_{11}A_{xx} + C_{12}(0+0)] dA_{xx} + \int_0^{A_{yy}} [C_{11}A_{yy} + C_{12}(A_{xx}+0)] dA_{yy} \\ & \quad + \int_0^{A_{zz}} [C_{11}A_{zz} + C_{12}(A_{xx}+A_{yy})] dA_{zz} \\ &= \frac{C_{11}}{2} \sum_i^{x,y,z} A_{ii}^2 + C_{12}(A_{xx}A_{yy} + A_{yy}A_{zz} + A_{zz}A_{xx}) \\ &= \frac{C_{12}}{2} \left(\sum_i^{x,y,z} A_{ii} \right)^2 + \frac{C_{11}-C_{12}}{2} \sum_i^{x,y,z} A_{ii}^2. \end{aligned} \quad (6.38)$$

$$\begin{aligned} \sum_{ij}^{xy,yz,zx} \int_0^{A_{ij}} \sigma_{ij} (2dA_{ij}) &= \sum_{ij}^{xy,yz,zx} \int_0^{A_{ij}} 2C_{44}A_{ij} (2dA_{ij}) = 2C_{44} \sum_{ij}^{xy,yz,zx} A_{ij}^2 \\ &= 2C_3 \sum_{ij}^{xy,yz,zx} A_{ij}^2. \end{aligned} \quad (6.39)$$

Note 3

$$F_{ms}(\alpha, A) = \sum_i^{x,y,z} U_i(\alpha) A_{ii} + \sum_{ij}^{xy,yz,zx} V_{ij}(\alpha) A_{ij}. \quad (6.40)$$

Expand $U_i(\alpha)$ and $V_{ij}(\alpha)$ into the power series of α_i satisfying the symmetry of cubic crystal as below.

① $U_i(\alpha)$

Analyze the $U_z(\alpha_x, \alpha_y, \alpha_z)A_{zz}$ term. If $\vec{M}$ direction is reversed, the signs of all α_i change but A_{zz} remains unchanged. Since the energy remains unchanged, it holds

$$U_z(\alpha_x, \alpha_y, \alpha_z) = U_z(-\alpha_x, -\alpha_y, -\alpha_z) = U_z(\alpha_x^2, \alpha_y^2, \alpha_z^2). \quad (6.41)$$

The transposition between α_x and α_y does not affect the energy, so

$$U_z(\alpha_x^2, \alpha_y^2, \alpha_z^2) = U_z(\alpha_y^2, \alpha_x^2, \alpha_z^2) = U_z(s, \alpha_z^2), \quad (6.42)$$

thus we get

$$U_i(\alpha) = U_i(s, \alpha_i^2). \quad (i = x, y, z) \quad (6.43)$$

Expanding it into the power series of α_i^2 and s we get corresponding terms in the right of (6.8).

② $V_{ij}(\alpha)$

Analyze the $V_{xy}(\alpha_x, \alpha_y, \alpha_z)A_{xy}$ term. The reflection on the (100) plane does not change α_y and α_z , but changes the signs of A_{xy} and α_x . The reflection on the (010) plane does not change α_x and α_z , but changes the signs of A_{xy} and α_y . The above reflection operations do not change energy. Therefore, it holds

$$V_{xy}(\alpha_x, \alpha_y, \alpha_z)A_{xy} = V_{xy}(-\alpha_x, \alpha_y, \alpha_z)(-A_{xy}) = V_{xy}(\alpha_x, -\alpha_y, \alpha_z)(-A_{xy}). \quad (6.44)$$

The expression of $V_{ij}(\alpha)A_{ij}$ which satisfies the above condition is

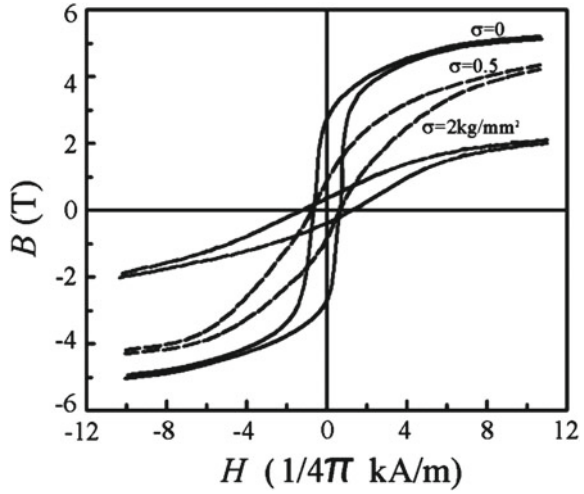
$$V_{ij}(\alpha_x, \alpha_y, \alpha_z)A_{ij} = 2a_2\alpha_i\alpha_jA_{ij} + \dots \quad (6.45)$$

6.2 Stress Energy

Figure 6.5 demonstrates the hysteresis loops of Ni metal under different tensile forces. The loops are measured in the tensile stress direction. It demonstrates that stress affects magnetization process. The effect is apparent for soft magnetic materials. The crystal structures of soft magnetic materials being cubic or amorphous, the stress-related energies for cubic crystals and isotropic magnetic materials will be analyzed below.

Analyze the effect of stress tensor (σ) on the thermal potential of a magnetic crystal. Let (A^σ) denote the strain tensor induced by the stress. The total strain tensor is $(A) = (A^0 + A^\sigma)$, and the thermal potential is

Fig. 6.5 Effect of tensile stress on the hysteresis loop of Ni metal [1]



$$\begin{aligned}
 G(\alpha, A) &= F_K(\alpha, A) - \sum_i^{x,y,z} \sigma_{ii} A_{ii} - \sum_{ij}^{xy,yz,zx} 2\sigma_{ij} A_{ij} \quad ((1.90)) \\
 &= F_K^0(\alpha) + F_{ms}(\alpha, A^0) + F_{ms}(\alpha, A^\sigma) + F_{el}(A^0 + A^\sigma) \\
 &\quad - \sum_i^{x,y,z} \sigma_{ii} (A_{ii}^0 + A_{ii}^\sigma) - \sum_{ij}^{xy,yz,zx} 2\sigma_{ij} (A_{ij}^0 + A_{ij}^\sigma) \quad ((6.10), (6.8)) \\
 &= F_K(\alpha) + F_{ms}(\alpha, A^\sigma) + F_{el}(A^0 + A^\sigma) - F_{el}(A^0) \quad ((6.13)) \\
 &\quad - \sum_i^{x,y,z} \sigma_{ii} (A_{ii}^0 + A_{ii}^\sigma) - \sum_{ij}^{xy,yz,zx} 2\sigma_{ij} (A_{ij}^0 + A_{ij}^\sigma), \quad (6.46)
 \end{aligned}$$

$$\begin{aligned}
 F_{ms}(\alpha, A^\sigma) &= \sum_{ij}^{xx,yy,zz,xy,yz,zx} \frac{\partial F_{ms}(\alpha, A)}{\partial A_{ij}} A_{ij}^\sigma = \sum_{ij}^{xx,yy,zz,xy,yz,zx} \frac{\partial F_{ms}(\alpha, A)}{\partial A_{ij}} \Big|_{A^0} A_{ij}^\sigma, \\
 &\quad (6.47)
 \end{aligned}$$

$$\begin{aligned}
 F_{el}(A^0 + A^\sigma) - F_{el}(A^0) &= \sum_{ij}^{xx,yy,zz,xy,yz,zx} \frac{\partial F_{el}(A)}{\partial A_{ij}} \Big|_{A^0} A_{ij}^\sigma
 \end{aligned}$$

$$\begin{aligned}
& xx, yy, zz, \\
& + \frac{1}{2} \sum_{ij,kl}^{xy, yz, zx} \frac{\partial^2 F_{\text{el}}(A)}{\partial A_{ij} \partial A_{kl}} \Big|_{A^0} A_{ij}^{\sigma} A_{kl}^{\sigma} \\
& = \sum_{ij}^{xx, yy, zz, xy, yz, zx} \frac{\partial F_{\text{el}}(A)}{\partial A_{ij}} \Big|_{A^0} A_{ij}^{\sigma} \\
& + F_{\text{el}}(A^{\sigma}), \quad (\text{Note 1 of this section}) \quad (6.48)
\end{aligned}$$

$$\frac{\partial F_{\text{ms}}(\alpha, A)}{\partial A_{ij}} \Big|_{A^0} + \frac{\partial F_{\text{el}}(A)}{\partial A_{ij}} \Big|_{A^0} = 0. \quad (6.49)$$

Inserting (6.47)–(6.49) into the last expression of (6.46), we get

$$G(\alpha, A) = F_K(\alpha) + F_{\text{el}}(A^{\sigma}) - \sum_i^{x,y,z} \sigma_{ii} \left(A_{ii}^0 + A_{ii}^{\sigma} \right) - \sum_{ij}^{xy,yz,zx} 2\sigma_{ij} \left(A_{ij}^0 + A_{ij}^{\sigma} \right). \quad (6.50)$$

At the equilibrium strain state, the derivatives of the thermal potential with respect $\{A_{ij}^{\sigma}\}$ are zero:

$$\frac{\partial G(\alpha, A)}{\partial A_{ii}^{\sigma}} = \frac{\partial F_{\text{el}}(A^{\sigma})}{\partial A_{ii}^{\sigma}} - \sigma_{ii} = 0, \quad (i = x, y, z) \quad (6.51)$$

$$\frac{\partial G(\alpha, A)}{\partial A_{ij}^{\sigma}} = \frac{\partial F_{\text{el}}(A^{\sigma})}{\partial A_{ij}^{\sigma}} - 2\sigma_{ij} = 0. \quad (ij = xy, yz, zx) \quad (6.52)$$

Equations (6.51) and (6.52) show that $\{A_{ij}^{\sigma}\} (ij = xx, yy, zz, xy, yz, zx)$ are functions of applied stress and are irrelevant to α . Terms irrelevant to α being neglected (6.50) simplifies to

$$G(\alpha, A^0 + A^{\sigma}) = F_K(\alpha) + F_{\sigma}(\alpha, \sigma), \quad (6.53)$$

in which

$$F_{\sigma} = - \sum_i^{x,y,z} \sigma_{ii} A_{ii}^0 - \sum_{ij}^{xy,yz,zx} 2\sigma_{ij} A_{ij}^0 \quad (6.54)$$

is called stress energy.

If a tensile stress σ is applied in the direction of direction cosines $\{\gamma_i\} (i=x, y, z)$, the stress tensor elements are

$$\sigma_{ij} = \sigma \gamma_i \gamma_j. \quad (\text{Note 2 of this section}) \quad (6.55)$$

Inserting (6.55) and (6.19) into (6.54) we get the stress energy as

$$F_\sigma(\alpha, \sigma) = -\frac{3}{2} \lambda_{100} \sigma \sum_i^{x,y,z} \alpha_i^2 \gamma_i^2 - 3 \lambda_{111} \sigma \sum_{ij}^{xy,yz,zx} \alpha_i \alpha_j \gamma_i \gamma_j. \quad (6.56)$$

Let θ denote the angle between the directions of $\vec{M}$ and tensile stress. If the direction of $\vec{M}$ or stress is parallel to the [100] axis, (6.56) becomes

$$F_\sigma = -\frac{3}{2} \lambda_{100} \sigma \cos^2 \theta. \quad (6.57)$$

If the direction of $\vec{M}$ or tensile stress is parallel to the [111] axis, (6.56) becomes

$$F_\sigma = -\frac{3}{2} \lambda_{111} \sigma \cos^2 \theta. \quad (6.58)$$

If $\lambda_{100} = \lambda_{111} = \lambda_s$, (6.56) simplifies to

$$F_\sigma = -\frac{3}{2} \lambda_s \sigma \cos^2 \theta. \quad (6.59)$$

The stress energy for an isotropic polycrystal of saturation magnetization is also

$$F_\sigma = -\frac{3}{2} \lambda_s \sigma \cos^2 \theta. \quad \left(\lambda_s \equiv \frac{2}{5} \lambda_{100} + \frac{3}{5} \lambda_{111} \right) \quad (6.60)$$

Note 1

If $\varphi(x_1, x_2, \dots, x_l)$ is a differentiable and homogeneous function of degree n , that is

$$\varphi(kx_1, kx_2, \dots, kx_l) = k^n \varphi(x_1, x_2, \dots, x_l) \quad (6.61)$$

for arbitrary k ,

$$\begin{aligned} \frac{\partial}{\partial k} \varphi(kx_1, kx_2, \dots, kx_l) &= \sum_i x_i \frac{\partial}{\partial(kx_i)} \varphi(kx_1, kx_2, \dots, kx_l) \\ &= nk^{n-1} \varphi(x_1, x_2, \dots, x_l). \end{aligned} \quad (6.62)$$

By taking $k = 1$ we get

$$\sum_i^{1,2,\dots,l} \frac{\partial \varphi}{\partial x_i} x_i = n \varphi. \quad (6.63)$$

Exploiting this relation we get

$$\begin{aligned} \sum_j \frac{\partial}{\partial x_j} \left(\sum_i \frac{\partial \varphi}{\partial x_i} x_i \right) x_j &= \sum_j n \frac{\partial \varphi}{\partial x_j} x_j = n^2 \varphi \\ &= \sum_{i,j} \frac{\partial^2 \varphi}{\partial x_i \partial x_j} x_i x_j + \sum_j \frac{\partial \varphi}{\partial x_j} x_j = \sum_{i,j} \frac{\partial^2 \varphi}{\partial x_i \partial x_j} x_i x_j + n \varphi, \end{aligned} \quad (6.64)$$

so

$$\sum_{i,j} \frac{\partial^2 \varphi}{\partial x_i \partial x_j} x_i x_j = n(n-1) \varphi. \quad (6.65)$$

Applying (6.65) on the homogeneous function F_{el} of $n = 2$, we get

$$\begin{array}{cc} xx, yy, zz, & xx, yy, zz, \\ xy, yz, zx & xy, yz, zx \\ \sum_{i,j,kl} \frac{\partial^2 F_{\text{el}}(A)}{\partial A_{ij} \partial A_{kl}} A_{ij}^{\sigma} A_{kl}^{\sigma} = & \sum_{i,j,kl} \frac{\partial^2 F_{\text{el}}(A^{\sigma})}{\partial A_{ij}^{\sigma} \partial A_{kl}^{\sigma}} A_{ij}^{\sigma} A_{kl}^{\sigma} = 2 F_{\text{el}}(A^{\sigma}). \end{array} \quad (6.66)$$

Note 2

Consider a column of equal cross-section area S . A tensile stress σ per unit area of S is acting in the column axis direction. Let S' denote the section area parallel to the (100) plane, $S = \gamma_x S'$. So the tensile stress per unit area of section S' is $\sigma \gamma_x$. The project of this stress in the [010] direction, that is σ_{yx} equals to $\sigma \gamma_x \gamma_y$. In the same way arbitrary σ_{ij} is expressed by (6.55).

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Chapter 7

Magnetic Domain

Weiss (1907) proposed the hypothesis of magnetic domain, Bitter (1931) first observed the domain patterns, and Landau and Lifshitz (1935) founded the theory of the domain. The theory assumes that a magnetic body constitutes of magnetic domains and magnetic walls. In each domain it is spontaneously magnetized to saturation, and inhomogeneous magnetization is restricted only in the domain walls.

At equilibrium state at constant temperature an isolated magnetic body should have a minimum free energy (Sect. 1.4.3). When it is magnetized to saturation along any easy axis, both exchange energy and magnetic anisotropy energy are the smallest. But there appears magnetic charges of same sign on one side surface and those of opposite sign on the other side surface of the body, which produces a large demagnetizing field and hence a large magnetostatic energy. Under the action of the demagnetizing field, the magnetizations of some part of the body reverse to different easy directions forming magnetic domains to decrease the magnetostatic energy.

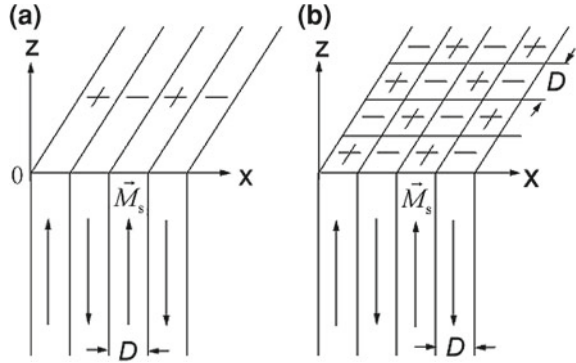
This chapter contains the sections of Magnetostatic energies of strip and chessboard domain structures; Magnetic domain wall; and Magnetic domain structure.

7.1 Magnetostatic Energies of Strip and Chessboard Domain Structures

Consider an infinite magnetic object of uniaxial anisotropy occupying the half space of $z \leq 0$. The easy axis is parallel to the z -axis and the strip domains of infinite dimensions in the yz plane and width D along the x -axis are magnetized parallel and antiparallel to the z -axis alternately (Fig. 7.1a). The surface magnetic charge density distribution is

$$\sigma_m(x) = \begin{cases} J_s, & [2lD < x < (2l+1)D, l : 0 \text{ or integer}] \\ -J_s, & [(2l+1)D < x < 2(l+1)D] \end{cases} \quad ((1.39)) \quad (7.1)$$

Fig. 7.1 $\vec{M}_s$ and magnetic charge distributions in the magnetic object occupying half space of $z \leq 0$. (a) Strip domains; (b) chessboard domains



The magnetic potential V_m is the function of x and z and satisfies the Laplace equation

$$\frac{\partial^2 V_m(x, z)}{\partial x^2} + \frac{\partial^2 V_m(x, z)}{\partial z^2} \equiv V_m^{xx}(x, z) + V_m^{zz}(x, z) = 0 \quad (z \neq 0) \quad (7.2)$$

under the boundary conditions of

$$\begin{aligned} \frac{\partial V_m(x, +0)}{\partial z} - \frac{\partial V_m(x, -0)}{\partial z} &\equiv V_m^z(x, +0) - V_m^z(x, -0) \\ &= -\frac{\sigma_m(x)}{\mu_0}, \quad ((1.32), (1.34)) \\ V_m(x, z \rightarrow \pm\infty) &= 0. \end{aligned} \quad (7.3)$$

The magnetic field being symmetrical with respect to the reflection on the $z = 0$ plane the first relation of (7.3) simplifies to

$$V_m^z(x, +0) = -V_m^z(x, -0) = -\frac{\sigma_m(x)}{2\mu_0}. \quad (7.4)$$

$V_m(x, z)$ is a periodic function of x with period $2D$ and is symmetrical with respect to the reflection on the $x = D(1/2 + l)$ plane. Therefore, its Fourier expansion with respect x is

$$V_m(x, z) = \sum_{n=1,3,5,\dots} C_n f_n(z) \sin \frac{n\pi x}{D}. \quad (7.5)$$

Inserting (7.5) into (7.2) and by taking into account that $V_m(x, z \rightarrow \pm\infty) = 0$, we get

$$f_n(z > 0) = \exp \frac{-n\pi z}{D}, \quad f_n(z < 0) = \exp \frac{n\pi z}{D}. \quad (7.6)$$

Inserting (7.1), (7.5), and (7.6) into (7.4), we get

$$-2\frac{\pi}{D} \sum_n^{1,3,5,\dots} n C_n \sin \frac{n\pi x}{D} = \begin{cases} -M_s, & [2lD < x < (2l+1)D] \\ M_s, & [(2l+1)D < x < 2(l+1)D] \end{cases} \quad (7.7)$$

Multiply (7.7) by $\sin(n\pi x/D)$ and then integrate from $x = 0$ to $2D$,

$$-2\frac{\pi}{D} n C_n \int_0^{2D} \sin^2 \frac{n\pi x}{D} dx = -M_s \left(\int_0^D \sin \frac{n\pi x}{D} dx - \int_D^{2D} \sin \frac{n\pi x}{D} dx \right), \quad (7.8)$$

from which we get

$$C_n = \frac{2M_s D}{\pi^2 n^2}. \quad (7.9)$$

Inserting (7.9), (7.6) into (7.5) we get

$$V_m(x, 0) = \frac{2M_s D}{\pi^2} \sum_n^{1,3,5,\dots} \frac{1}{n^2} \sin \frac{n\pi x}{D} \quad (7.10)$$

and the magnetostatic energy density per unit surface area

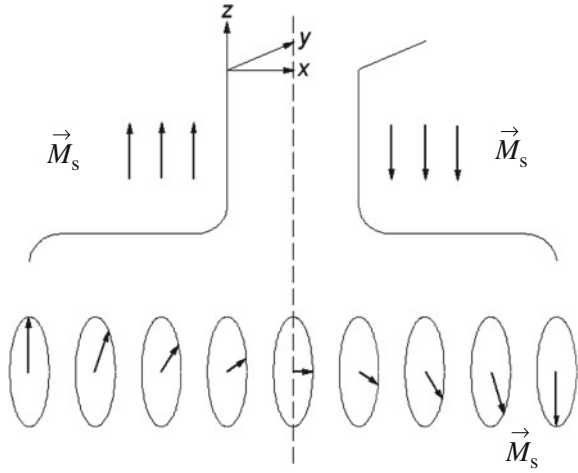
$$\begin{aligned} F_d &= \frac{1}{D} \int_0^D \frac{1}{2} \sigma_m V_m(x, 0) dx = \frac{2\mu_0 M_s^2 D}{\pi^3} \sum_n^{1,3,5,\dots} \frac{1}{n^3} = 1.052 \frac{2\mu_0 M_s^2 D}{\pi^3} \\ &= 0.852 \times 10^{-7} M_s^2 D. \end{aligned} \quad (7.11)$$

By using the same method, we get the magnetostatic energy surface density for the chessboard domain systems (Fig. 7.1b) as

$$F_d = 0.53 \times 10^{-7} M_s^2 D, \quad (7.12)$$

which is also proportional to $M_s^2 D$ but the proportional coefficient is apparently smaller than that of (7.11) for the strip domain system (Fig. 7.1a).

Equations (7.11) and (7.12) show that the formation of the domains transforms the uniform magnetic charge distribution on the $z = 0$ surface to alternately changing sign magnetic charge distribution. The denser the alteration of the sign of magnetic charge the smaller the magnetostatic energy. The formation of domains, however, accompanies the creation of domain walls and hence domain wall energy which is proportional to the domain wall area.

Fig. 7.2 180° Bloch wall

7.2 Magnetic Domain Wall

7.2.1 Bloch Wall

Consider an infinite plane domain wall. The normal of the wall is along the x -axis. With shift from one domain to the neighboring domain $\vec{M}_s$ rotates gradually from the $\vec{M}_s$ direction in the first domain to that in the neighboring domain (Fig. 7.2). Under the condition of no appearance of magnetic charge to make the magnetostatic energy zero, the $\vec{M}_s$ distribution in the domain wall should satisfy that the component of it normal to the wall remains unchanged at any position x . The domain wall which satisfies this condition is called Bloch wall. A domain wall in a bulk magnetic object is considered Bloch wall.

7.2.2 General Expressions of the Structure and Energy of Bloch Wall

Consider a domain wall centered at the origin of x coordinate and $\vec{M}_s(x)$ is within the wall plane. Let $\theta(x)$ denote the angle between $\vec{M}_s(x)$ and $\vec{M}_s(-\infty)$, and $g[\theta(x)]$ the anisotropy energy density with respect to that within the domains. The domain wall energy density per unit wall area γ_w is the sum of the exchange and anisotropy energies:

$$\gamma_w = \int_{-\infty}^{\infty} \left\{ A \left[\frac{d\theta(x)}{dx} \right]^2 + g[\theta(x)] \right\} dx. \quad (4.113) \quad (7.13)$$

At the equilibrium state, the variation of the energy with respect $\theta(x)$ should be zero:

$$\delta\gamma_w = \int_{-\infty}^{\infty} \delta \left[A \left(\frac{d\theta}{dx} \right)^2 + g(\theta) \right] dx = 0 \quad (7.14)$$

under the boundary conditions of

$$g[\theta(\pm\infty)] = \frac{d\theta(\pm\infty)}{dx} = 0. \quad (7.15)$$

Inserting the relations of

$$\begin{aligned} \int_{-\infty}^{\infty} \delta \left[A \left(\frac{d\theta}{dx} \right)^2 \right] dx &= 2A \int_{-\infty}^{\infty} \frac{d\theta}{dx} \delta \left(\frac{d\theta}{dx} \right) dx = 2A \int_{-\infty}^{\infty} \frac{d\theta}{dx} \frac{d}{dx} (\delta\theta) dx \\ &= 2A \left[\frac{d\theta}{dx} \delta\theta \right]_{-\infty}^{\infty} - 2A \int_{-\infty}^{\infty} \frac{d^2\theta}{dx^2} \delta\theta dx = -2A \int_{-\infty}^{\infty} \frac{d^2\theta}{dx^2} \delta\theta dx, \end{aligned} \quad (7.16)$$

$$\int_{-\infty}^{\infty} \delta g(\theta) dx = \int_{-\infty}^{\infty} \frac{dg(\theta)}{d\theta} \delta\theta dx \quad (7.17)$$

into (7.14), we get

$$\delta\gamma_w = \int_{-\infty}^{\infty} \left[-2A \frac{d^2\theta}{dx^2} + \frac{dg(\theta)}{d\theta} \right] \delta\theta dx = 0. \quad (7.18)$$

$\delta\theta$ is arbitrary, and hence the integrand should be zero, that is the Euler equation

$$-2A \frac{d^2\theta}{dx^2} + \frac{dg(\theta)}{d\theta} = 0 \quad (7.19)$$

holds. Multiply (7.19) with $d\theta/dx$ and integrate from $x = -\infty$ to x . Under the boundary conditions of (7.15) we get

$$A \left[\frac{d\theta(x)}{dx} \right]^2 = g[\theta(x)], \quad (7.20)$$

that is, the exchange energy density equals to the anisotropy energy density at arbitrary position. From (7.20) we get the following general formula for the Bloch wall

structure:

$$x = \int_{\theta(0)}^{\theta(x)} \sqrt{\frac{A}{g(\theta)}} d\theta. \quad (7.21)$$

Inserting (7.20) into (7.13) we get general formula for the Bloch wall energy density as

$$\gamma_w = 2\sqrt{A} \int_{\theta(-\infty)}^{\theta(\infty)} \sqrt{g(\theta)} d\theta. \quad (7.22)$$

Some typical Bloch wall structures and domain wall energies will be analyzed below on the basis of (7.21) and (7.22). Suppose $K_{i>1} = 0$.

7.2.3 180° Wall of Easy Axis Crystal

$$\theta(-\infty) = \frac{d\theta(\pm\infty)}{dx} = 0, \quad \theta(0) = \frac{\pi}{2}, \quad \theta(\infty) = \pi, \quad (7.23)$$

$$g(\theta) = K_1 \sin^2 \theta, \quad (7.24)$$

$$x(\theta) = \sqrt{\frac{A}{K_1}} \ln \operatorname{tg} \frac{\theta}{2}. \quad \left(\int \frac{d\theta}{\sin \theta} = \ln \operatorname{tg} \frac{\theta}{2} + \text{const.} \right) \quad (7.25)$$

The curve in Fig.7.3 shows the domain wall structure. It can be seen that there is no clear-cut boundary between the wall and the domain. Defining the domain wall thickness δ_w by the x coordinate difference $x_+ - x_-$ of the intersections of the tangent of the $\theta(x)$ curve at the origin with the straight lines of $\theta = \pi$ and 0 we get

$$\delta_w = \pi \delta_0, \quad (7.26)$$

where

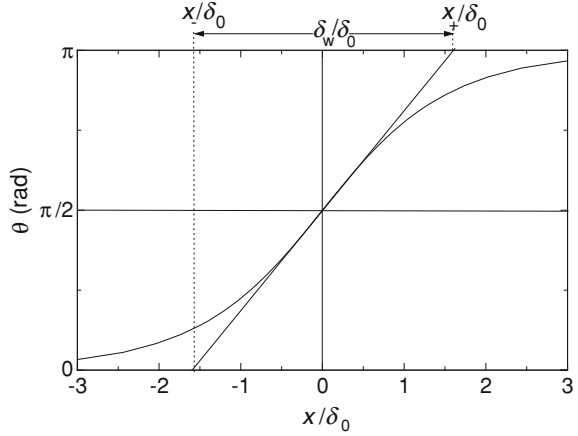
$$\delta_0 \equiv \sqrt{\frac{A}{K_1}} \quad (7.27)$$

is called exchange length. Inserting (7.24) into (7.22) and integrating the latter we get

$$\gamma_w = 4\gamma_0, \quad (7.28)$$

$$\gamma_0 \equiv \sqrt{AK_1}. \quad (7.29)$$

Fig. 7.3 Domain wall structure of 180° wall for easy axis crystal



7.2.4 90° Wall of Cubic Crystal

Take the wall parallel to the (100) plane in the crystal of easy axes along the $\langle 100 \rangle$ axes as an example.

$$\theta(-\infty) = \frac{d\theta(\pm\infty)}{dx} = 0, \quad \theta(0) = \frac{\pi}{4}, \quad \theta(\infty) = \frac{\pi}{2}, \quad (7.30)$$

$$g(\theta) = K_1 \sin^2 \theta \cos^2 \theta, \quad (7.31)$$

$$x(\theta) = \sqrt{\frac{A}{K_1}} \int_{\theta(0)}^{\theta(x)} \frac{d\theta}{\sin \theta \cos \theta} = \sqrt{\frac{A}{K_1}} \ln \operatorname{tg} \theta. \quad (7.32)$$

Defining the wall thickness by the difference of the x coordinates of the intersections of the tangent of the $\theta(x)$ curve at the origin with the straight lines of $\theta = \pi/2$ and 0 as in the above Sect. 7.2.3 we get

$$\delta_w = \pi \delta_0, \quad (7.33)$$

$$\gamma_w = \gamma_0. \quad (7.34)$$

7.2.5 180° Wall of Cubic Crystal Under Stress

Suppose a tensile or compressive stress σ is applied in the direction of $\theta = 0$ in the above Sect. 7.2.4 and $\lambda_{100} = \lambda_{111} = \lambda_s$.

$$g(\theta) = \begin{cases} K_1 \sin^2 \theta \cos^2 \theta - \frac{3}{2} \lambda_s \sigma (\cos^2 \theta - 1), & (\lambda_s \sigma > 0) \\ K_1 \sin^2 \theta \cos^2 \theta - \frac{3}{2} \lambda_s \sigma (\cos^2 \theta - 0), & (\lambda_s \sigma < 0) \end{cases} \quad ((6.59)) \quad (7.35)$$

Table 7.1 The values of δ_w and γ_w for some magnetic materials

Material	δ_w/nm	$\gamma_w/(10^{-3} \text{ J/m}^2)$
Ni	90 ~ 210	0.06 ~ 0.3
Fe	40 ~ 140	0.7 ~ 2
Co	~16	~8
Nd ₂ Fe ₁₄ B	4.2	~30
SmCo ₅	~5	~90

The domain wall energy density is

$$\begin{aligned}
 \gamma_w &= \begin{cases} 2\sqrt{A} \int_0^\pi \sqrt{K_1 \sin^2 \theta \cos^2 \theta + \frac{3}{2} \lambda_s \sigma \sin^2 \theta} d\theta, & (\lambda_s \sigma > 0) \\ 2\sqrt{A} \int_{-\pi/2}^{\pi/2} \sqrt{K_1 \sin^2 \theta \cos^2 \theta - \frac{3}{2} \lambda_s \sigma \cos^2 \theta} d\theta & (\lambda_s \sigma < 0) \end{cases} \\
 &= 2\sqrt{A} \int_0^\pi \sqrt{K_1 \cos^2 \theta + \frac{3}{2} |\lambda_s \sigma| \sin \theta} d\theta. \quad (\text{arbitrary sign of } \lambda_s \sigma < 0) \quad (7.36)
 \end{aligned}$$

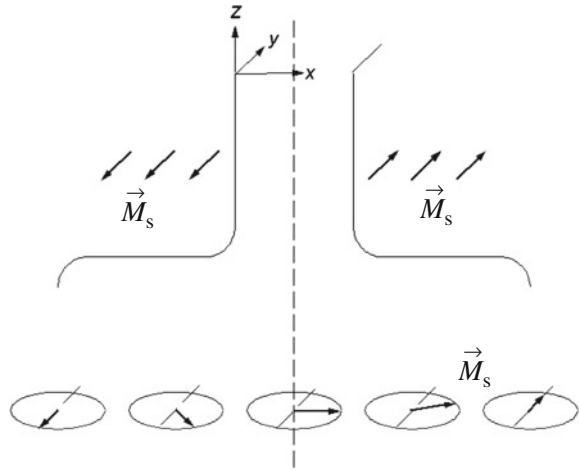
7.2.6 Typical Values of δ_w and γ_w

Table 7.1 shows the values of δ_w and γ_w for some magnetic materials.

The dimension of real domain wall is finite, but the above results for infinite wall holds if the dimension is much larger than δ_w .

7.2.7 Néel Wall

In general, the easy plane shape anisotropy of thin films with the demagnetizing factors of $N_\perp \approx 0$ and $N_z \approx 1$ ((5.72) and (5.69)) being very large, the easy axis of the film is in the film plane. The dimension of a Bloch wall normal to the film plane is the film thickness. The surface magnetic charges appear on the belts of intersections of the wall with the film surfaces. Thus the domain wall energy also contains magnetostatic energy. The proportion of the magnetostatic energy increases with decrease of the film thickness. When the thickness decreases to around the wall width, the energy of the domain wall in which the magnetic vector rotates within the film plane with shift of position x (Fig. 7.4) becomes smaller than that of the Bloch wall, and hence the former replaces the latter. This kind of domain wall is called Néel wall. In the transition film thicknesses criss-cross wall is formed (Fig. 7.5a). In this structure the Bloch wall and Néel wall are alternately arranged along the principal domain wall line along with pairs of arms on the two sides of the Bloch

Fig. 7.4 Néel wall

wall. This structure is advantageous to reduce magnetic charges thus decreasing the magnetostatic energy (Fig. 7.5b).

7.3 Magnetic Domain Structure

Innumerable domain structures have been observed so far. The domain structure is very multifarious and in many cases is very complicated. The structure depends not only on the intrinsic magnetic properties such as spontaneous magnetization, magnetic anisotropy, magnetostriction etc, but also sensibly depends on the shape and dimension of the body and microstructures such as grain size and their distribution, defects, internal stresses, impurities, etc.

7.3.1 Methods of Domain Observation

There are many methods of observation. Some typical methods will be introduced briefly.

7.3.1.1 Magnetic Powder Method (Bitter Pattern Method)

This is the method used by Bitter in the earliest days and is still used widely nowadays. A drop of a water-based colloidal suspension of Fe_3O_4 is placed on the specimen surface. The stray magnetic fields along the domain wall lines produced by the magnetic surface charge on the end of domain walls on the surface attract the magnetic particles and form patterns outlining the underlying domains. The size of the particle d should be appropriate (~ 10 nm). If it is too small, the assembly of the particles onto

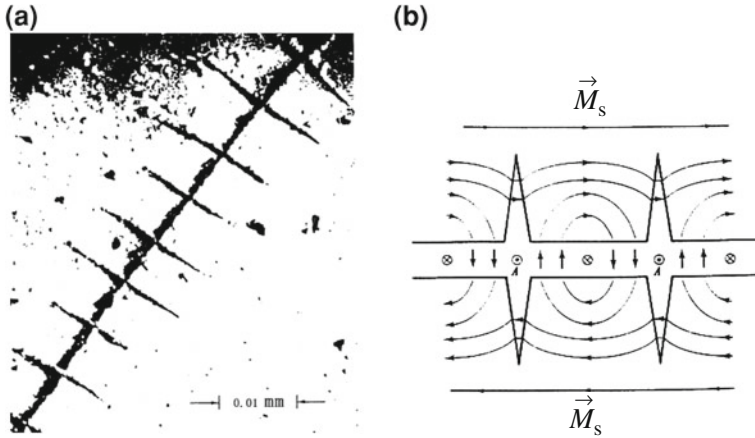


Fig. 7.5 Criss-cross wall in 30 nm thick Fe-80%Ni film (a) and its magnetic structure (b) [1]

the lines is not distinct (the distribution density of the particle $\propto \exp(p_J H / k_B T)$, where $p_J \propto d^3$ is the magnetic polarization moment of the particle and H is the stray field). If it is too large, the particles conglomerate themselves (probability of two particles to get together $\propto \exp\{[3(\vec{p}_{J1} \cdot \vec{r})(\vec{p}_{J2} \cdot \vec{r})/r^5 - \vec{p}_{J1} \cdot \vec{p}_{J2}/r^3]/4\pi\mu_0 k_B T\} \propto \exp(d^3)$ ((5.22), $r \approx d$).

The resulting Bitter pattern is usually viewed with a metallographic microscope of magnification $100 \sim 1000$. Figure 7.5a is the domain wall structure observed by the powder method. Sometimes domains are observed with a scanning electron microscope after the colloid is dried (colloid-SEM method).

7.3.1.2 Faraday Effect Method

An incident natural light passes through a polarizer, a thin transparent specimen and analyzer successively, and reaches the ocular piece of microscope (Fig. 7.6). The light that went through the polarizer is linearly polarized. The plane of polarization is rotated about light propagation direction after transmitting a domain of the specimen. The rotation angle is proportional to the component of the $\vec{M}_s$ in the propagation direction and the thickness of the specimen, and the rotation direction depends on the sign of the component. The analyzer is rotated to an angle to make the images of one kind of domains completely dark (the transmission axis of the analyzer is set normal to the polarization plane of the light). The domains can then be distinguished from differences of the brightness.

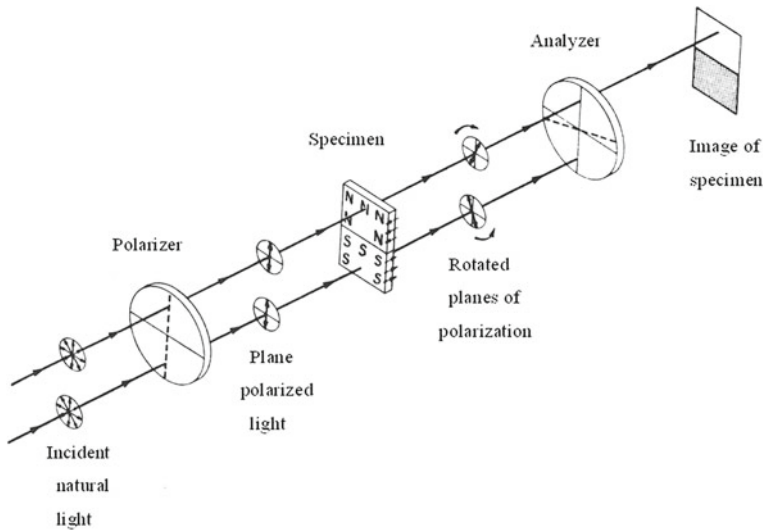


Fig. 7.6 Faraday effect method of domain observation [2]

7.3.1.3 Kerr Effect Method

The principle of Kerr effect method is similar to that of Faraday effect method. The difference is that the polarized light is reflected from the specimen surface.

The domains observed by the powder method and Kerr effect are those of specimen surface, and the domains observed by the Faraday effect are those within the specimen.

The Kerr and Faraday effect methods can observe the dynamic variation of domain structure during a magnetization process.

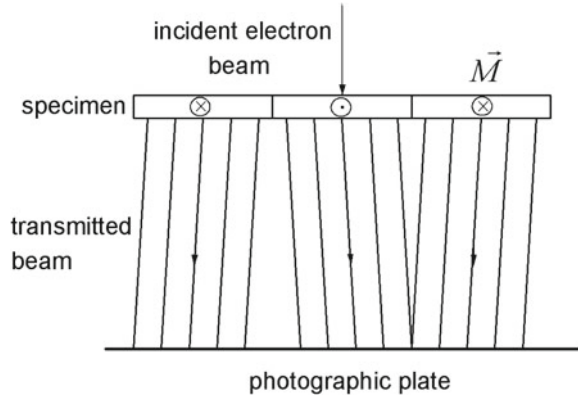
7.3.1.4 Magnetic Force Microscopy Method

The principle of Magnetic Force Microscopy (MFM) is similar to that of the powder method, but the method is different. A very small magnetized cantilever tip (dozens nm) scans over the specimen at a constant height (~ 10 nm) and records the distribution of the force felt by the tip in the stray field. Typical resolution of ~ 30 nm is reached which is an order higher than that of Kerr effect method.

7.3.1.5 Transmission Electron Microscopy (Lorentz microscope) Method

The electron beam deflects under the action of Lorentz force (1.1) during transmission through an ultra thin specimen. The deflection direction is different for the beams

Fig. 7.7 Lorentz microscope for domain observation



transmitting different domains, thus making the brightness of domain wall image darker or brighter than that of domains (Fig. 7.7). Resolution of this method can reach <10 nm.

7.3.2 Analyses of Domain Structures of Easy Axis Crystal Plate

Take a $h = 1$ mm thick Co plate c -axis which is normal to the plate as an example. $M_s = 1.43$ MA/m, $K_1 = 410$ kJ/m³, $K_2 = 140$ kJ/m³ and $\gamma_w = 8 \times 10^{-3}$ J/m² at R.T.. Several possible domain structure models will be proposed, analyzed, and compared with each other. The structure which has the smallest energy should be the closest to the real structure among the models. The values of energy density will be per unit area of the plate.

7.3.2.1 Single Domain with $\vec{M}_s$ Normal to the Plate

The energy is the largest magnetostatic energy (Fig. 7.8a),

$$F = \frac{\mu_0}{2} M_s^2 h \approx 1.3 \times 10^3 \text{ (J/m}^2\text{)}. \quad (7.37)$$

7.3.2.2 Single Domain with $\vec{M}_s$ in the Plane

The energy is the largest magnetocrystalline anisotropy energy (Fig. 7.8b),

$$F = (K_1 + K_2)h = 0.6 \times 10^3 \text{ (J/m}^2\text{)}. \quad (7.38)$$

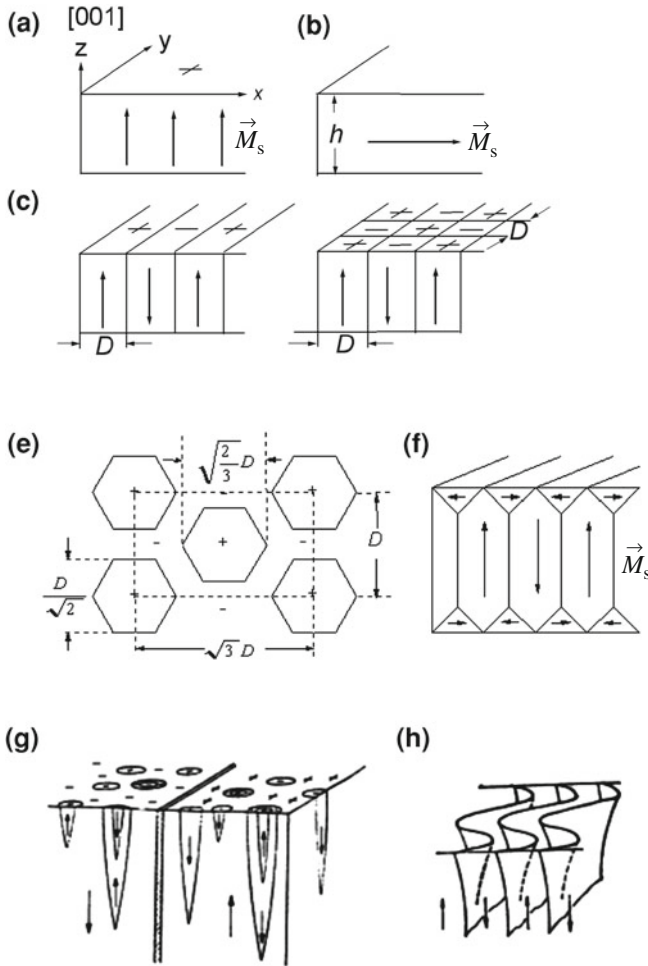


Fig. 7.8 Models of domain structure for Co crystal plate of c axis normal to the plate. (a) Saturated normal to the plate; (b) saturated in the plate plane; (c) strip domains; (d) chessboard domains; (e) beehive domains; (f) strip domains with closure domains; (g) spike-like domains near the surface of the plate [1]; (h) strip domains which become wavy near the surface of the plate [3]

The energy is almost half of (7.37) (Fig. 7.8a) and hence the state is more stable.

7.3.2.3 Strip Domains

Let D denote the domain width. $\vec{M}_s$ of each domain is along the easy axis normal to the plate and changes the direction periodically along the x -axis thus producing the magnetic surface charges of positive and negative signs distributed in turn (Fig. 7.8c).

Suppose $D \ll h$. The magnetostatic and domain wall energies are

$$F_d(D) = 2 \times 0.852 \times 10^{-7} M_s^2 D, \quad (7.11) \quad (7.39)$$

$$F_W(D) = \frac{\gamma_w h}{D}. \quad (7.40)$$

From minimum condition of the total energy

$$\frac{dF}{dD} = \frac{d(F_d + F_W)}{dD} = 0 \quad (7.41)$$

we get the width of the domain and corresponding total energy

$$D = \frac{1}{M_s} \sqrt{\frac{\gamma_w h}{1.7 \times 10^{-7}}} = 5 \text{ (}\mu\text{m)}, \quad (7.42)$$

$$F = 2M_s \sqrt{1.7 \times 10^{-7} \gamma_w h} = 3.3 \text{ (J/m}^2\text{)}. \quad (7.43)$$

Equation (7.42) justifies the assumption of $D \ll h$ and hence that the magnetic field energy is stored near each surface and the energy for the plate is twice that of the field energy of the magnetic charges on one side of the surface (7.39). It is notable that the energy of this structure is three orders smaller than those of the single-domain structures (7.37), (7.38). The result clearly demonstrates that the formation of magnetic domains is strikingly effective to reduce the energy of the object.

7.3.2.4 Chessboard Domains

The magnetostatic energy of the chessboard domain structure (Fig. 7.8d) is apparently smaller than that of strip domain structure (7.11), (7.12). From minimum condition of total energy

$$\frac{d}{dD} \left(2 \times 0.53 \times 10^{-7} M_s^2 D + 2 \frac{\gamma_w h}{D} \right) = 0 \quad (7.44)$$

we get

$$D = \frac{1}{M_s} \sqrt{\frac{\gamma_w h}{0.53 \times 10^{-7}}} = 8.7 \text{ (}\mu\text{m)}, \quad (7.45)$$

$$F = 2M_s \sqrt{2.12 \times 10^{-7} \gamma_w h} = 3.7 \text{ (J/m}^2\text{)}. \quad (7.46)$$

The total energy is a bit larger than that of strip domain structure, which is caused by that the increase in domain wall energy surpasses the decrease in magnetostatic energy.

7.3.2.5 Beehive Domains

Domains are magnetized along the easy axis. The island domains of positive magnetization distribute in the network domain of negative magnetization. The volumes of the two are the same. The period in the x and y direction is $\sqrt{3}D$ and D , respectively (Fig. 7.8e). The magnetostatic energy is 1/2.6 folds and domain wall energy is 2.8 folds of those of strip domain structure and the total energy is between those of strip and chessboard domain structures.

7.3.2.6 Strip Domains with Closed Surface Domains

By attaching the closed surface domains (Fig. 7.8f), the magnetostatic energy decreases to zero. The price is increase of magnetocrystalline anisotropy energy in the closed domains and domain wall energy of them. The total energy is mainly the magnetocrystalline anisotropy energy of the closed domains and domain wall energy of the principal domains:

$$F(D) \approx \frac{K_1 D}{2} + \gamma_w \frac{h}{D}. \quad (7.47)$$

From minimum condition of F we get

$$D = \sqrt{\frac{2\gamma_w h}{K_1}} = 5 \text{ (}\mu\text{m)}, \quad (7.48)$$

$$F \approx \sqrt{2K_1 \gamma_w h} = 3.1 \text{ (J/m}^2\text{)}. \quad (7.49)$$

The energy is a bit smaller than 3.3 J/m^2 of the strip domains without the closed surface domains.

7.3.2.7 Strip Domains with Spike-Like or Wavy Surface Domains

On the one hand this structure being strip domains inside the plate, which takes up most part of the plate, it is advantageous in reducing the domain wall energy. On the other hand the structure having chessboard-like domains on the surfaces (Fig. 7.8g, h) it is advantageous in reducing the magnetostatic energy. The thicker the plate the more advantageous the structure.

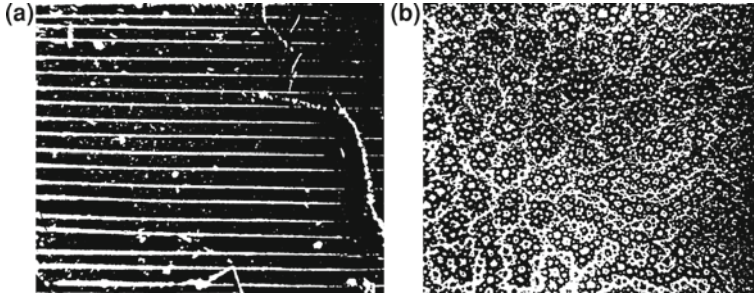


Fig. 7.9 Bitter patterns of Co plate. (a) [001]//plate; (b) (001)//plate

7.3.3 Domain Structures of Easy Axis Crystal Plates Observed in Experiment

7.3.3.1 Strip Domains with Spike-Like Surface Domains in a Single Crystal Co Plate

Figure 7.9 demonstrates the strip domains with spike-like surface domains observed in a single crystal Co plate [4].

7.3.3.2 Domains in Single Crystal $\text{PbO} \cdot 6\text{Fe}_2\text{O}_3$ Plates of Different Thickness

Figure 7.10 shows the Bitter patterns on the (001) plate surfaces of $\text{PbO} \cdot 6\text{Fe}_2\text{O}_3$ single crystals of different thickness. For very thin crystal of $h = 0.03$ mm it has a strip domain structure (Fig. 7.10a). It becomes wavy or rickrack for $h = 0.08$ mm (Fig. 7.10b). Circles, which are the ends of spike-like domains (Fig. 7.8g) appear when $h = 0.36$ mm (Fig. 7.10c). The pattern in Fig. 7.10d is for $h = 2.5$ mm. This complex pattern has many spike-like domains and is similar to the pattern for the Co crystal (Fig. 7.9b).

7.3.4 Measurement of γ_w and A Values

Experimental value of γ_w can be obtained exploiting the first relation of (7.42) by using the experimental values of M_s , h , and D of the strip domains.

Experimental value of A can be obtained exploiting (7.28) and (7.29) by using the experimental values of K_1 and γ_w .

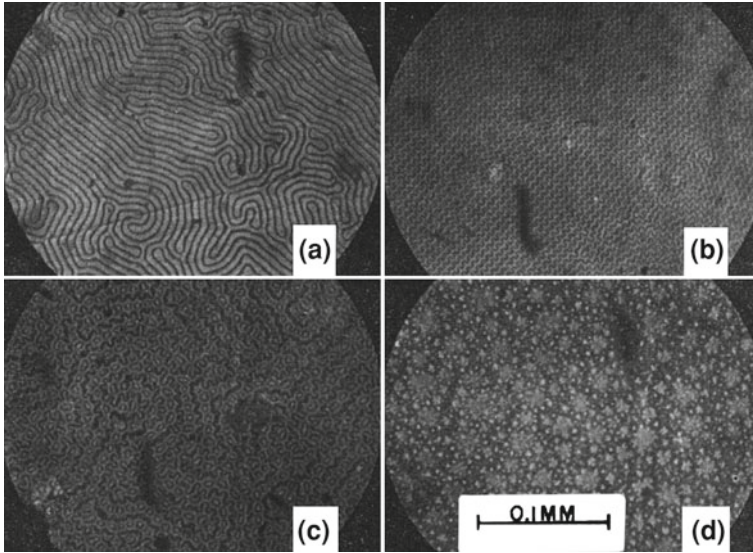


Fig. 7.10 Bitter patterns on (001) plate surfaces of $\text{PbO-6Fe}_2\text{O}_3$ single crystals [2]. $h = 0.03$ mm (a), 0.08 mm (b), 0.36 mm (c), 2.5 mm (d)



Fig. 7.11 Formation of magnetic bubbles (Kerr effect patterns). $H = 0$ (a); 1.6×10^3 A/m (b); 2.2×10^3 A/m (c) [5]

7.3.5 Magnetic Bubble

7.3.5.1 Formation of Magnetic Bubble

Consider the variation of strip domain structure (Fig. 7.11a) under the action of a magnetic field H applied normal to the film plane. With increase of H the domains of $\vec{M}_s$ in the field direction expand and those of opposite direction contract (Fig. 7.11b). When H is increased to a critical value, the opposite $\vec{M}_s$ direction domains split into isolated columnar domains (Fig. 7.11c). The columns are called magnetic bubbles. When H is increased further to a second critical value the bubbles disappear.

7.3.5.2 Stabilization Conditions of Magnetic Bubble

Let d denote the diameter of the bubble. The thermal potential of a bubble consists of the domain wall energy E_w , Zeeman energy E_H relative to the energy of $\vec{M}_s$ parallel to the static bias field $\vec{H}$, and magnetostatic energy E_d . They are

$$E_w = \pi d h \gamma_w, \quad (7.50)$$

$$E_H = \left[\pi \left(\frac{d}{2} \right)^2 h \right] (2J_s H), \quad (7.51)$$

and E_d of complicated expression. At stabilized state the differential of the total energy with respect to d is zero:

$$\pi h \gamma_w + \pi d h J_s H + \frac{\partial E_d}{\partial d} = 0, \quad (7.52)$$

where [6]

$$\frac{\partial E_d}{\partial d} = -\pi h^2 \mu_0 M_s^2 f \left(\frac{d}{h} \right), \quad (7.53)$$

$$f \left(\frac{d}{h} \right) = \begin{cases} \frac{d}{h} - \frac{2}{\pi} \left(\frac{d}{h} \right)^2 + \frac{1}{4} \left(\frac{d}{h} \right)^3 - \frac{3}{64} \left(\frac{d}{h} \right)^4 + \dots, & (d < h) \\ \frac{1}{\pi} \left\{ \left[\frac{1}{2} + \frac{3}{32} \left(\frac{h}{d} \right)^2 - \frac{3}{64} \left(\frac{h}{d} \right)^4 + \dots \right] \right. \\ \left. + \left[1 - \frac{1}{8} \left(\frac{h}{d} \right)^2 + \frac{3}{64} \left(\frac{h}{d} \right)^4 \dots \right] \ln \frac{4d}{h} \right\}, & (d > h) \end{cases} \quad (7.54)$$

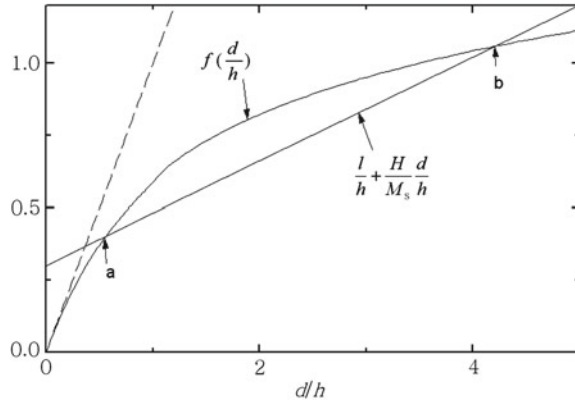
The first two terms in the left of (7.52) are positive which represent the compressing force acting on the domain wall inward, and the third term $\partial E_d / \partial d$ is negative that means $-\partial E_d / \partial d$ is an expansion force acting outward. The equation shows the equilibrium condition of the forces. To get the solution of d graphically rewrite (7.52) as

$$\frac{l}{h} + \frac{H}{M_s} \frac{d}{h} = f \left(\frac{d}{h} \right), \quad (7.55)$$

$$l \equiv \frac{\gamma_w}{\mu_0 M_s^2}. \quad (7.56)$$

Take d/h as abscissa and the right and left of (7.55) ordinates. The right is a curve irrelevant to H and passing through the origin which increases with increase of d/h but more and more slowly. The left is a straight line of slope H/M_s passing through the fixed point $(d/h = 0, l/h)$ on the ordinate axis (Fig. 7.12). When $H = 0$ the straight line is parallel to the abscissa and intersects with the curve at point a. When $H \neq 0$, the straight line also intersects at another point b. At these two points the compressing force equals the expansive force. Point a is unstable such as if d

Fig. 7.12 Left and right of (7.55) versus d/h



decreases a bit under thermal fluctuation, the compressing force becomes larger than the expanding force leading to extermination of the bubble. In the same way it can be concluded that point b is stable. The value of d can be obtained from the abscissa of point b. With increase of H the slope of the straight line increases thus shifting point b toward point a which makes d smaller. When point b coincides with point a at a critical value of H the bubble becomes unstable. Above the critical field the straight line and the curve does not intersect any more and the bubble annihilates.

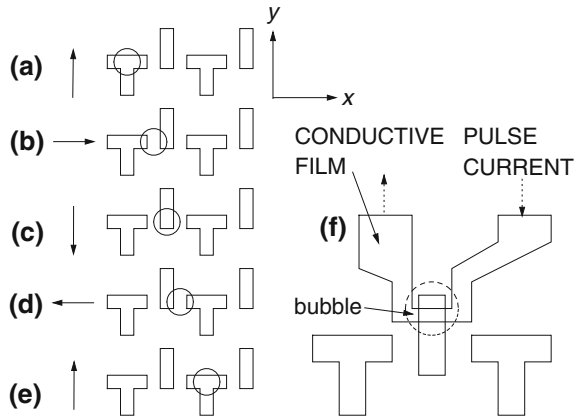
7.3.5.3 Magnetic Bubble Memory

A magnetic bubble can be made smaller than $1\ \mu\text{m}$ which can move by high speed. After the bubble is reported first in 1967, bubble memory started out as a promising technology in the 1970s, but failed commercially as the hard disk prices fell rapidly in the 1980s.

Principle of bubble memory: Take an early memory made of garnet single crystal film as an example. $h \sim 5\ \mu\text{m}$, $d \sim 10\ \mu\text{m}$, and $H = \sim 10^3\ \text{A/m}$. A closed chain of many T- and I- shaped Fe-80Ni film strip pairs are evaporated on the film surface (Fig. 7.13). When a bubble moves beneath a T strip the magnetic flux originating from top of the bubble spreads through the strip and returns into the garnet film. The decrease of the magnetostatic energy makes the bubble pinned at the position (Fig. 7.13a).

- (1) **Storage.** A T-I strip pair which has a bubble records number 1 and that has no bubble records number 0. Thus the $\{0,1\}$ information is stored in the T-I strip pair chain. During the operation of the storage a weak high frequency rotating magnetic field is applied parallel to the film plane. Suppose a bubble is beneath a T strip. When the field is in the y -axis direction the bubble is attracted to the top of T strip by the magnetic charge distributed there (Fig. 7.13a); when the field is rotated toward the x -axis direction the bubble shifts to the middle of the T-I

Fig. 7.13 Principle of bubble memory



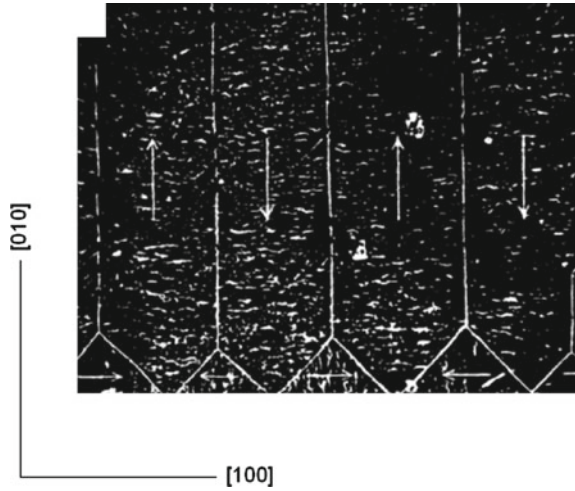
strip pair (Fig. 7.13b); when the field rotates to $-y$ direction the bubble shifts to the bottom of the I strip (Fig. 7.13c); . . . ; when the field rotates back to the y -axis direction again, the bubble shifts a T-I strip pair distance (Fig. 7.13e). Thus the group of the bubbles shifts along one direction in synchronism with the rotating field.

- (2) **Input.** Initially there is no bubble on the T-I strip pair chain, that is, the information stored in the chain is $\{0, 0, \dots\}$. A conductive film is installed upon a I strip (Fig. 7.13f). A series of pulses of current representing the information flow the conductive film synchronously with the rotating field. A pulse represents number 1 and no pulse represents 0. The pulse current produces a large enough pulse magnetic field below the I strip in the direction opposite to the static bias field direction and produces a bubble beneath the I strip, so 1 is written there. When a next pulse current flows the existed bubble had moved to the next T-I strip pair. Thus, the information $\{0, 1\}$ of the electric current pulse is input in series.
- (3) **Output.** A magnetoresistant probe is installed upon a I strip. When a bubble moves in the I strip position the magnetic field produced by the bubble changes the electric resistance of the probe. The data stored in the chain can be read through measuring the electric resistance of the probe synchronously with the rotating magnetic field.

7.3.6 Domains in Cubic Crystal Plate

Consider the case of $K_1 > 0$.

Fig. 7.14 Bitter pattern of Fe-4%Si single crystal plate [2]



7.3.6.1 Domains in Fe-4%Si Crystal Plate Parallel to (001) Plane

Figure 7.14 shows the strip domains along the $[010]$ axis with closed domains at the ends observed in a Fe-Si alloy crystal plate parallel to the $\{100\}$ faces. The structure has neither magnetostatic energy nor magnetocrystalline anisotropy energy but has elastic energy. Let L denote the length of the plate along the $[010]$ axis. All of the domains contract $\lambda_{100}/2$ per unit length along the $[001]$ axis normal to the plate. Along the $[100]$ and $[010]$ axis, however, the closed domains tend to stretch by λ_{100} and contract by $\lambda_{100}/2$ contrary to that the principal domains tend to contract by $\lambda_{100}/2$ and stretch by λ_{100} , respectively (6.20). Suppose the principal domains stretch and contract freely. The closed domains, being rigidly coupled with the principal domains, are forced to strain by $A_{xx} = -3\lambda_{100}/2$ and $A_{yy} = 3\lambda_{100}/2$. The elastic energy density produced by the strain is $(C_{11} - C_{12})(3\lambda_{100}/2)^2$ (6.6). By neglecting the domain wall energy of the closed domains, the total energy density per unit area of (010) face is the sum of the elastic energy and the domain wall energy of the principal domains:

$$F(D) = (C_{11} - C_{12}) \left(\frac{3\lambda_{100}}{2} \right)^2 \frac{D}{2} + \frac{\gamma_w L}{D}. \quad (7.57)$$

From minimum condition of F we get

$$D = \frac{2}{3\lambda_{100}} \sqrt{\frac{2\gamma_w L}{C_{11} - C_{12}}}, \quad (7.58)$$

$$F = \frac{3\lambda_{100}}{2} \sqrt{2\gamma_w L (C_{11} - C_{12})}. \quad (7.59)$$

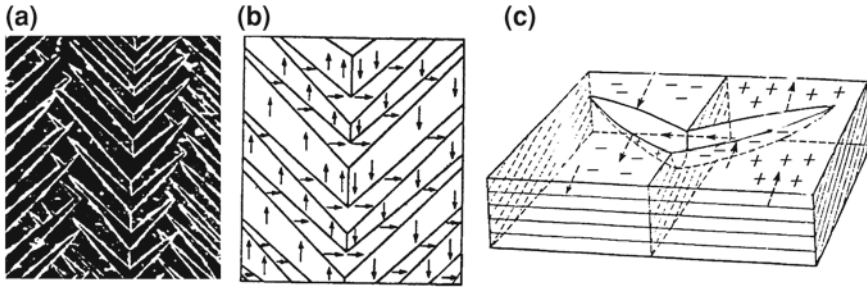


Fig. 7.15 Tree pattern domain structure on a Fe-4%Si crystal plate inclined a few degrees from (001) plane [4]

7.3.6.2 Domains in Fe-4%Si Crystal Plate Inclined a Few Degrees From (001) Plane

If the crystal plane in the above Sect. 7.3.6.1 is inclined from (001) face, there appears surface magnetic charges on the surfaces of the plate. To reduce the demagnetizing energy produced by the magnetic charges, tapered (tree) surface domains are formed on the surfaces (Fig. 7.15a). The tree domains transmit a part of magnetic flux from one principal domain to the adjacent principal domain thus decreasing the magnetic charges and hence demagnetizing energy (Fig. 7.15b–c).

7.3.7 Domains Observed in Polycrystals

The patterns observed on many surfaces of the grains are strip domains. Often a domain in a grain strides across the grain boundary and extends into adjacent grain so that no large magnetic charge appears on the grain boundary. But when the angle between the easy directions of adjacent grains is large a large surface magnetic charge appears. In such cases spike-like domains appear on the grain boundary to decrease magnetostatic energy (Fig. 7.16a).

Magnetization vectors interrupt at a void, impurity, etc. Spike-like domains are often formed at such places to decrease magnetostatic energy (Fig. 7.16b).

If a domain wall spans an impurity, void et al., the domain wall energy is decreased by decreasing both the area of the wall and magnetostatic energy. Therefore, domain wall tends to pin at such positions.

7.3.8 Single Domain

Above arguments show that magnetostatic energy plays a key role in forming multi-domain structure. The magnetostatic energy E_d of a single-domain body of size d is proportional to d^3 , and domain wall energy of multi-domain body is proportional

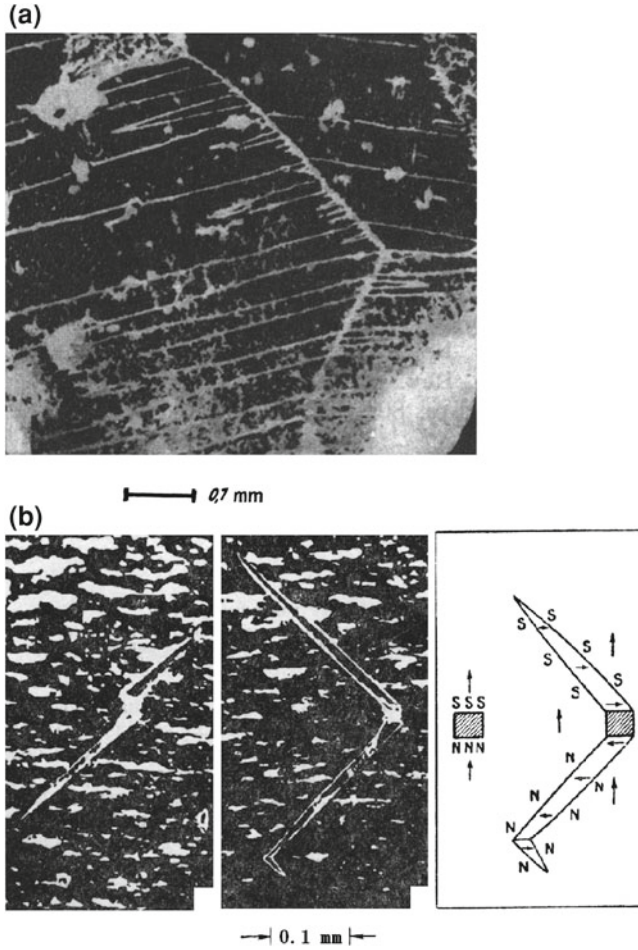


Fig. 7.16 Bitter patterns in polycrystalline Fe-Si. (a) [1], (b) [4]

to d^2 . With decrease of d , E_d decreases faster than the domain wall energy, and below a critical size d_0 the E_d becomes smaller than the sum of domain wall and magnetostatic energies of multi-domain structure making single-domain structure more stable. d_0 is called critical size for single domain. The value of d_0 is estimated roughly for a spherical particle as below. The energy of a single-domain sphere (Fig. 7.17a) is the magnetostatic energy

$$E_s = E_d = \frac{1}{3} \frac{\mu_0 M_s^2}{2} \frac{4\pi}{3} \left(\frac{d}{2} \right)^3 = \frac{\pi}{36} \mu_0 M_s^2 d^3. \quad ((5.69), (5.70)) \quad (7.60)$$

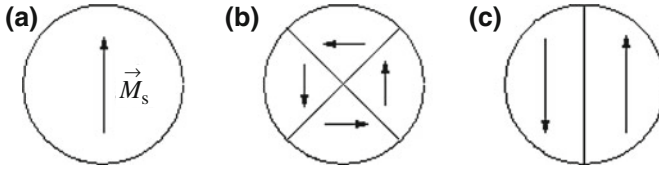


Fig. 7.17 Domain structures of a particle

Table 7.2 Values of d_0 for some magnetic materials

Material	d_0
Fe metal	~ 40 nm
Co metal	~ 60 nm
BaO·6Fe ₂ O ₃	~ 0.9 μ m
Nd ₂ Fe ₁₄ B	~ 0.2 μ m
SmCo ₅	~ 1.3 μ m

The energy of the four-domain sphere of Fig. 7.17b for cubic crystal of $K_1 > 0$ is mostly the domain wall energy

$$E_{4d} \approx E_w = 2\pi \left(\frac{d}{2}\right)^2 \gamma_w. \quad (7.61)$$

The energy of the two-domain sphere of Fig. 7.18c for uniaxial crystal of $K_1 > 0$ is the sum of magnetostatic energy and domain wall energy

$$E_{2d} \approx \frac{1}{2} \frac{1}{3} \frac{\mu_0 M_s^2}{2} \frac{4\pi}{3} \left(\frac{d}{2}\right)^3 + \pi \left(\frac{d}{2}\right)^2 \gamma_w. \quad (7.62)$$

From the conditions of $E_s = E_{4d}$ and $E_s = E_{2d}$ we get the same result of

$$d_0 = \frac{18\gamma_w}{\mu_0 M_s^2}. \quad (7.63)$$

Table 7.2 shows the values of d_0 at R.T. for some magnetic materials.

7.3.9 $\vec{M}_s$ Distribution in Submicron-Scale Dots

For a submicron-scale dot of very small magnetocrystalline anisotropy alloys the shape anisotropy has a major effect on the magnetic structure. Take a small circular Fe-80%Ni dot as an example. If the diameter of the dot is in the range of 200 nm to some μ m and the thickness is dozens of nm, the $\vec{M}_s$ is mostly parallel to the circumference to decrease magnetostatic energy. Such magnetic config-

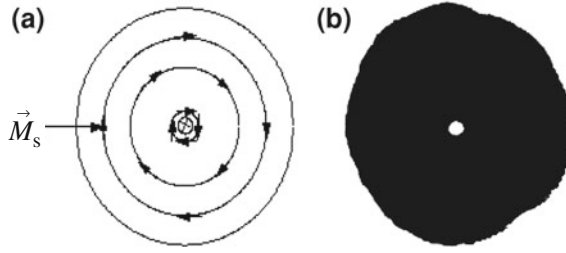


Fig. 7.18 Magnetic structure of Fe-80%Ni dot [7]

uration, however, gives rise to very large exchange energy density near the center ($A \sum_i^{x,y,z} (\nabla \alpha_i)^2 = A/r^2$, r : radius). To decrease the exchange energy the $\vec{M}_s$ near the center within diameter $\sim \delta_0$ tilts toward the normal of the dot (Fig. 7.18). Such structure is called spin vortex. The white region in Fig. 7.18b is the microscopic image of spin vortex observed by use of MFM. If the diameter of the dot decreases below 100 nm and the thickness to some nm, the dot becomes single domain with the $\vec{M}_s$ in the dot plane. If the diameter is around 10 nm and the thickness exceeds 10 nm, the $\vec{M}_s$ is arranged normal to the dot.

7.3.10 Superparamagnetism

If the volume of a single-domain particle v becomes small so that thermal energy fluctuation $k_B T$ becomes comparable with the anisotropy energy barrier Kv , the probability of magnetization rotation from one easy direction to the another, which is proportional to $\exp(-Kv/k_B T)$, becomes not negligible. In the absence of magnetic field, the $\vec{M}_s$ not only fluctuates about an easy direction but also flip-flops between the two easy directions making the average in time magnetization zero.

In a magnetic field the magnetization is

$$M = N \frac{M_s v \int_0^\pi \exp\left(\frac{J_s v H \cos \theta}{k_B T}\right) \cos \theta \sin \theta d\theta}{\int_0^\pi \exp\left(\frac{J_s v H \cos \theta}{k_B T}\right) \sin \theta d\theta} = N M_s v L\left(\frac{J_s v H}{k_B T}\right), \quad (7.64)$$

where N is the number of the particles in a unit volume and

$$L(x) \equiv \coth x - \frac{1}{x} = B_\infty(x) \quad (7.65)$$

is the Langevin function. Equation (7.64) corresponds to the magnetization of paramagnetic atoms:

$$M = \frac{N \sum_{M_J}^{-J, -J+1, \dots, J} -g_J M_J \mu_B \exp\left(-\frac{g_J M_J \mu_B H}{k_B T}\right)}{\mu_0 \sum_{M_J}^{-J, -J+1, \dots, J} \exp\left(-\frac{g_J M_J \mu_B H}{k_B T}\right)} = \frac{N g_J J \mu_B}{\mu_0} B_J(x). \quad (2.120)$$

Here the magnetic moment of the particle $M_s v$ is much larger than $g_J J \mu_B / \mu_0$ of an atom. Such magnetism is called superparamagnetism.

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Chapter 8

Micromagnetism

The theory of magnetic domain is based on the assumption that a magnetically ordered object constitutes of domains and domain walls. The domains are uniformly magnetized to saturation and non-uniform magnetization is distributed only in the walls. In some cases, however, $\vec{M}_s$ distribution is out of domain structure category. The $\vec{M}_s$ distribution in a small object of transition dimension from single domain size to multi-domain size and its variation during magnetization processes should be nonuniform which cannot be treated by the domain model. Even in a bulk object, when an applied magnetic field is decreased from a sufficiently large value, the magnetization decreases from saturation along the upper hysteresis curve. At some critical field there should form a nucleus of reverse domain before it grows up to an observable spike-like domain of opposite magnetization. The nucleus is a small local region of non-uniform magnetization which is neither a domain nor a domain wall.

Micromagnetism intends to find the $\vec{M}_s$ space distribution either directly from minimum condition of the free energy or thermal potential of a magnetic object (Brown 1940–1963) [1]. This chapter introduces the principle of micromagnetism and demonstrates some numerical calculations of magnetization for nanocrystalline NdFeB permanent magnets. The chapter contains the sections of Brown's equation; and Finite element method.

8.1 Brown's Equation

8.1.1 Brown's Equation

Consider a magnetic crystal in the applied magnetic field $\vec{H} = H\vec{e}_z$. Let $\vec{e}_M(\vec{r})$ and $\alpha_\beta(\vec{r})$ ($\beta = x, y, z$) denote the unit vector of $\vec{M}_s$ and its direction cosine at position $\vec{r}$:

$$\vec{M}_s(\vec{r}) = M_s \vec{e}_M(\vec{r}), \quad (8.1)$$

$$\vec{e}_M(\vec{r}) = \sum_{\beta}^{x,y,z} \alpha_{\beta}(\vec{r}) \vec{e}_{\beta}, \quad (8.2)$$

$\vec{H}_m$ and V_m the magnetic field and magnetic potential produced by the crystal, G , F_{ex} , F_K , and F_H the densities of thermal potential, exchange energy, magnetocrystalline anisotropy energy, and Zeeman energy, and $\int_{\infty} F_d dv$ the demagnetizing energy of the crystal.

$$\begin{aligned} \int G dv &= \int (F_{ex} + F_K + F_d + F_H) dv \\ &= \int \left\{ A \sum_{\beta}^{x,y,z} (\nabla \alpha_{\beta})^2 + F_K [\alpha_x, \alpha_y, \alpha_z(\alpha_x, \alpha_y)] \right. \\ &\quad \left. - \vec{J}_s [\alpha_x, \alpha_y, \alpha_z(\alpha_x, \alpha_y)] \cdot \left(\frac{1}{2} \vec{H}_m + \vec{H} \right) \right\} dv, \quad (\alpha_z^2 = 1 - \alpha_x^2 - \alpha_y^2) \end{aligned} \quad (8.3)$$

$$\vec{H}_m = -\nabla V_m, \quad (1.34)$$

$$\nabla^2 V_m = \nabla \cdot \vec{M}_s. \quad ((1.10), (1.6)) \quad (8.4)$$

Let $\vec{e}_n$ and n represent the unit vector and displacement along the normal of the magnetic object surface from inside to outside, and $V_m(-)$ and $V_m(+)$ the V_m just inside and outside the surface. V_m satisfies the boundary conditions on the surface:

$$V_m(-) = V_m(+), \quad (8.5)$$

$$\frac{\partial V_m(-)}{\partial n} - \frac{\partial V_m(+)}{\partial n} = \vec{M}_s \cdot \vec{e}_n. \quad (8.6)$$

From minimum condition of the thermal energy with respect to $\{\alpha_{\beta}(\vec{r})\}$

$$\delta \int G dv = 0 \quad (8.7)$$

we get the Brown's equations

$$-2A \left(\nabla^2 \alpha_x - \frac{\alpha_x}{\alpha_z} \nabla^2 \alpha_z \right) + \frac{\partial F_K}{\partial \alpha_x} + J_s \left(\frac{\partial V_m}{\partial x} - \frac{\alpha_x}{\alpha_z} \frac{\partial V_m}{\partial z} \right) + J_s H \frac{\alpha_x}{\alpha_z} = 0, \quad (8.8)$$

$$-2A \left(\nabla^2 \alpha_y - \frac{\alpha_y}{\alpha_z} \nabla^2 \alpha_z \right) + \frac{\partial F_K}{\partial \alpha_y} + J_s \left(\frac{\partial V_m}{\partial y} - \frac{\alpha_y}{\alpha_z} \frac{\partial V_m}{\partial z} \right) + J_s H \frac{\alpha_y}{\alpha_z} = 0 \quad (8.9)$$

inside the crystal and

$$\frac{\partial \alpha_x}{\partial n} - \frac{\alpha_x}{\alpha_z} \frac{\partial \alpha_z}{\partial n} = \frac{\partial \alpha_y}{\partial n} - \frac{\alpha_y}{\alpha_z} \frac{\partial \alpha_z}{\partial n} = 0 \quad (8.10)$$

on the surface (Note 1 of this section). Equations (8.8), (8.9), and (8.10) can be formulated by the vector equations of

$$J_s \vec{e}_M(\vec{r}) \times \left[\frac{2A}{J_s} \nabla^2 \vec{e}_M(\vec{r}) + \vec{H}_K + \vec{H}_m(\vec{r}) + \vec{H} \right] = 0, \quad (8.11)$$

$$\vec{H}_K \equiv -\frac{1}{J_s} \left(\frac{\partial F_K}{\partial \alpha_x} \vec{e}_x + \frac{\partial F_K}{\partial \alpha_y} \vec{e}_y \right) \quad (8.12)$$

inside the crystal and

$$\vec{e}_M \times \frac{\partial \vec{e}_M}{\partial n} = 0 \quad (8.13)$$

on the surface (Note 2 of this section). $\frac{2A}{J_s} \nabla^2 \vec{e}_M(\vec{r})$ and $\vec{H}_K$ in the bracket of (8.11) are the effective fields of exchange interaction and magnetocrystalline anisotropy. Equation (8.11) shows that $\vec{J}_s$ is parallel to the total effective field direction everywhere.

Brown's equations can be solved analytically only for very limited simple cases. An example is in the next Sect. 8.1.2.

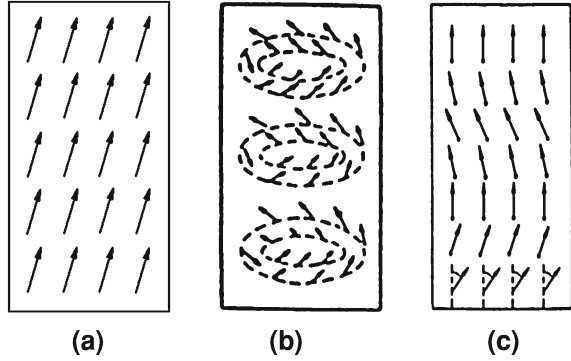
8.1.2 Nucleation of Magnetization Reversal in Infinite Long Cylindrical Crystal

Consider an infinitely long uniaxial anisotropy single crystal cylinder of radius R . The easy axis is parallel to the cylindrical axis (z axis). Initially the crystal is magnetized to saturation in the z direction. A magnetic field is applied in $-z$ direction and the magnetization distribution begins to deviate from the saturation at the nucleation field of magnetization reversal H_n . H_n will be analyzed below. Let r denote the radial coordinate, then

$$\alpha_x, \quad \alpha_y \ll 1, \quad \alpha_z \approx 1, \quad (8.14)$$

$$\nabla^2 V_m = \begin{cases} M_s \left(\frac{\partial \alpha_x}{\partial x} + \frac{\partial \alpha_y}{\partial y} \right), & (r < R, (8.4)) \\ 0, & (r > R) \end{cases} \quad (8.15)$$

Fig. 8.1 Three kinds of nucleation mode of magnetization reversal. **a** Coherent mode; **b** vortex mode; **c** buckling mode



$$V_m(R_-) = V_m(R_+), \quad (8.5)$$

$$\frac{\partial V_m(R_-)}{\partial n} - \frac{\partial V_m(R_+)}{\partial n} = \vec{M}_s \cdot \vec{e}_n, \quad (8.6) \quad (8.16)$$

$$-\frac{2A}{J_s}(\nabla^2 \alpha_x - \alpha_x \nabla^2 \alpha_z) + \frac{\partial V_m}{\partial x} + \left(-\frac{\partial V_m}{\partial z} - H_K + H\right) \alpha_x = 0, \quad ((8.8), (5.21)) \quad (8.17)$$

$$-\frac{2A}{J_s}(\nabla^2 \alpha_y - \alpha_y \nabla^2 \alpha_z) + \frac{\partial V_m}{\partial y} + \left(-\frac{\partial V_m}{\partial z} - H_K + H\right) \alpha_y = 0, \quad (8.9) \quad (8.18)$$

$$\frac{\partial \alpha_x}{\partial n} = \frac{\partial \alpha_y}{\partial n} = 0. \quad (8.10) \quad (8.19)$$

Omitting details of calculation processes only the results will be presented [2]. There are three kinds of nucleation mode of magnetization reversal:

① Coherent Mode

$\vec{M}_s$ rotates coherently (preserving the parallel alignment of $\vec{M}_s$. Fig. 8.1a), and

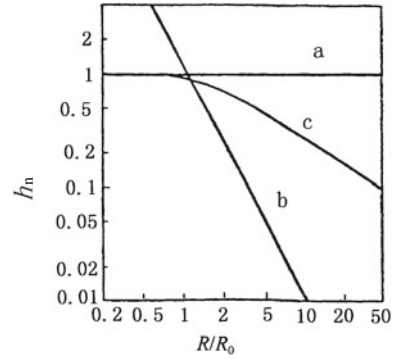
$$H_n = \frac{M_s}{2} + H_K, \quad (8.20)$$

where $M_s/2$ is the anisotropy field of the cylinder (Note 3 of this section). H_n is independent of r . This result is the same with that calculated by the single domain model.

② Vortex Mode

$\vec{M}_s$ on a cylindrical surface of radius r tilts toward the circumference by small angle. The angle is a function of r (Fig. 8.1b), and

Fig. 8.2 h_n versus R/R_0 .
a Coherent mode; **b** vortex mode; **c** buckling mode



$$H_n = 10.8 \left(\frac{R_0}{R} \right)^2 \left(\frac{M_s}{2} + H_K \right), \quad (8.21)$$

$$R_0 \equiv \sqrt{\frac{4\pi A}{\mu_0 M_s^2}}. \quad (8.22)$$

③ Buckling Mode

$\vec{M}_s$ on a cross-section normal to the z axis tilt toward the section. The tilt angle is a periodical function of z (Fig. 8.1c). H_n is the same with that of coherent rotation mode (8.20) if R/R_0 is smaller than ~ 0.8 , and decreases with increase of R/R_0 above ~ 0.8 (Fig. 8.2).

Figure 8.2 shows $h_n \equiv H_n/(M_s/2 + H_K)$ as a function of R/R_0 for the three modes. The nucleation proceeds by the mode of smallest H_n , that is, if $R/R_0 < \sim 0.8$ it proceeds by coherent or buckling mode, if $\sim 0.8 < R/R_0 < 1.04$ by buckling mode, and if $R/R_0 > 1.04$ by vortex mode. Due to mathematical difficulty the variation of magnetic structure after the nucleation cannot be solved analytically.

Note 1

$$\delta\alpha_z = -\frac{\alpha_x\delta\alpha_x + \alpha_y\delta\alpha_y}{\alpha_z}, \quad \left(\sum_{\beta}^{x,y,z} \alpha_{\beta}^2 = 1 \right) \quad (8.23)$$

$$\delta \int F_{\text{ex}} dv = A \int \delta \sum_{\beta}^{x,y,z} (\nabla\alpha_{\beta})^2 dv = 2A \int \sum_{\beta}^{x,y,z} (\nabla\alpha_{\beta}) \cdot (\nabla\delta\alpha_{\beta}) dv \quad (4.113)$$

$$= 2A \oint_S \sum_{\beta}^{x,y,z} [(\nabla\alpha_{\beta})\delta\alpha_{\beta}] \cdot d\vec{S} - 2A \int \sum_{\beta}^{x,y,z} (\nabla^2\alpha_{\beta})\delta\alpha_{\beta} dv \quad (\text{a3.28})$$

$$\begin{aligned}
&= 2A \oint_S \left[\left(\nabla \alpha_x - \frac{\alpha_x}{\alpha_z} \nabla \alpha_z \right) \delta \alpha_x + \left(\nabla \alpha_y - \frac{\alpha_y}{\alpha_z} \nabla \alpha_z \right) \delta \alpha_y \right] \cdot d\vec{S} \\
&- 2A \int \left[\left(\nabla^2 \alpha_x - \frac{\alpha_x}{\alpha_z} \nabla^2 \alpha_z \right) \delta \alpha_x + \left(\nabla^2 \alpha_y - \frac{\alpha_y}{\alpha_z} \nabla^2 \alpha_z \right) \delta \alpha_y \right] dv, \quad (8.23) \quad (8.24)
\end{aligned}$$

$$\begin{aligned}
F_K[\alpha_x, \alpha_y, \alpha_z(\alpha_x, \alpha_y)] &= F_K(\alpha_x, \alpha_y), \\
\delta \int F_K(\alpha_x, \alpha_y) dv &= \int \left(\frac{\partial F_K}{\partial \alpha_x} \delta \alpha_x + \frac{\partial F_K}{\partial \alpha_y} \delta \alpha_y \right) dv, \quad (8.25)
\end{aligned}$$

$$\delta \int F_d dv = \frac{\mu_0}{2} \delta \int_{\infty} \vec{H}_m^2 dv = \frac{1}{2} \delta \int_{\infty} \vec{H}_m \cdot (\vec{B} - \mu_0 \vec{H} - \vec{J}_s) dv, \quad (8.26)$$

in which $\vec{H}$ is a constant vector,

$$\int_{\infty} \vec{H}_m \cdot \vec{B} dv = 0, \quad (1.73)$$

$$\int_{\infty} \vec{H}_m dv = - \int_{\infty} \nabla V_m dv = 0, \quad \left(\int_{-\infty}^{\infty} \frac{\partial V_m}{\partial \beta} d\beta = V_m(\infty) - V_m(-\infty) = 0 \right) \quad (8.27)$$

$$\begin{aligned}
\int \delta \vec{H}_m \cdot \vec{J}_s dv &= \frac{1}{4\pi} \int \int \left\{ \frac{3[\delta \vec{J}_s(\vec{r}') \cdot (\vec{r} - \vec{r}')] [\vec{J}_s(\vec{r}) \cdot (\vec{r} - \vec{r}')] }{|\vec{r} - \vec{r}'|^5} - \frac{\delta \vec{J}(\vec{r}') \cdot \vec{J}(\vec{r})}{|\vec{r} - \vec{r}'|^3} \right\} dv dv' \\
&= \int \vec{H}_m \cdot \delta \vec{J}_s dv, \quad (1.46) \quad (8.28)
\end{aligned}$$

therefore (8.26) becomes

$$\begin{aligned}
\delta \int F_d dv &= - \frac{1}{2} \int (\delta \vec{H}_m \cdot \vec{J}_s + \vec{H}_m \cdot \delta \vec{J}_s) dv = \int \nabla V_m \cdot \delta \vec{J}_s dv \\
&= J_s \int \left[\left(\frac{\partial V_m}{\partial x} - \frac{\alpha_x}{\alpha_z} \frac{\partial V_m}{\partial z} \right) \delta \alpha_x + \left(\frac{\partial V_m}{\partial y} - \frac{\alpha_y}{\alpha_z} \frac{\partial V_m}{\partial z} \right) \delta \alpha_y \right] dv. \quad (8.29)
\end{aligned}$$

$$\delta \int F_H dv = - \int J_s H \delta \alpha_z dv = J_s H \int \frac{\alpha_x \delta \alpha_x + \alpha_y \delta \alpha_y}{\alpha_z} dv. \quad (8.30)$$

From

$$\delta \int (F_{ex} + F_K + F_d + F_H) dv = 0 \quad (8.31)$$

we get (8.8)–(8.10).

Note 2

Each term of y component of (8.11) divided by $-\alpha_z$ equals to corresponding term of (8.8). In fact

$$-\frac{2A}{\alpha_z} \begin{vmatrix} \vec{e}_x & \vec{e}_y & \vec{e}_z \\ \alpha_x & \alpha_y & \alpha_z \\ \nabla^2 \alpha_x & \nabla^2 \alpha_y & \nabla^2 \alpha_z \end{vmatrix}_y = -2A \left(\nabla^2 \alpha_x - \frac{\alpha_x}{\alpha_z} \nabla^2 \alpha_z \right), \quad (8.32)$$

$$-\frac{J_s}{\alpha_z} \begin{vmatrix} \vec{e}_x & \vec{e}_y & \vec{e}_z \\ \alpha_x & \alpha_y & \alpha_z \\ -\frac{1}{J_s} \frac{\partial F_K}{\partial \alpha_x} & -\frac{1}{J_s} \frac{\partial F_K}{\partial \alpha_x} & 0 \end{vmatrix}_y = \frac{\partial F_K}{\partial \alpha_x}, \quad (8.33)$$

$$-\frac{J_s}{\alpha_z} \begin{vmatrix} \vec{e}_x & \vec{e}_y & \vec{e}_z \\ \alpha_x & \alpha_y & \alpha_z \\ -\frac{\partial V_m}{\partial x} & -\frac{\partial V_m}{\partial y} & -\frac{\partial V_m}{\partial y} \end{vmatrix}_y = J_s \left(\frac{\partial V_m}{\partial x} - \frac{\alpha_x}{\alpha_z} \frac{\partial V_m}{\partial z} \right), \quad (8.34)$$

$$-\frac{J_s}{\alpha_z} \begin{vmatrix} \vec{e}_x & \vec{e}_y & \vec{e}_z \\ \alpha_x & \alpha_y & \alpha_z \\ 0 & 0 & H \end{vmatrix}_y = J_s H \frac{\alpha_x}{\alpha_z}. \quad (8.35)$$

Note 3

The shape anisotropy energy density of the cylinder being

$$F_d = \frac{\mu_0 M_s^2}{4} \sin^2 \theta \quad ((5.73), N_z = 0, N_\perp = 1/2) \quad (8.36)$$

the anisotropy field of the anisotropy is

$$\frac{2}{J_s} \frac{\mu_0 M_s^2}{4} = \frac{M_s}{2}. \quad (\text{Sect. 5.1.3}) \quad (8.37)$$

8.2 Finite Element Method

The function of computer being developed at such a high level, almost all of micromagnetic calculations adopt numerical method nowadays. In this method the magnetic object and its surrounding space are partitioned into many elements.

Independent $\vec{J}_s$ directions are calculated only for finite positions instead of finding out it as a continuous function of position vector $\vec{r}$. In this way $\vec{J}_s$ space distribution is approximately obtained from distribution of $\{\vec{J}_s(\vec{r}_i)\}$ (i : integral) of finite number.

The magnetization and magnetic structure can be calculated either from minimization of total energy or by solving the equations of precession motion of $\vec{J}_s(\vec{r}_i)$ (3.103). This section introduces basic characteristics of finite element method through analyses of NdFeB magnet by minimization of the total energy by use of conjugate gradient method [3].

8.2.1 Domain Wall in Bulk $\text{Nd}_2\text{Fe}_{14}\text{B}$

$\text{Nd}_2\text{Fe}_{14}\text{B}$ has easy c axis at R.T. (Sect. 5.1.2). Take the c axis z axis and analyze a domain wall normal to the x axis centered at $x = 0$. Let θ denote the angle between $\vec{J}_s$ and z axis. $\theta(-\infty) = 0$ and $\theta(\infty) = \pi$.

Each side from the wall center is partitioned to 100 regions. The width of each region is D . Two kinds of model, G and S, are employed. In the G model θ is constant in each region and hence $\theta(x)$ is a discontinuous step function. Let $\theta_i \equiv \theta(iD \leq x < (i+1)D)$ ($i = -100, -99, \dots, 100$). In model S $\theta_i \equiv \theta(iD)$ and $\theta(x)$ is a linear function within each region making it a continuous function. The domain wall energy density γ_G and γ_S for the two models is approximated by

$$\gamma_G = D \sum_{i=-100, -99, \dots, 100} \left[A \left(\frac{\theta_{i+1} - \theta_i}{D} \right)^2 + K_1 \sin^2 \theta_i \right] \quad (8.38)$$

and

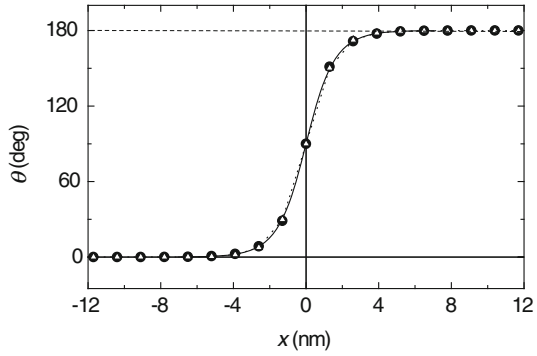
$$\gamma_S = \sum_{i=-100, -99, \dots, 100} \left[DA \left(\frac{\theta_{i+1} - \theta_i}{D} \right)^2 + \int_0^D K_1 \sin^2 \left(\theta_i + \frac{\theta_{i+1} - \theta_i}{D} x \right) dx \right], \quad (8.39)$$

respectively. The domain structure is calculated from minimum condition of γ_G or γ_S with respect to the set of $\{\theta_i\}$ under the boundary conditions of $\theta(-100D) = 0$ and $\theta(100D) = \pi$. If D is taken $1.7 \text{ nm} \approx 0.4\delta_w$, the errors of γ_G and γ_S with respect to the rigorous solution γ_w [(7.28)] are smaller than 2% and the differences of $\{\theta(i)\}$ from rigorous solution [(7.25)] are very small (Fig. 8.3) [4].

8.2.2 Models of Nanocrystalline NdFeB

Hereafter nanocrystalline NdFeB magnet will be analyzed. A rapid quenched NdFeB magnet consists of dozens nm size $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains surrounded by a thin Nd-rich non-magnetic grain boundary phase network. The c axis of the grains are randomly oriented and the magnet is isotropic.

Fig. 8.3 Domain wall structure of $\text{Nd}_2\text{Fe}_{14}\text{B}$ calculated by G model (full circle), S model (triangle+dashed line), and (7.25) (full curve)



The model magnet consists of limited number of randomly oriented isometric cubic or tetrakaidecahedral $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains. There is no grain boundary phase and the grains densely contact each other. Each grain is partitioned into isometric cubic or tetrahedral elements. The volume of the element is about $(1.5 \text{ nm} \approx \delta_w/3)^3$. Three kinds of model are considered [4, 5].

8.2.2.1 Cubic Grain Models

The magnet consists of $N = n \times n \times n$ cubic grains of size L . Each grain is partitioned into $m \times m \times m$ isometric cubic regions.

Model G considers a cubic region (i, j, k) (i, j, k : integers) a single domain element exchange coupling with the six adjacent elements of $(i \pm 1, j, k)$, $(i, j \pm 1, k)$ and $(i, j, k \pm 1)$. The exchange energy between (i, j, k) and $(i+1, j, k)$ elements, for instance, is approximated by

$$\begin{aligned}
 E_{\text{ex}} &= \left(\frac{L}{m}\right)^2 \int_i^{i+1} A \sum_{\beta}^{x,y,z} \left(\frac{\partial \alpha_{\beta}}{\partial x}\right)^2 dx \approx \left(\frac{L}{m}\right)^2 A \sum_{\beta}^{x,y,z} \left[\frac{\alpha_{\beta}(i+1, j, k) - \alpha_{\beta}(i, j, k)}{L/m} \right]^2 \frac{L}{m} \\
 &= \frac{2LA}{m} \left[1 - \frac{\vec{J}_s(i+1, j, k) \cdot \vec{J}_s(i, j, k)}{J_s^2} \right], \tag{8.40}
 \end{aligned}$$

where α_{β} is the direction cosine of $\vec{J}_s$ and the integral in the second expression is between the centers of (i, j, k) and $(i+1, j, k)$ elements. The exchange energy between the elements separated by the grain boundary is assumed the same with the energy between the elements within a grain unless otherwise mentioned. In this model the number of independent variables of $\{\vec{J}_s(i, j, k)\}$ is $2(n \times m)^3$.

Model S partitions each cubic region into 24 isometric tetrahedral elements further. One vertex of the element is at the body-center (point CC in Fig. 8.4a) and another 3 vertexes are on a same face of the cubic region (FC (face-center), V1 and V2 (vertexes) in Fig. 8.4a).

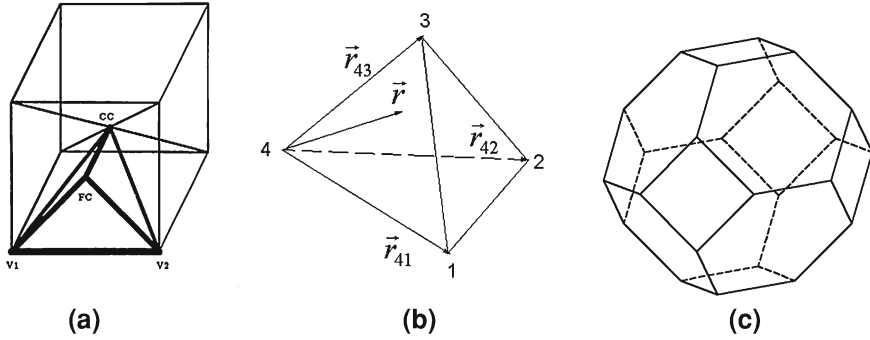


Fig. 8.4 A tetrahedral element in a cubic region (a), symbols for a tetrahedral element (b) and tetrakaidecahedral grain (c)

Let $\vec{e}_i$ denote the unit vector of $\vec{J}_s$ at the i^{th} vertex of the element and assume that $\vec{e}(\vec{r}) \equiv \vec{J}_s(\vec{r})/J_s$ changes linearly within each element, that is

$$\vec{e}(\vec{r}) = \sum_i^{1,2,3,4} \vec{e}_i \eta_i(\vec{r}), \quad (8.41)$$

$$\begin{aligned} \eta_1(\vec{r}) &= \frac{\vec{r} \cdot (\vec{r}_{42} \times \vec{r}_{43})}{\vec{r}_{41} \cdot (\vec{r}_{42} \times \vec{r}_{43})}, & \eta_2(\vec{r}) &= \frac{\vec{r} \cdot (\vec{r}_{43} \times \vec{r}_{41})}{\vec{r}_{42} \cdot (\vec{r}_{43} \times \vec{r}_{41})}, \\ \eta_3(\vec{r}) &= \frac{\vec{r} \cdot (\vec{r}_{41} \times \vec{r}_{42})}{\vec{r}_{43} \cdot (\vec{r}_{41} \times \vec{r}_{42})}, & \eta_4(\vec{r}) &= 1 - \sum_{i=1,2,3} \eta_i(\vec{r}), \end{aligned} \quad (8.42)$$

where $\vec{r}$ and $\vec{r}_{4i}$ ($i = 1, 2, 3$) represent the position vectors from vertex 4 to the viewpoint and vertex i (Fig. 8.4b). The exchange energy of an element, for instance, is

$$\int_{\text{element}} F_{\text{ex}} dV = \int A \sum_{\beta}^{x,y,z} [\nabla \alpha_{\beta}(\vec{r})]^2 dV = A v_{\text{el}} \sum_{i,j}^{1,2,3,4} (\vec{e}_i \cdot \vec{e}_j) (\nabla \eta_i \cdot \nabla \eta_j), \quad (8.43)$$

where $v_{\text{el}} = (1/24)(L/m)^3$ is the volume of an element.

8.2.2.2 Tetrakaidecahedral Grain Model

The tetrakaidecahedral grain model (Fig. 8.4c) is constructed on the basis of a cubic object densely piled up by n^3 cubes. The center of a grain is on the body-center or the vertex of a cube. The 14 faces of a grain bisect perpendicularly the straight lines

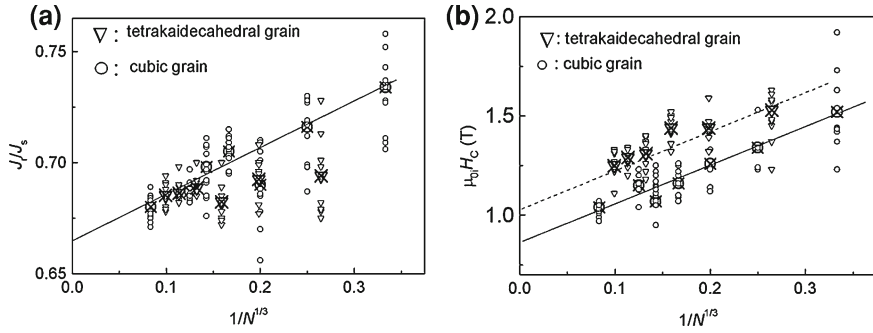


Fig. 8.5 J_r/J_s (a) and $\mu_{0i}H_c$ (b) of calculation versus $1/N^{1/3}$ for nanocrystalline NdFeB. Open symbols with $\times$ symbol represent the average for different $\vec{H}$ directions for the $1/N^{1/3}$ [5]

connecting the center and the 14 centers of the neighbor grains 8 or 6 of which are the vertexes and 6 or 8 neighbor body-centers. Each tetrakaidecahedral grain is also partitioned into many isometric tetrahedral elements of same shape.

8.2.3 Effects of $\vec{H}$ Direction and the Value of N on the Calculation of Hysteresis Curve of Nanocrystalline NdFeB

The hysteresis loop is calculated by decreasing H from 4 to -4 MA/m by step $\Delta H \approx -0.08$ MA/m. The thermal potential is the sum of the exchange interaction, magnetocrystalline anisotropy, Zeeman energy, and magnetostatic energy. The $\vec{J}_s$ space distribution can also be obtained simultaneously if necessary.

Quantitatively reliable calculations of J become much onerous due to the effects of $\vec{H}$ direction and the value of N , which seems inherent in the calculations for nanocrystalline polycrystals consisted of large number of exchange coupled grains. If there is no intergrain exchange interaction in the G model (Stoner–Wohlfarth model), the calculated hysteresis curve for as small as $n = 3$ is already nearly the same with that of $n = \infty$ which is irrelevant to the $\vec{H}$ direction. The situation becomes quite different if the exchange interactions are taken into account. The demagnetization curve depends on both $\vec{H}$ direction and the value of $N = n^3$. Figure 8.5 demonstrates normalized remanence (a) and coercivity (b) as a function of $1/N^{1/3}$ calculated for $L = 20$ nm cubic grains with $m = 4$ by S model and for the same grain volume tetrakaidecahedral grain model. The different values for given $1/N^{1/3}$ are the results calculated in different $\vec{H}$ directions. It can be seen that with decrease of $1/N^{1/3}$ both J_r/J_s and $\mu_{0i}H_c$ decrease along with the range of scattering of them in different $\vec{H}$ directions. The results of G model are close to those of S model. Apparently the final results which we need should be the extensions of the averages for each $1/N^{1/3}$ to $1/N^{1/3} \rightarrow \infty$. Figure 8.5 shows that the averages of J_r/J_s and $\mu_{0i}H_c$ for different $\vec{H}$ directions calculated by the tetrakaidecahedral grain model

Fig. 8.6 $\mu_{0i}H_c$ versus d for nanocrystalline NdFeB

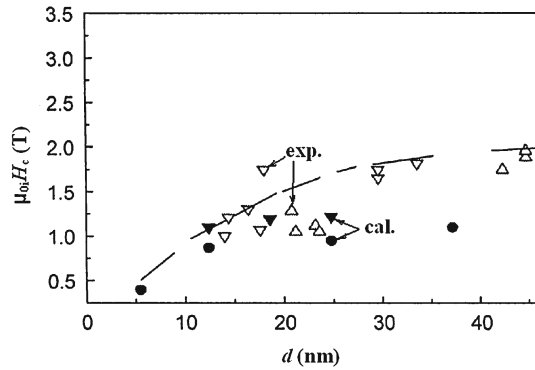
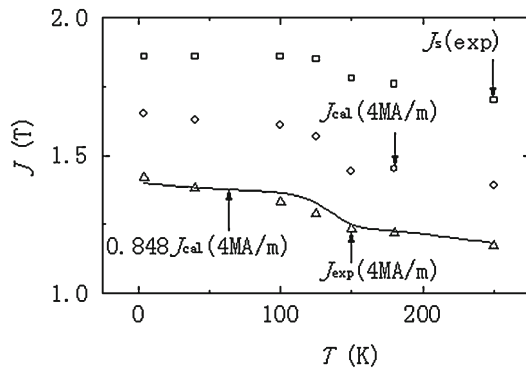


Fig. 8.7 J (4 MA/m) versus T for nanocrystalline NdFeB



are somewhat smaller and larger than those calculated by the cubic grain model. The results are thought to give rise from smaller intergrain exchange interactions in the tetrakaidecahedral grain model due to the smaller ratio of surface area to the volume for the grain. Compared to the effects of N and $\vec{H}$ direction, however, the effect of grain shape is secondary.

In brief conclusion, to get a credible result of J for given H it is necessary to repeat several dozens of $J(\vec{H}, N)$ calculations for different $\vec{H}$ directions and N values and the largest $1/N^{1/3}$ should reach ~ 10 .

8.2.4 Hysteresis Curve of Nanocrystalline NdFeB

8.2.4.1 Coercivity as a Function of Grain Size

Figure 8.6 demonstrates R.T. $\mu_{0i}H_c$ ($N \rightarrow \infty$) as a function of grain size d (defined by the diameter of a sphere of same grain volume) for nanocrystalline NdFeB magnets calculated by cubic (●) [4] and tetrakaidecahedral (▼) [5] grain models.

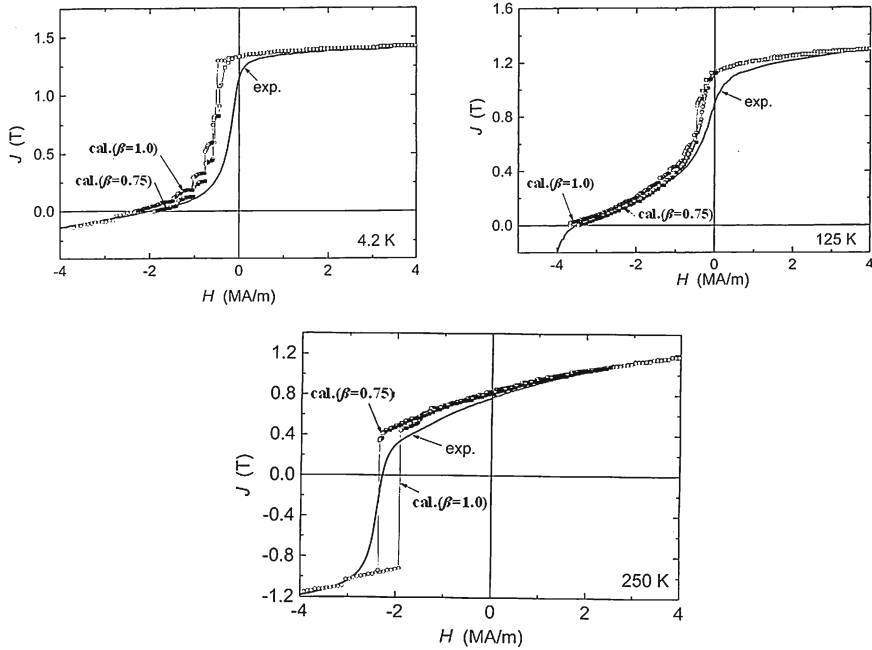


Fig. 8.8 Upper half hysteresis loops of nanocrystalline NdFeB

The periodical boundary conditions hold for the magnets. The experimental data are for melt-spun $\text{Nd}_{2.33}\text{Fe}_{14}\text{B}_{1.06}\text{Si}_{0.21}$ magnets [6]. The mean grain sizes are measured on the free (Δ) and roll (∇) sides of the ribbons. The calculations coincide with experiments very well for small grain sizes. But with increase of grain size, the calculations increase slower than the experiments. The discrepancy arises from the neglect of the effect of non-magnetic boundary phase in the calculations which assumes that the intergrain exchange interaction is the same with the intragrain exchange interaction. The composition of the magnets in the experiments being fixed the thickness of the grain boundary phase increases linearly with increase of the grain size, which causes decrease in the intergrain exchange interaction leading to increase of iH_c with increase of the grain size.

8.2.4.2 Hysteresis Curves at Different Temperatures

The calculations in this paragraph are on the G model magnet of $n = 6$ ($N = 216$), $m = 14$ and $L = 20$ nm. The periodical boundary conditions do not hold for the magnet. The expression of magnetocrystalline anisotropy energy density is

$$F_K = K_1 \sin^2 \theta(i) + K_2 \sin^4 \theta(i) + K_3 \sin^4 \theta(i) \cos[6\phi(i)]. \quad (5.3) \quad (8.44)$$

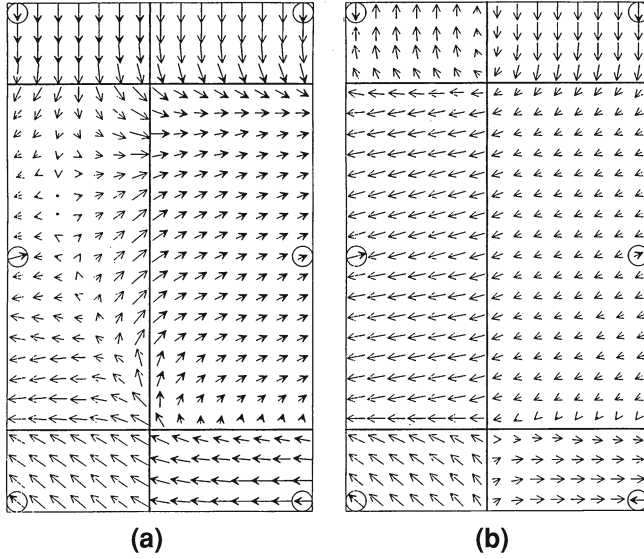


Fig. 8.9 $\vec{J}_s(\vec{r})/J_s$ distribution at the state of $J/J_s = 0.244$ (a) and -0.717 (b)

Preliminarily, a dozen of hysteresis loops at R.T. are calculated in different $\vec{H}$ directions. The following results are for the $\vec{H}$ direction along which iH_c is the smallest.

① $J(4 \text{ MA/m})$ as a Function of Temperature [7]

Figure 8.7 shows the temperature dependences of $0.848J(4 \text{ MA/m})$ of calculations and experimental result of $J(4 \text{ MA/m})$ for nanocrystalline $\text{Nd}_{14}\text{Fe}_{77}\text{B}_{10}$ magnet [8]. The two coincide very well, which shows that the $\text{Nd}_{14}\text{Fe}_{77}\text{B}_{10}$ magnet contains $\sim 15\%$ volume non-magnetic boundary phase.

② Hysteresis Curves at Different Temperatures [7]

In the calculations below the effects of the grain boundary are taken into account by multiplying coefficient β (≤ 1) on (8.40) for the intergrain exchange interactions.

Figure 8.8 demonstrates upper half hysteresis loops of calculation and experiment [8] at 4.2, 125, and 250 K.

Though the calculations reproduce the experiments fairly well, J of the demagnetization curves are larger than the experiments, and the curves have large steps in contrast to the smooth curves of the experiments. Larger value of N should be taken for better quality of the calculations.

8.2.4.3 Space Distribution of $\vec{J}_s/J_s$

Figure 8.9 demonstrates a $\vec{J}_s/J_s$ distribution and its variation near $-iH_c$ during demagnetization process from saturation at 250 K [8]. The calculations are on the G model magnet of $n = 3$ ($N = 27$), $m = 17$, and $L = 20 \text{ nm}$. The periodical boundary

conditions hold for the magnet. The section is cut through the center of the cubic grain model magnet parallel to the magnet surface. $\vec{H}$ is normal to the section. The bold straight lines represent the grain boundaries. The arrows in the circles are the easy direction unit vectors and those outside the circles $\vec{J}_s(\vec{r})/J_s$ in the grains. The length of an arrow represents the projection of $\vec{J}_s(\vec{r})/J_s$ onto the section. The bold arrows represent that the projection of $\vec{J}_s$ on the positive field direction is positive, that is, the vector is not reversed yet, and the thin arrows represent that $\vec{J}_s$ are reversed. Figure 8.9a is at the state of $J/J_s = 0.244$ and Fig. 8.9b at the state of $J/J_s = -0.717$ after H is decreased by a negative step of $\Delta H = -0.08$ MA/m to below $-iH_c$. It can be seen that the magnetization is nonuniform within each grain especially near the grain boundaries and the magnetization reverses through non-coherent rotation even though 20 nm of grain size is one order smaller than 200 nm of critical size for single domain.

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Part II

Magnetic Materials

Chapter 9

Soft Magnetism

Magnetization process has been discussed by both rotation magnetization and domain wall displacement. These two processes are explained to be able to understand easily and intuitively. When the magnetic materials are applied for devices various losses are produced. Hence, the origin of losses is briefly explained. Various kinds of soft magnetic materials have been reported so far. Typical alloys and their magnetic characteristics will be shown.

9.1 Magnetization Process

In the preceding chapter, the concepts of magnetic moment (saturation magnetization), exchange interaction (Curie temperature), magnetic anisotropy, and magnetostriction are discussed. The magnetic characteristics obtained by discussing it phenomenologically using the physical quantity to actually use the magnetic substance as a practical material in that chapter becomes important. Application of a field H causes the magnetization in the direction of field. The most common way to show the magnetic properties of ferromagnetic materials is by plots of magnetization M or magnetic induction B for various field strengths H which is called a magnetization curve. Generally, the process of the magnetization may be divided as shown in Fig. 9.1. Each magnetization proceeds by the rotation of the magnetization or the displacement of the magnetic domain wall which requires less energy than magnetization rotation process.

9.1.1 Rotation Magnetization

Assuming that a material is homogeneous with the same uniaxial anisotropy anywhere in the material, the magnetic field is applied by the angle θ_0 from the direction

Fig. 9.1 Magnetization process

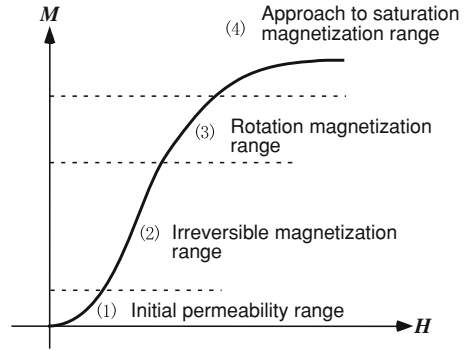
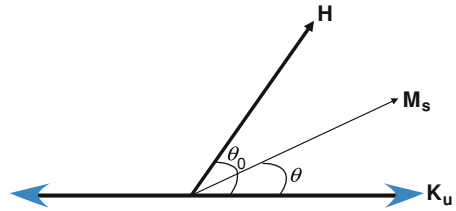


Fig. 9.2 Rotation of magnetization from the easy axis



of the uniaxial magnetic anisotropy as shown in Fig. 9.2. Then the magnetization suitable for a magnetic easy direction may be rotated by the angle θ from the direction of magnetic easy axis.

The energy for each unit volume of the system is given by

$$E = K_u \sin^2 \theta - \mu_0 M_s H \cos (\theta_0 - \theta), \quad (9.1)$$

where K_u is a magnetic uniaxial anisotropy constant. An angle θ may be determined by the minimum condition of the energy of system;

$$\frac{\partial E}{\partial \theta} = 0 \quad \frac{\partial^2 E}{\partial \theta^2} > 0.$$

Thus, a component of the magnetization along the direction of the magnetic field is given by the equation $M_s \cos (\theta_0 - \theta)$. A magnetization curve is obtained by increasing an external magnetic field stronger gradually, and having plotted the magnetic field on the horizontal axis with fixed angle θ_0 . Let us consider how the magnetization changes as the magnetic field increases along some external magnetic fields, though it may be omitted here because the details of calculation have been described in a lot of textbooks. Figure 9.3 shows the change in the energy shown by (9.1), when the magnetic field is applied from the state that the magnetization is suitable for the direction of 0° to the opposite direction (180°). In this figure, $H_k (=2K_u/\mu_0 M_s)$ is an anisotropic magnetic field which may be converted into the magnetic field. Even

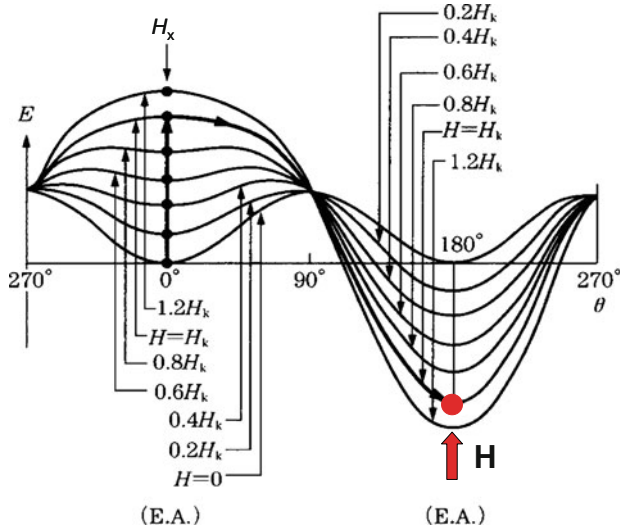


Fig. 9.3 Change in energy when magnetic field is applied in an easy axis of magnetization

if a magnetic field is increased up to $H = H_k$ as shown in Fig. 9.3, a magnetization stays in the minimum point $\theta = 0$ of energy E . At $H = H_k$ the magnetization is suitable for the direction of the magnetic field at $\theta = \theta_0$ that slips down over the top of energy. Next, let us consider the case where the magnetic field is applied in the direction of middle ($\theta = 135^\circ$) between an easy axis and a hard axis (Fig. 9.4).

With a gradual increase in H , a minimal position of energy $\theta = \theta_0$ is moved to right slowly. Correspondingly, it is shifted into the middle between the magnetic field and the direction of 180° higher than $H = 0.5H_k$. In addition, when the magnetic field is made stronger, the position of minimum energy gradually approaches the direction of magnetic field.

Figure 9.5 indicates the case where the magnetic field is applied in the direction of a hard axis. In this case, it is understood that the position of the minimum energy gradually moves from the former magnetic easy direction to the right side by application of small magnetic field. The magnetic field dependence of the magnetization ($M_s \cos(\theta - \theta_0)$) is summarized in Fig. 9.6, when the magnetic field is applied along these three directions $\theta = 180^\circ, 135^\circ$, and 90° . At $\theta_0 = 180^\circ$, the change of magnetization does not occur less than $H = H_k$. However, the magnetization changes from the plus sign into the minus one momentarily at $H = H_k$. At $\theta_0 = 135^\circ$, the magnetization decreases gradually with H up to $H = H_k/2$, which suddenly changes into the minus and approaches the saturation value afterwards. At $\theta_0 = 90^\circ$, it is understood that the magnetization decreases linearly with a decrease of H .

Table 9.1 summarizes both calculated and experimental results of relative permeability (μ_i) by the rotation of magnetization for hexagonal (Co) and cubic (Fe, Ni) crystals. The experimental values are larger by one order compared with the calculated ones.

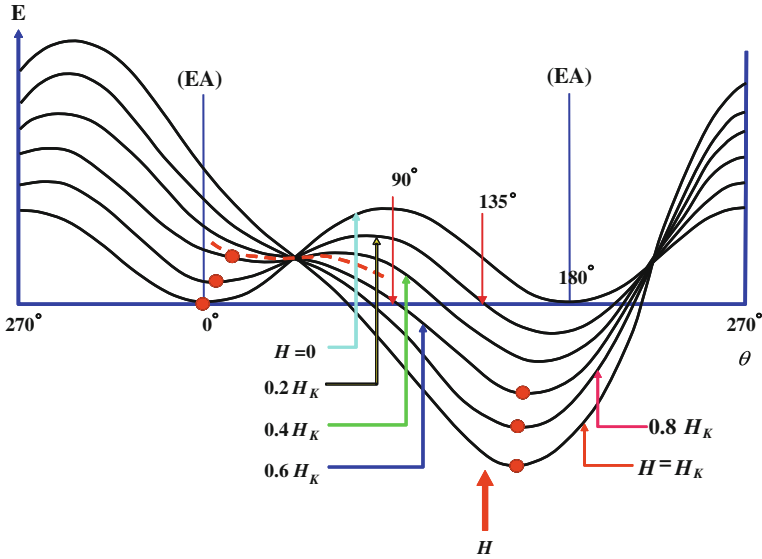
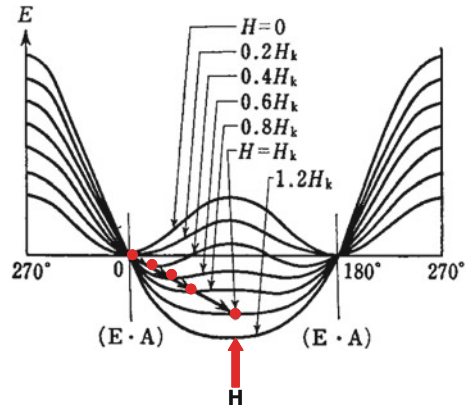


Fig. 9.4 Change in energy when magnetic field is applied in the direction of middle between an easy axis and a hard axis of magnetization

Fig. 9.5 Change in energy when magnetic field is in a hard axis of magnetization



9.1.2 Asteroid Curve

The magnetization in bulk samples in general advances by magnetic wall movement in a small range of field but by the rotation in a large magnetic field. However, a single magnetic domain occurs if the size of magnetic substance is reduced, and the magnetization advances entirely there only by the rotation. The magnetization advances only by the rotation in MRA, etc., the flux reversal of which may be discussed by using the asteroid curve. Then, let us obtain this curve. From the condition

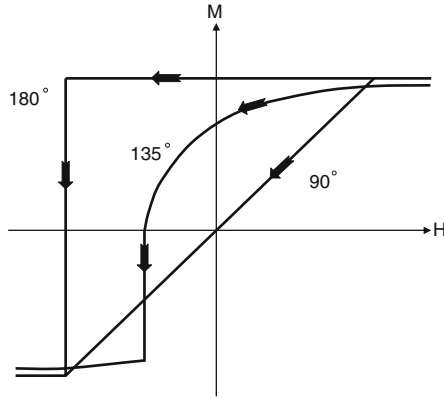


Fig. 9.6 Hysteresis curves calculated by rotation model of magnetization

Table 9.1 Initial permeabilities calculated based on the rotation model and experimental values for Fe, Co, and Ni

Crystal structure	Initial permeability	Calculated	Experiment
Hexagonal (Uniaxial anis.)	$\frac{\mu_0 M_s^2}{3K_u} + 1$	3 (Co)	70
Cubic ($K_1 > 0$)	$\frac{\mu_0 M_s^2}{3K_1} + 1$	30 (Fe)	250
Cubic ($K_1 < 0$)	$-\frac{\mu_0 M_s^2}{2K_1} + 1$	30 (Ni)	300

of stability of energy expressed in the preceding section, we have

$$\frac{\partial E}{\partial \theta} = 0, \quad \frac{\partial^2 E}{\partial \theta^2} > 0$$

Then, we have

$$\frac{1}{2} \sin 2\theta - h \sin (\theta_0 - \theta) = 0 \quad (9.2)$$

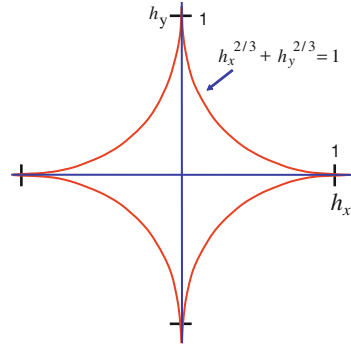
$$\cos 2\theta + h \cos (\theta_0 - \theta) > 0 \quad (9.3)$$

where $h = H/H_k$ and $H_k = 2K_u/\mu_0 M_s$.

Moreover, assuming that ε is an energy normalized with $\mu_0 M_s H_k$,

$$\varepsilon = \frac{1}{2} \sin^2 \theta - h \cos (\theta_0 - \theta). \quad (9.4)$$

Putting $h \cos \theta_0 = h_x$ (element of abscissa of the external field) and $h \sin \theta_0 = h_y$ (element of ordinate of the external field), rewriting (9.4), (9.2), and (9.3), whence

Fig. 9.7 Asteroid curve

$$\varepsilon = \frac{1}{2} \sin^2 \theta - h_x \cos \theta - h_y \sin \theta \quad (9.5)$$

$$\frac{1}{2} \sin 2\theta - h_y \cos \theta + h_x \sin \theta = 0 \quad (9.6)$$

$$\cos 2\theta + h_x \cos \theta + h_y \sin \theta > 0 \quad (9.7)$$

Thus, from these equations,

$$h_x^{2/3} + h_y^{2/3} = 1 \quad (9.8)$$

The relation between both h_x and h_y may be shown for x and y axis, in Fig. 9.7, which is called the Asteroid curve. The magnetization reversal occurs in the magnetic field outside but it does not reverse within the curve.

9.1.3 Magnetic Domain Wall Displacement

The boundary of the magnetic domains is termed as the magnetic domain wall. The magnetization advances with displacement of the magnetic domain wall. To facilitate understanding, let us consider a simple 180° magnetic domain. First of all, the magnetic domain wall is at the position in which the magnetic wall energy is minimized as shown in Fig. 9.8. It is assumed that an external magnetic field is applied along the domain wall, an angle is θ between a magnetic field and a direction of downward magnetization, and x is the shifted distance (Fig. 9.9).

The energy of the state is given by

$$E = U_w - 2\mu_0 M_s H \cos \theta x \quad (9.9)$$

The energy of magnetic domain wall depends on the position. For $-2\mu_0 M_s H \cos \theta x$ of (9.9), the coefficient 2 is adhered on energy by magnetic field because a minus (opposite direction) part is changed into the plus one to the magnetization.

Fig. 9.8 180° domain wall and change of domain wall energy

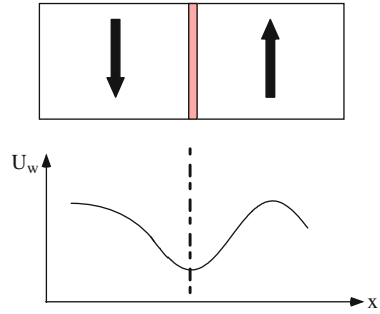
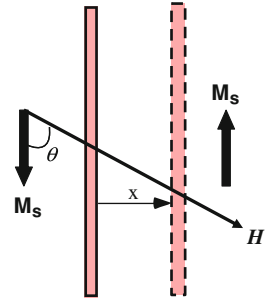


Fig. 9.9 Displacement of 180° domain wall



The position of the magnetic domain wall by applied magnetic field is determined by differentiation of energy of (9.9),

$$\frac{\partial E}{\partial x} = \frac{\partial U_w}{\partial x} - 2\mu_0 M_s H \cos \theta = 0. \quad (9.10)$$

Let us consider how magnetic hysteresis curve can be shown by the magnetic wall movement on magnetizing. The 180° magnetic domain is still assumed for simplicity as shown in Fig. 9.10a, where magnetic field is assumed to be parallel to the magnetic domain. Figure 9.10b shows the change in internal energy of the magnetic domain wall in the sample, and figure (c) shows positional dependence of inclination ($\partial U_w / \partial x$) in internal energy. The magnetic domain wall is situated first at the position where U_w at the center of sample is minimum. The magnetic domain wall moves from the center to the right side, that is, the position where the relation of the (9.2) is satisfied as the magnetic field is increased gradually. The magnetic domain wall returns to the origin through the same route, reducing H to 0 between 0 and point of a . However, the magnetic domain wall goes directly from a to b point when the term $2\mu_0 M_s H$ is increased over the gradient (dU_w/dx) at a point. In addition, the magnetic domain wall reaches d point at a dash when the magnetic field is made stronger and over c point, the magnetization is saturated. (d) the route $0 \rightarrow a \rightarrow b \rightarrow c \rightarrow d$ in the figure shows the magnetization curve corresponding to that of (c). Figure 9.10 of (d); $0 \rightarrow a \rightarrow b \rightarrow c \rightarrow d$ shows magnetization curve corresponding to the one in figure (c).

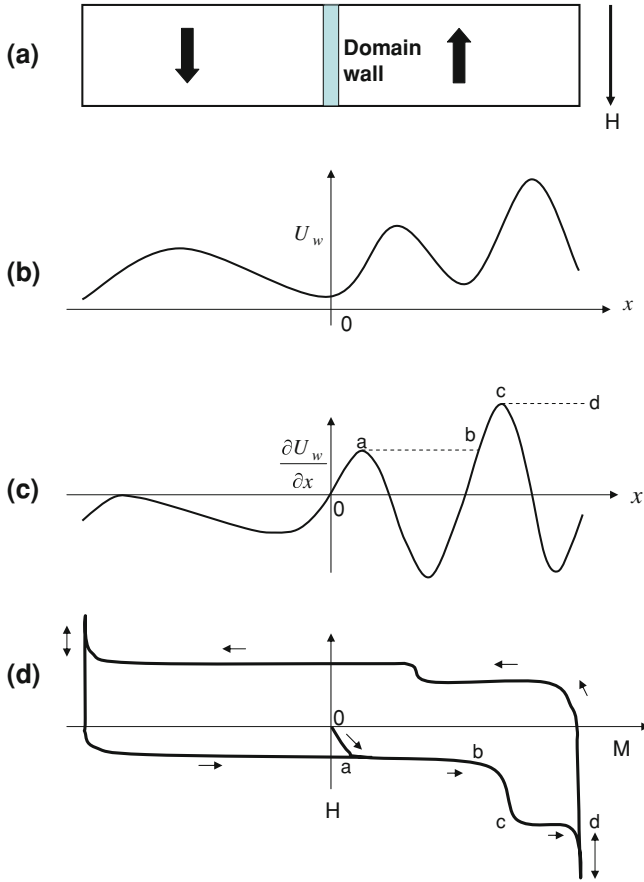


Fig. 9.10 Model of domain wall displacement and corresponding hysteresis curve

That is, a hysteresis with one cycle is shown in (d) where dU_w/dx is assumed in figure (c). Exchanging a horizontal axis for a vertical one, and having made it a usual magnetic hysteresis curve, Fig. 9.11a is obtained. It is, however, assumed that a demagnetizing field slightly is applied to the sample with inclined loops to some extent in order to compare with the experimental result in Fig. 9.11b. Figure 9.11b shows the experimental data of the hysteresis curve of an amorphous $\text{Fe}_5\text{Co}_{70}\text{Si}_{15}\text{B}_{10}$ alloy (rapidly quenched thin film). The feature that the hysteresis loop may advance rapidly by the magnetization at a certain magnetic field (jump of the magnetization), and non-symmetric loop calculated by assuming a magnetic wall displacement may account for the experimental results well. In the next step, it must be clarified why the magnetic wall energy depends on the position of domain wall.

Two models were proposed for the problem years old. On one hand, a stress theory is by Kersten. The stress may be thought not to be homogeneous within the

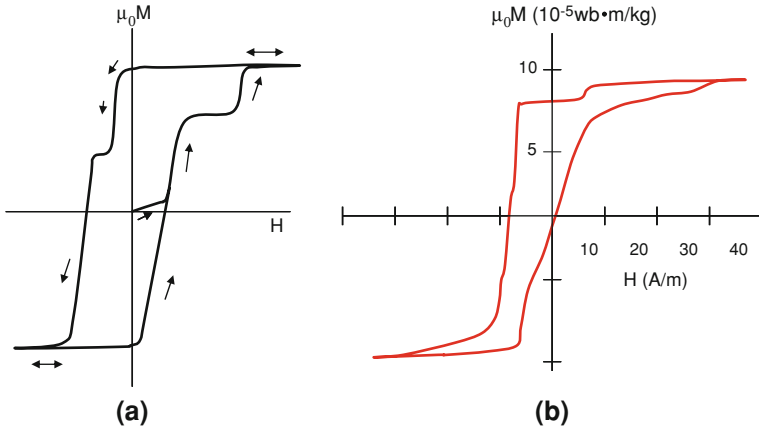
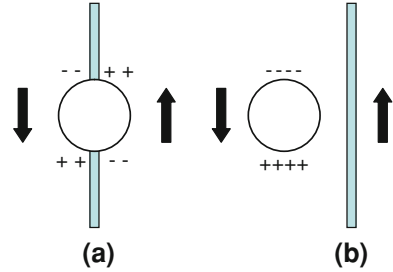


Fig. 9.11 Hysteresis curve calculated by domain wall displacement (a) and hysteresis curve measured for $\text{Fe}_5\text{Co}_{70}\text{Si}_{15}\text{B}_{10}$ amorphous alloy (b)

Fig. 9.12 Model for the change of domain wall

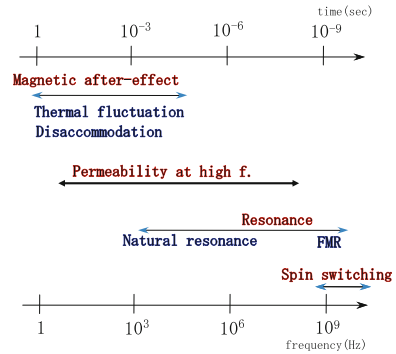


sample. In that case, it is required to convert K in a magnetic wall energy $U_w = C\sqrt{AK}$ to $K + 3\lambda\sigma/2$ (A : the exchange constant, K : anisotropy constant). An initial permeability or a coercive force is discussed simply, assuming that σ may behave in a sinusoidal way like $\sigma = \sigma_0 \cos \frac{2\pi x}{\ell}$. For instance, the initial permeability is

calculated $\frac{2\mu_0 M_s^2}{\pi^2 \lambda \sigma_0} \cdot \frac{\ell}{\delta}$ for the 180° magnetic domain wall and $\frac{4\mu_0 M_s^2}{3\pi \lambda_{100} \sigma_0}$ for the 90° magnetic domain wall, respectively, where δ : the width of the magnetic domain wall, and λ_{100} : magnetostriction for the $[100]$ direction.

The results may be changed largely by how to choose the values of the physical constants such as σ_0 and ℓ . Therefore, a strict discussion is difficult though the values of about 100–200 are obtained. The other one includes the impurity theory of Néel. It is an idea (Fig. 9.12) that the magnetic domain wall is trapped by non-magnetic impurities (defects of various origins, etc.) within the material. Kersten thought that the trapped magnetic domain wall is in the part reduced. On the other hand, Néel thought that about half of magneto-static energy of magnetic domain wall may be decreased by being trapped by impurities. A considerably detailed examination case-

Fig. 9.13 Time scale of the phenomena related to movement of spin



by-case is required to specify either the internal stress change theory of Kersten or the impurity theory of Néel, because the energy $\mu_0 M_s H = 10^{-1} \text{ J/m}^3$ ($M_s H = 10^2 - 10 \text{ erg/cc}$) is negligibly small.

9.1.4 AC Magnetization and Loss

When AC magnetic field is applied to the magnetic material, the accompanying variation in magnetization is called a dynamic magnetization. Over the order of the seconds and 10^{-9} s as shown in Fig. 9.13, various phenomena occur by the time range, and various terms are given to them. A magnetic after effect is called for slow one in timescale by the change of the magnetism that occurs from a small conformational change of the ion or spin in the magnetic substance at room temperature over the wide time range from 10^{-4} s to several hours. Especially, the high frequency permeability after the demagnetization returns to the former value in Mn–Zn ferrite or an amorphous magnetic substance, etc., which degrades permeability with time. Such a phenomenon is especially called disaccommodation (disaccommodation: DA for short), as a time decrease of the real part of the initial permeability following a demagnetization of the sample. On the other hand, ferromagnetic fine particle energy vK_u (v : volume and K_u : magnetic uniaxial anisotropic energy) becomes the same level as thermal energy $k_B T$ when the volume becomes small in a ferromagnetic particle, so that the directions of the magnetization is at random. Thus, the magnetization disappears. This is one of the important problems that should be solved for the development of a high density magnetic recording medium, which is called the thermal fluctuation aftereffect. A signal disappears therefore by thermal fluctuation though the medium should be made of fine particles to increase coercive force of magnetic substance. Moreover, the disappearance of the signal becomes a problem decreasing in the size of the cell even the development of magnetic memory (MRAM) that uses tunnel reluctance (TMR) element (make to a large capacity). In general, magnetic phenomenon which is greatly enhanced at angular frequency acted upon by

an external periodic driving field is called a magnetic resonance. It does not necessarily resonate at the Larmor frequency because the movement is decided by the position (effective field) that the electron feels though the characteristic frequency for the electron (spin) is in principle a Larmor frequency. When the frequency of magnetic field applied to ferromagnetic substance is increased, it reaches to satisfy the resonance condition. In the so-called size resonance or natural resonance, a permeability shows the peak at a certain frequency (order of MHz). On the other hand, when a spin is made to move in a high frequency magnetic field of the small amplitude (order of GHz), and the DC field is increased to reach the resonance condition, ferromagnetic resonance (FMR) or paramagnetic resonance (ESR) occurs. Therefore, the dynamics of the spin from MHz to GHz order will be handled in resonance phenomena. The direction of the magnetization (spin) turns around by the order of nanosecond, when the ferromagnetic substance is applied by the pulse magnetic field, which is called spin switching. One of the advantages in which the magnetic substance is used as a memory is required for very short, and high speed; moreover, it is possible to read rapidly. The scale of the time of the phenomenon is equal to that of FMR mentioned above. The research of the phenomenon mentioned above has been carried out since years old, and it is undesirable on the application, however, the material research that uses these has been done for the resonance and spin switching. Especially, the device comes to be researched, using the phenomenon including MRAM recently, which is interesting to the dynamics of spin at high speed less than 10^{-6} s. The current in which polarized spin is injected into ferromagnetic/insulator/ferromagnetic tunnel junction, and especially, the idea to reverse the magnetization (spin) is important in the development of a large magnetic memory, the indispensable one, and drawn hot attention to the technology that is related to this. Permeability at various f in the table is described here, which explains some losses. Switching in dynamics and MRAM of spin will be described by the accompanying phenomenon in part II spintronics in Chap. 13.

9.1.4.1 Imaginary Part of Permeability and Loss

When the magnetic substance is magnetized by ac magnetic field, $H = H_0 \cos \omega t$, the magnetization (magnetic induction) is delayed in the change of the magnetic field. Then, magnetic induction $B = B_0 \cos(\omega t - \delta)$ may be expressed, assuming δ the delay of the phase. Showing by exponential $H = H_0 e^{j\omega t}$, and $B = B_0 e^{j(\omega t - \delta)}$

$$\mu = \frac{B}{\mu_0 H} = \frac{B_0 e^{j(\omega t - \delta)}}{\mu_0 H_0 e^{j\omega t}} = \frac{B_0}{\mu_0 H_0} e^{-j\delta} = \frac{B_0}{\mu_0 H_0} \cos \delta - j \frac{B_0}{\mu_0 H_0} \sin \delta. \quad (9.11)$$

Putting the real part for $\mu' = \frac{B_0}{\mu_0 H_0} \cos \delta$ and the imaginary part for $\mu'' = \frac{B_0}{\mu_0 H_0} \sin \delta$ Here, we put the real part and the imaginary part of permeability, respectively as follows,

$$\mu = \mu' - j\mu''. \quad (9.12)$$

When the phase has a delay, $\delta > 0$, while the phase has no delay, $\delta = 0$.

Energy consumption per second for each unit volume W is given as, $W = \frac{\omega}{2\pi} \int H dB = \frac{\omega}{2\pi} \int_0^{\frac{2\pi}{\omega}} H \frac{dB}{dt} dt$ $H = H_0 \cos \omega t$, $B = B_0 e^{j(\omega t - \delta)}$ are inserted into the above equation and calculated, whence

$$\begin{aligned} W &= \frac{\omega}{2\pi} \int_0^{\frac{2\pi}{\omega}} -H_0 B_0 \omega \cos \omega t \cdot \sin (\omega t - \delta) dt = \frac{\omega^2}{2\pi} H_0 B_0 \int_0^{\frac{2\pi}{\omega}} \cos^2 \omega t \cdot \sin \delta dt \\ &= \frac{1}{2} \omega H_0 B_0 \sin \delta = \frac{1}{2} \omega \mu'' \mu_0 H_0^2. \end{aligned} \quad (9.13)$$

For soft magnetic material, it is hopeful that μ' is large but μ'' is small. In other words, it is preferable that μ''/μ' is small. Ratio of both quantities

$$\frac{\mu''}{\mu'} = \frac{(B_0/H_0) \sin \delta}{(B_0/H_0) \cos \delta} = \tan \delta \quad (9.14)$$

where $\tan \delta$ or loss factor is expected to be small. Loss factor is considered as the index of the quality of a high frequency magnetic material. Other $\tan \delta/\mu_r$ or $\tan \delta/\mu_i$ etc. is used as an evaluation index.

9.1.4.2 Origin of Losses

The losses, the hysteresis loss and the eddy current loss, are predominant in metals with a small resistivity though it differs in the frequency. On the other hand, the resonance loss that grows by the high frequency besides the hysteresis loss becomes predominant in the ferrites with a large resistivity, and the loss by the eddy current is small. It explains some hysteresis losses and the eddy current losses here.

(a) Hysteresis loss

When the magnetic field is increased a little in addition, the magnetization changes linearly. Moreover, to an additional magnetic field when only little magnetic field is applied to the magnetic substance, the hysteresis appears as shown in Fig. 9.14. This magnetization is given by

$$M = \mu_i H + \frac{1}{2} \eta H^2. \quad (9.15)$$

In the right side of (9.15), the first term expresses the part of M proportional to H and the second term an irreversible part of M to H (see the right side Fig. 9.14), where η is called Rayleigh constant. Note here η is positive for the rising curve and η is negative in the descent curve in the magnetization of $b \rightarrow a$ in figure.

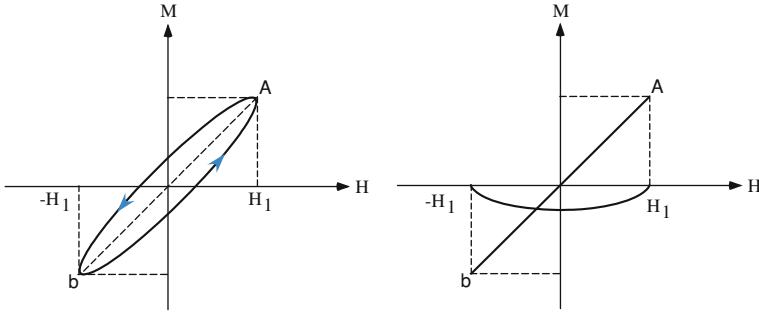


Fig. 9.14 Rayleigh loop

$$M = (\mu_i + \eta H_1) H + \frac{1}{2} \eta (H^2 - H_1^2), \quad (9.16)$$

$$M = (\mu_i + \eta H_1) H - \frac{1}{2} \eta (H^2 - H_1^2). \quad (9.17)$$

Both the ascending and the descending curves can be shown in each of (9.16) and (9.17) by transforming (9.15). Using the magnetization given by (9.16) and (9.17), a loss corresponding to area of hysteresis in one cycle is obtained,

$$W_h = \oint \mu_0 M dH = \frac{4}{3} \eta \mu_0 H_1^3. \quad (9.18)$$

When we show this by describing the loss

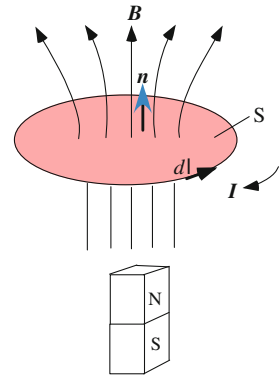
$$\tan \delta_h = \frac{4\eta H_1}{3\pi \mu_i} \quad (9.19)$$

(b) Eddy current loss

Let us recall the Faraday's law of the electromagnetic induction learnt by the electricity and magnetism (Fig. 9.15). When the flux of magnetic induction is changed at time, on this law to cause the current in the direction that decreases the caused flux of magnetic induction. The electromotive force (EMF) produced around a closed path is proportional to the rate of change of the magnetic flux through any surface that is bounded by that path.

In practice, this means that an electrical current will be induced in any closed circuit when the magnetic flux through a surface bounded by the conductor changes. This applies whether the field itself changes in strength or the conductor is moved through it. Electromagnetic induction underlies the operation of generators, all electric motors, transformers, induction motors, synchronous motors, solenoids, and most other electrical machines.

Faraday's law of electromagnetic induction states that: $\varepsilon = -N \frac{d\Phi_B}{dt}$ where ε is the EMF in volts, N is the number of turns of wire, Φ_B is the magnetic flux in webers

Fig. 9.15 Faraday's law

through a single loop. This energy (eddy current) can naturally depend on the shape of the sample, and a special case may be shown by (9.20), where W_e is an energy per one cycle.

$$W_e f = \pi^2 d^2 B^2 f^2 / C \rho \quad (9.20)$$

where an energy or eddy current depends on the shape of the specimen. While $C = 6$ for an infinitely wide board with thickness d , $C = 16$; for an infinitely long cylinder with diameter d , and $C = 20$ for a solid sphere with a diameter d . Additionally, (9.20) may also be given by

$$\tan \delta_e = \frac{\mu \pi d^2 f}{C \rho} \quad (9.21)$$

The loss is small in ferrites which is used for the high frequency (Mz order) while the eddy current loss in the metal is large. However, it originates in a magnetic wall resonance and size resonance peculiar to a high frequency field though most eddy current losses are 0, the peak of μ'' appears, and the loss grows.

9.2 Soft Magnetic Material

9.2.1 Brief Outline

Soft magnetic material is a term that has been used as one of which divides the magnetic materials in two types, comparing it with another hard magnetic material which will be explained in the next chapter. The researcher also composes each group of soft and hard materials and has been researching independently. Because the field of the magnetic material is so wide, one researcher is considerably serious to cover both of them. A huge magnetoresistance effect of a metallic artificial lattice (effect of GMR) is researched actively; however, the classification used

decreases gradually as a reading head is based on the GMR effect. Distinguishing between the soft material and the hard material is even felt old fashioned recently. The application of magnetism is divided into two basically. One is an application as power. A permanent magnet generates the magnetic field. When a current-carrying conductor is located in an external magnetic field perpendicular to the conductor, the conductor experiences a force perpendicular to itself and to the external magnetic field. When the current is flowed simultaneously, the coil receives the moment of power, and rotates the coil. A principal example is a motor in the field where a lot of permanent magnets are used. The material related to hard magnetic properties is as cores in power. The application of the other is a sensor, which was applied to an azimuth measurement device invented in the age of first to third century in China or twelfth to thirteenth century in Orient. The history of magnetism as the sensor develops gradually afterwards, and remarkable development is shown as a magnetic head, living body magnetic engineering, and various rotation sensors of the drive on a hard disk especially recently. The magnetic material related to such a sensor material is a soft magnetic material. This chapter gives what a typical soft magnetic material is here, and it explains historical details of its development. Next, it explains each characteristic among these in order of Permalloy (Fe–Ni alloy) that is a magnetic soft material and the Fe–Co–Ni alloy, the Sendust alloy, and the Fe–Si alloy (directional silicon steel board). We explain simply a magnetic amorphous, a nanocrystal, and a ferrite material.

9.2.2 Details of Development Research of Magnetic Metallic Soft Material

A magnetization of soft magnetic material is changed strongly by a negligibly small magnetic field in general. These materials may be divided roughly by using these in applied fields. One of the magnetic fields covers several A/m~several kA/m (from several to several 10 Oe) of extent in which the hysteresis of the material is a problem from a practicable viewpoint. Another one operates in less than 1 A/m (several mOe) and a very small magnetic field. The core of the transformer is given as an example of the former, and the magnetic head is the typical application example as the latter. As materials, Fe–Si, Fe–Ni (Permalloy), and Fe–Al–Si (Sendust) are given respectively. Such a soft magnetic material has done of the magnetic material with a hard magnetic material of which permanent magnet is representative. It is thought that the research of a soft magnetic material originates the edge near the discovery of the invar alloy (36Ni–Fe alloy and thermal expansion coefficient $\alpha = +1.2 \times 10^{-6}$) by Guillaume in the 1890s. He was given the Nobel prize for the discovery of the invar alloy and the precision measurement in a physics field in 1920. A research of a soft metallic magnetic material accomplished brilliant development by the discovery of Permalloy (21.5Fe–Ni) of Arnold and Elmen in the Bell Telephone laboratory later in 1923, the discovery of the directionality silicon steel board by Goss in 1934,

and the discovery of Sendust alloy (Fe–Al–Si) by Yamamoto in 1932. This field did not advance for a while after the epoch-making development. The research of amorphous alloys started in 1970s, it developed into a soft material of amorphous soft material and the microcrystalline metal and the alloy thereafter, and it extended to the present.

First of all, the saturation magnetization of the magnetic substance should be large as described in the preceding section so that the magnetization applied by a weak magnetic field may change remarkably. It is more important that the obstacle that disturbs the change in the magnetization may be neglected. On the phenomenological consideration of the magnetization mechanism that has been researched so far (the magnetization changes), the movement of the magnetic domain wall and the rotation of the magnetization are thought to be essential. Moreover, the obstacle for the movement of domain wall or the rotation of the magnetization is magnetic anisotropy. The physical quantity in which the extension of magnetic anisotropy of this metal and alloy is a crystalline magnetic anisotropy (K_1 , K_2) and magnetostriction (λ_s) of the alloys. Therefore, if the saturation magnetization is large to some degree at the room temperature, and both of magnetic crystalline anisotropy (K_1 , K_2) and λ_s are zero, a soft magnetic material can be developed, according to this guideline. The development of a soft magnetic material afterwards is based on a metallurgy academic idea excluding a technological idea since then. It is possible to make the state of the material with K_1 zero by not a crystal but keeping amorphous. Then, making the amorphous alloy, K_1 and λ_s become zero simultaneously. The research of amorphous alloys actually used by this guideline has been developed. The saturated magnetic induction for these alloys is not so large, less than 1.1 T (11 kG) as like as or less than that of Sendust. Therefore, the magnetic characteristic for recording head is insufficient. It is required that B_s should be 1.5 in this field. The soft magnetic material is demanded with 1.5 T (15 kG) or more and the researches have been aggressive. The research on this was done about the alloy system that assumed Fe to be a principal ingredient. If the grain size of the crystal was reduced in that case, without keeping amorphous, the research that generated a thin ribbon or the thin film whose λ_s was zero and a set of the microscopic crystal grain became a main current because effective crystalline magnetic anisotropy $\langle K_1 \rangle$ became almost zero. A specific face of crystal is adopted as another method of decreasing $\langle K_1 \rangle$ as far as possible and the method for the distribution is adopted on the film side (sample side) in parallel. Table 9.2 summarizes the approach to get a soft magnetic material.

Anyway, these researches were advanced in these about 20 years. The human lust is unlimited, and is hoped for the material development that B_s is larger, and the one $B_s > 2$ T (20 kG) or more is researched recently. The alloy that satisfies this condition is limited, and the Fe–Co alloy is a subject.

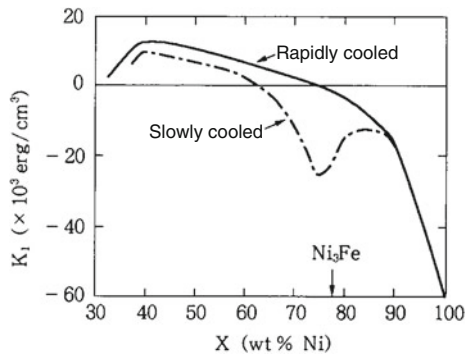
9.2.2.1 Permalloy

Elmen searched for soft magnetism (high permeability material) that was more excellent than the Fe–Si alloy, and found high permeability 30–90 %Ni in the Fe–Ni alloy

Table 9.2 Approach to obtain a soft magnetic material

i) Search an alloy with, $K_1 = 0$, $\lambda_s = 0$ at R.T.		
ii) $\lambda_s = 0$, $\langle K_1 \rangle$	Make an amorphous or fine crystalline alloy	0
	→	
iii) $\lambda_s = 0$, $\langle K_1 \rangle$	Preferred orientation	0
	→	

Fig. 9.16 Crystalline magnetic anisotropy constant of Fe–Ni alloys



system in 1913 according to fine book “Ferromagnetism” by Bozorth [1]. This is a meaning of high permeability alloy which is called Permalloy. The paper about this Permalloy was published in 1923 [2] which was 10 years later from the first finding. This alloy occupies the position as the grand champion of a soft magnetic material since then. If the composition is only chosen for the Fe–Ni alloy, soft magnetic property is not always achieved. Only if the composition shows that both K_1 and λ_s are 0 at room temperatures, then the alloy shows soft magnetic property.

Figures 9.16 and 9.17 show K_1 and λ_s as a function of Ni content for Fe–Ni alloy system. The ordered lattice of Ni_3Fe can be formed in the Fe–Ni alloy centering on 75% at Ni. The influence of ordered lattice on K_1 is especially large though it does not depend on the value of λ_s . That is, in case of slow cooling (ordered state), it becomes 0 at 65%Ni, and it is $1\text{--}2 \times 10^3 \text{ J/m}^3$ in 70–80%Ni. When cooled quickly (disordered state), K_1 becomes 0 in 75%Ni. To the contrary, λ_s hardly changes by the slow or rapid cooling, and it becomes 0 between 80 and 85%Ni. Therefore, to adjust λ_s to almost zero, the composition in the vicinity of 80%Ni should be chosen, cooled quickly. Then K_1 will be close to $\rightarrow 0$ and an initial permeability grows remarkably as indicated in Fig. 9.18.

Fig. 9.17 Magnetostriction of Fe–Ni alloys

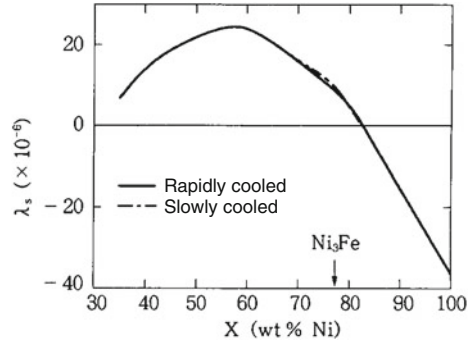
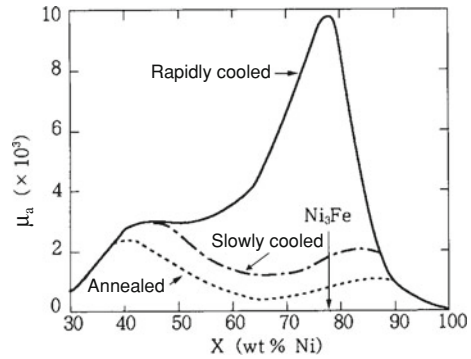


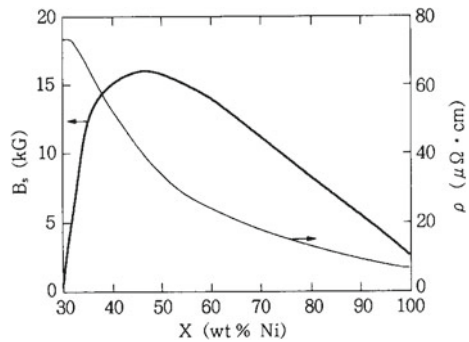
Fig. 9.18 Initial permeability in Fe–Ni alloy



The electromagnetic characteristics of the saturation magnetic induction and the resistivity, in addition to the initial permeability, are also important for the application as practical use of the material, especially as electronics. Figure 9.19 shows these composition dependencies. The electromagnetic characteristic varies greatly depending on the Ni content.

Therefore, Permalloy is classified into several kinds according to usage. Moreover, in order to stop the generation of the ordered lattice, to enlarge the resistivity of the material, or to improve the wear and abrasion resistance, the third elements such as Mo, Cr, Cu, and Nb 3–10% are added in the Fe–Ni alloy. In this case, the material name is given respectively with the addition elements [3, 4]. Permalloy containing 9%Nb, 79%Ni, and 12%Fe is called Hardperm, which is excellent in abrasive resistance, and so it has been useful for recording head. Permalloy is a champion of soft magnetic materials in an excellent soft magnetism, besides easy processing. In many cases, shapes wanted is processed by cutting or piercing after 25–100 μm is pressed. Furthermore, we should take into consideration an induced magnetic anisotropy. Induced magnetic anisotropy is the phenomenon where ferro-magnetic crystals are heated below Curie point and cooled down to room temperature in an externally applied magnetic field; a magnetic anisotropy is induced additionally in which the direction of easy magnetization is nearly parallel to the annealing field.

Fig. 9.19 Saturation magnetic flux density and resistivity of Fe–Ni alloys



A small hysteresis loop can result by heat treatment in a magnetic field transverse to its direction, while a square loop can occur by heat treatment in a longitudinal field. The magnetization curve is often useful in the direction of a magnetic easy axis due to the magnetic-induced anisotropy though it is practicably preferable to be reduced in many cases. The reason why it occurs is that constituent atoms of the alloy may be arranged directionally in the direction of the magnetic field at the high temperature. The usage of Permalloy is varied. There is, especially, a usage of the core for the magnetic head, the high frequency transformer, the pole piece, the magnetic shield, the magnetic amplifier, the reactor, the relay and the core, etc. of the transformer for the communication. Especially, 40 Ni–Fe alloy as the thin film magnetic head and 80 Ni–Fe alloy (Permalloy) as a reading magnetic head using the magneto resistive effect have been useful.

9.2.2.2 Fe–Co–Ni Alloy

As the high permeability material, it excels, and both Permalloy and Sendust alloys described in the next section have been put to practical use in various fields. However, the saturation magnetic induction is too small for a recording material in magnetic devices. B_s was about 1.4 T (14 kG) for the recording head material though the Fe–Ni alloy was used. The material development of larger B_s for a higher recording density was expected.

The composition of above-mentioned $\lambda_s = 0$ was looked for, which explains the Fe–Co–Ni alloy developed on the policy how to make it soft material. Figure 9.20 shows the composition dependence of the crystal structure and saturation magnetostriction constant of Fe–Ni–Co ternary alloys made by the liquid quenching method [5]. There is a composition line of $\lambda_s = 0$ in a composition near the phase boundary of fcc and bcc only in the rich Co composition as seen in the figure. The composition line of $\lambda_s = 0$ in the rich Ni composition is almost equal to the reports in the past. In the composition line neighborhood of $\lambda_s = 0$, B_s is comparatively large 1.8–2.0 T (18–20 kG) (Fig. 9.21) [1]. It is very interesting from a practical point of view, if this can be made magnetic soft material.

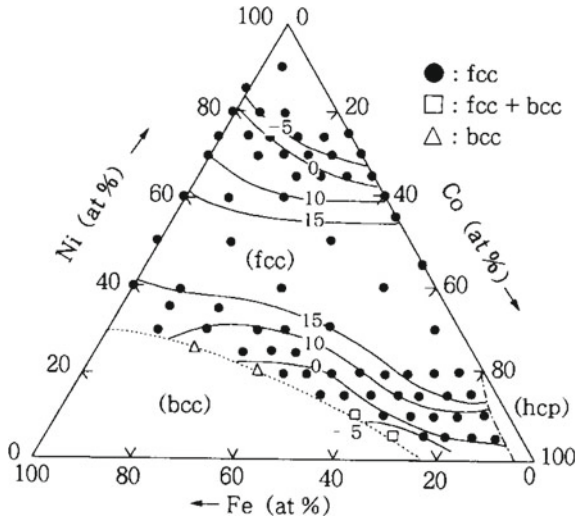


Fig. 9.20 Composition dependence of the crystal structure and saturation magnetostriction constant of Fe–Ni–Co ternary alloys. ●: fcc, □: fcc + bcc, △: bcc

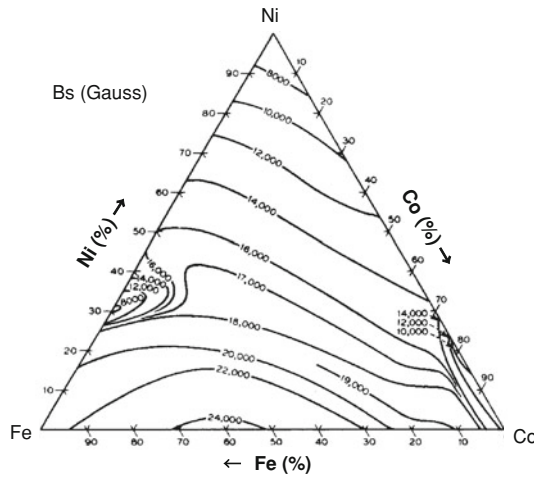


Fig. 9.21 Contours of the saturation magnetic flux density of annealed Fe–Co–Ni alloys (bulk)

Figure 9.22 [6] shows the composition dependence of the coercive force of ternary deposited films in Fe–Co–Ni alloy. The substrate temperature is 320°C with the film thickness about 1,000 Å. Wall coercive force H_w shows a comparatively small value 3–5 Oe in the vicinity of the line of $\lambda_s = 0$ in Fig. 9.20 along the line of $\lambda_s = 0$ as seen in Fig. 9.22. To make it magnetic soft material, we only have to take approach (ii) described first, microcrystalline aggregate. The $\text{Fe}_{26}\text{Co}_{50}\text{Ni}_{24}$ thin film with the film thickness of about 500 nm was made by the sputtering method afterwards, of

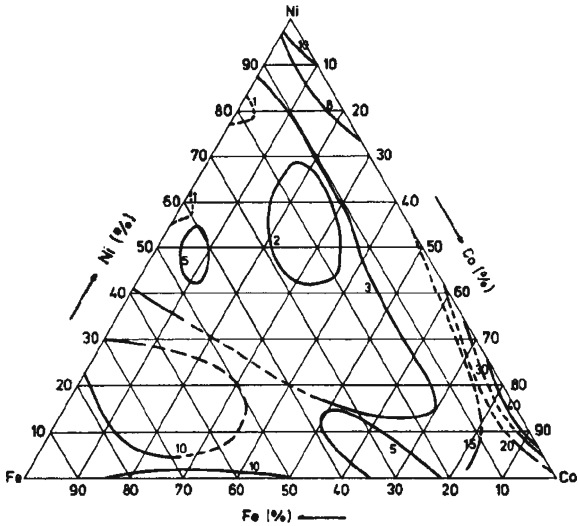


Fig. 9.22 Contours of the wall coercive force H_w (Oe) in evaporated Fe–Co–Ni alloy films

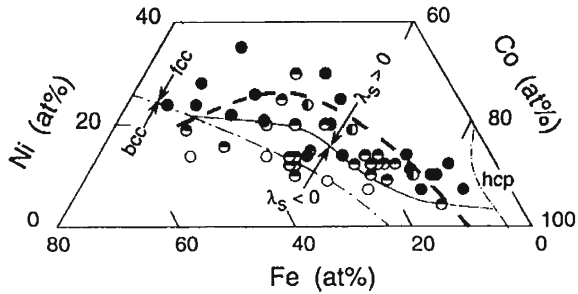


Fig. 9.23 Crystal structure of sputtered Fe–Co–Ni films. O : bcc phase (composite target), ◐ : bcc + fcc phases (composite target), ◑ : bcc + fcc phases (alloy target), ● : fcc phase (composite target). The dotted-and-dashed line shows the phase boundary between the fcc and bcc phases and the fcc and hcp phases for bulk samples. The solid line shows for bulk samples. The broken line shows the phase boundary between the fcc and bcc phases for film samples

which initial permeability $\mu' = 2,100$ in 10 MHz, $B_s = 1.8$ T, resistivity = $18 \mu\Omega \cdot \text{cm}$, and $\lambda_s = 11 \times 10^{-6}$ [7].

These magnetic characteristics, slightly worse than the expected value, are due to existence of the slightly mixed bcc phase in the fcc phase clearly shown afterwards. Though the phase boundary of the fcc phase and the bcc phase shifts to the side where Fe is few in the thin film, it can be returned to Fe-rich side by adding V as shown in Fig. 9.23 [8]. In 4%V doped $\text{Fe}_{26}\text{Co}_{50}\text{Ni}_{24}$ thin alloy film, the magnetic characteristics of $\mu' = 2,200$ (10 MHz), $B_s = 1.76$ T, $H_c = 95$ A/m (2 Oe), resistivity $44 \mu\Omega \cdot \text{cm}$, and $\lambda_s = 9 \times 10^{-6}$ are obtained (Miyazaki, unpublished)). The making of magnetic recording head is included in the formation process of the

thin magnetic film by electrodeposition. The excellent magnetic head material that has the characteristic of $B_s = 2.1 \text{ T}$, $H_c = 95 \text{ A/m}$ (1.2 Oe), and $\lambda_s = 1.8 \times 10^{-6}$ is developed in the $\text{Fe}_{15}\text{Co}_{73}\text{Ni}_{12}$ alloy film recently, though the development of the soft magnetic material for the recording magnetic head by electrodeposition is being advanced [9, 10].

9.2.2.3 Sendust

The alloys containing 9.6 %Si and 4.54 %Al around remainder Fe and 5–11 %Si, 3–8 %Al, and remainder Fe are named Sendust [11], which is a soft magnetic material that succeeds to Permalloy and silicon steel sheets. This was found by a detailed physical measurement of ternary Fe–Al–Si system alloy by combining Fe–Al alloys with an excellent electromagnetic characteristic as well as Fe–Si with an excellent soft magnetism at that time. In this alloy, both of initial permeability μ_i and maximum permeability $\mu_{\max}$ show a steep peak by the composition very limited as shown in Figs. 9.24 and 9.25. This excellent soft magnetism is due to the composition that both λ_s and K_1 are equal to zero, respectively.

The composition was original data of the polycrystalline sample by Zaimonvsky et al. for long time [12]. Two kinds of ordered alloys (B2 and DO3 phase) exist in Fe–Al–Si system alloy. In the single crystalline sample, the composition line [13] of $K_1 = 0$ and $\lambda_3 = 0$ of the DO3 phase (DO3 is generated in slow cooling) and the equal value line of μ_a and $\mu_{\max}$ by Yamamoto et al. are shown in Fig. 9.26. The peak of μ_i and $\mu_{\max}$ almost corresponds to the composition that both K_1 and λ_s are zero. Note that the composition line of $K_1 = 0$ in single crystalline materials is different from that of polycrystalline ones completely. Afterwards, the examination of K_1 and λ_s for the single crystalline samples for Fe–Ga–Si substituted Ga with Al of Fe–Al–Si and Ru doped. Fe–Ru–Ga–Si system alloy was carried out. As a result, the latter was reported to show that both λ_s and K_1 equal to zero and gave rise to the soft magnetism [14].

Figure 9.27 shows the contours of the crystalline magnetic anisotropy constant of Fe–Ga–Si + 8 %Ru alloys (a) and zero lines of λ_{100} , λ_{111} , and K_1 for Fe–Ga–Si + 8 %Ru alloys.

Furthermore, the thin film of alloys processed by sputtering method is reported to be excellent in high frequency magnetic characteristic [15, 16]. Sendust alloy is strong, fragile, and hard as well as Fe_3Si and Fe_3Al . Therefore, the attempt to make a lamina directly by thin film assembly methods [17, 18] from a practical material standpoint or methods [19, 20] of a rapid quenching of liquid has been done. However, a lamina can be done by cutting and grinding by the improvement of the casting process and the advancement of the high precision processing technology afterwards. Moreover, the improvement was added and an excellent Sendust in corrosion resistance was developed though it was easy to have rusted because the Sendust contains a lot of Fe. As the application of the Sendust alloy, the metal for audio and the video were for powder before, and recently used as a dust core hardened with insulation material. The usage as a soft magnetic film of the gap neighborhood in the

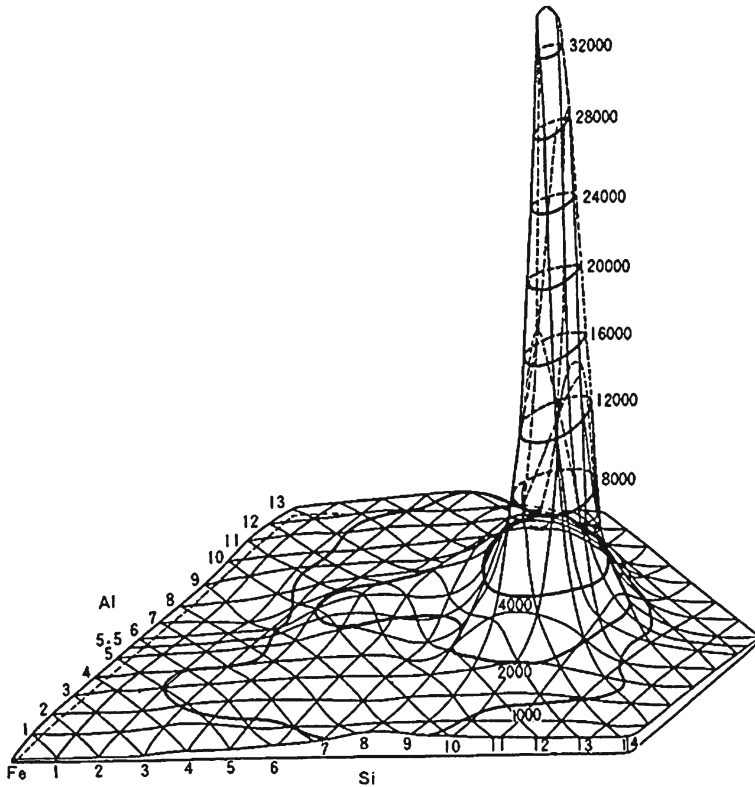


Fig. 9.24 Initial permeability of Sendust alloys

ferrite magnetic core is the majority as the gap compound magnetic head. A bulk of the Sendust system and an electromagnetism characteristic of the thin film were also shown with those of the Permalloy system in Table 9.3.

9.2.2.4 Amorphous, Microcrystal, and Ferrites

Alloys and Sendust were advanced on the principle that magnetostriction and magnetocrystalline anisotropy should be zero for the composition and heat treatment as described in Sect. 9.2. Afterwards, amorphous alloys such as an amorphous ribbon are made rapidly quenched, and it is expected that due to lack of a long range order, neither crystalline magnetic anisotropy nor magnetostriction appears. In the first, amorphous alloy which was found thus in $\text{Fe}_5\text{Co}_{70}\text{Si}_{15}\text{B}_{10}$ alloy [21, 22] is shown in Table 9.4.

Amorphous alloys contain 20–25 % non-magnetic elements that are called a metalloid such as Si and B in general. Therefore, the saturation magnetic induction

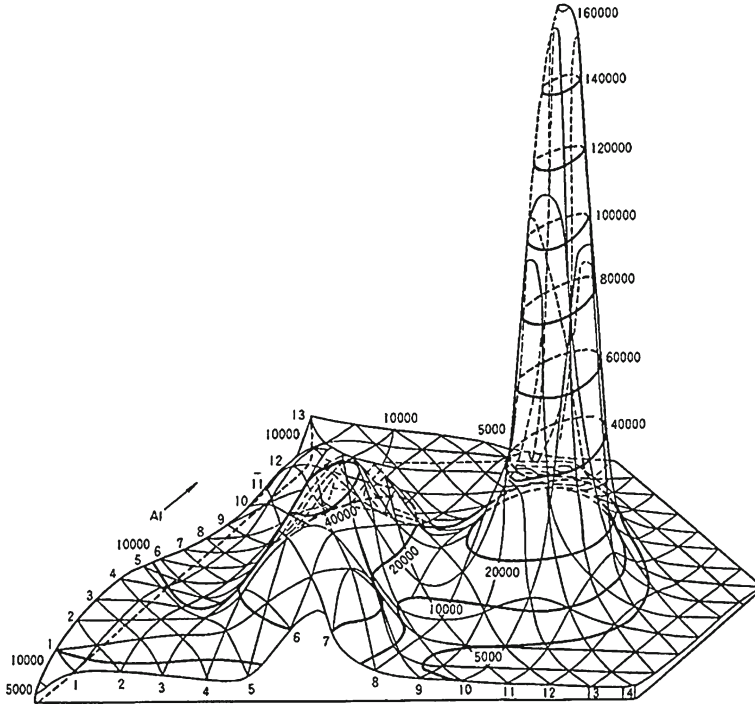


Fig. 9.25 Maximum permeability of Sendust alloys

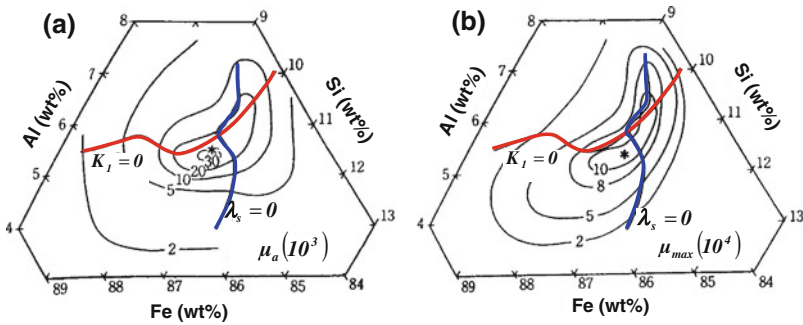


Fig. 9.26 Contours of the initial permeability and $\lambda_s = 0$ lines for Sendust alloys (a) and contours of the maximum permeability and $K_1 = 0$ and $\lambda_s = 0$ lines for Sendust alloys (b)

considerably becomes small compared with that of the Fe–Co alloy system. Moreover, because the amount of composition of Co is large, and Fe is few, B_s is so small as 5 kOe. On the other hand, B_s of the $\text{Fe}_{75}\text{Si}_{10}\text{B}_{15}$ alloy is as much as 14 kOe as seen in Table 9.4. The magnetostriction, however, is also as large as 20×10^{-6} . An alloy of whose magnetostriction is zero was expected for the application as the magnetic head at first. However, the alloy was hardly put to practical use because B_s was small.

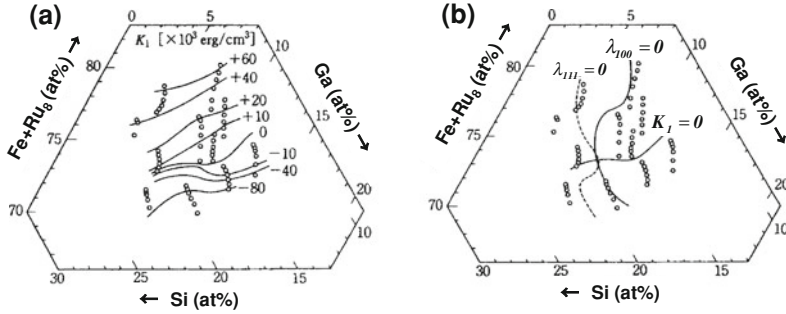


Fig. 9.27 Contours of the crystalline magnetic anisotropy constant of Fe–Ga–Si + 8 %Ru alloys (a) and zero lines of λ_{100} , λ_{111} and K_1 for Fe–Ga–Si + 8 %Ru alloys

On the other hand, the $\text{Fe}_{75}\text{Si}_{15}\text{B}_{10}$ alloy has been put to practical use as a transformer material because B_s is large, though the magnetostriction is large. Moreover, in the alloy of the Fe–Si–B system, 1 at%Cu and 3 at%Nb were doped, and then heat treatment was carried out at temperature before and behind 800 K. As a result, $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{Si}_{13.5}\text{B}_9$ alloy is developed, which is minute about 100 Å crystalline aggregates. [23, 24] The brand name FINEMET is given. The characteristics of two typical FINEMET are compared with those of amorphous and the ferrite which is shown in the table.

9.2.2.5 Mechanism of Soft Magnetic Property for Crystalline Aggregates

The development of a soft magnetic material proceeds, and the material that exceeds the initial permeability expected by the theory by as much as one order has appeared. The discussion of taking influence of macroscopic structures of the material (crystal grain) to the discussion about a coercive force or the initial permeability came to be done. Here we will discuss the softness of fine crystalline aggregate based on the report by Alben et al. [25] and Herzer [26]. Let us consider that the magnetization has been changed as shifting from a magnetic easy direction of the average, and waving as shown in Fig. 9.28.

It is assumed as the wavelength of the wave of this magnetization (characteristic length). Using a magnetocrystalline anisotropic constant K_1 and the exchange stiffness constant A , we have

$$L_{\text{ex}} = (A/K_1)^{1/2}. \quad (9.22)$$

The coercive force and the permeability of the material may be determined from the relation between L_{ex} and crystalline particle size D .

(i) Small grain size of the crystal ($D < L_{\text{ex}}$)

Table 9.3 Magnetic properties of Permalloy, Sendust, and Sofmax alloys

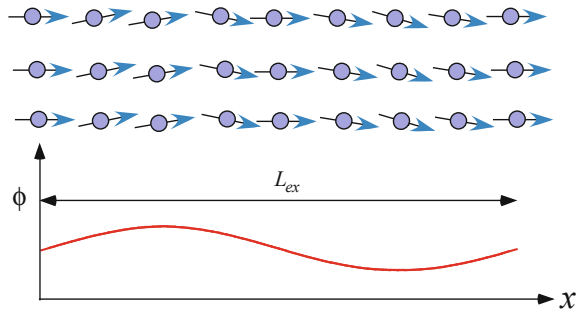
Materials	Composition	$H_c(Oe)$	$\mu_0(10^{-3})$	$\mu_i(10^{-3})$	$\mu_m(10^{-3})$	$B_s(T)$	$T_c(^{\circ}C)$	$\rho(\mu\Omega \cdot cm)$	Remark	Ref.
Permalloy	78.5Ni-Fe	0.05	18	4.3 (1kHz)	100	1.08	400	16	$D = 8.6(g/cm^3)$	1
Permalloy	80Mn-Fe	0.01						60		
Hardperm	79.6Ni ₁₂ Fe ₄ Nb	0.01	42		153	0.66		69		4
Sendust	9.62Si5.38Al balFe	0.62	35.1		117.5	1.1	440	81		12
Sendust	9.66Si6.21Al balFe	0.02	27.3		162	1.1	440			12
Sendust	F-Fe-Al-Si	0.5		1.5-2 (5MHz)		1.0-1.1				
Sofmax	F-Fe ₇₁ Ru ₄ Ga ₇ Si ₁₈			2.3 (1kHz)		1.25	520	130	$D = 7.7$	16
Sofmax	F-Fe ₆₅ Ru ₈ Ga ₈ Si ₁₉					1.0	490	140	$D = 7.9$	17

F: Film

Table 9.4 Magnetic properties of Amorphous, FINEMET and Ferrites

Alloy	$t(\mu\text{m})$	B_s (T)	T_c (K)	$\lambda_s(\times 10^{-6})$	H_c (A/m)	μi (1 kHz)	Loss (kW/m ³)
Fe-Si-B	20	1.41	631	20	6.9	6,000	460
Co-Fe-Si-B	18	0.53	453	0	0.32	80,000	300
FT-1M	20	1.35	843	+2.3	1.3	70,000	350
FT-1L	20	1.35	843	+2.3	1.6	22,000	310
Ni-ZnFerrite		0.38	473	-7.8	30	500	
Mn-ZnFerrite		0.44	>423	-0.6	8	5,300	1,200
Mn-ZnFerrite		0.49	>473	-0.6	12	2,400	680

Loss at 100kHz, 0.2T

Fig. 9.28 Local change of magnetization direction and characteristic length L_{ex} 

Let us consider the volume L_{ex}^3 in the sample (Fig. 9.29). In this volume number $N = (L_{ex}/D)^3$ crystal grains exist and direction of each crystal grain in this volume may be assumed to be random. Therefore, the axis of easy magnetization of individual crystal grain is distributed at random like the arrows in the figure. Then, effective magnetic anisotropy in this area is given

$$\langle K \rangle = K_1 / \sqrt{N}. \quad (9.23)$$

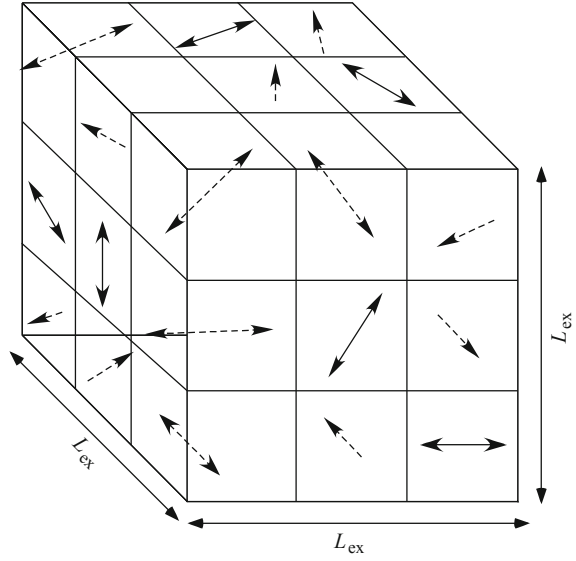
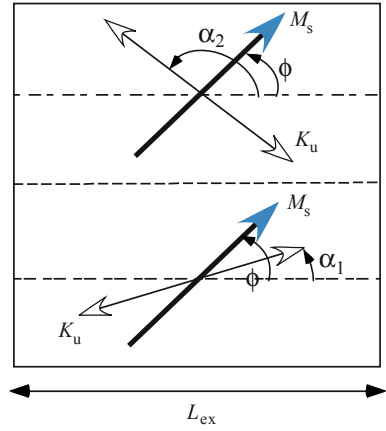
It may be considered about this as follows. The two pieces of the crystalline aggregates are assumed to exist in the area for simpleness (Fig. 9.30).

The angle between the standard and the average magnetization direction is assumed to be ϕ , and α_1 or α_2 in each crystal grain. Here ϕ is the angle between M_s and standard and α_1, α_2 the angle between the standard and easy axis. Then, assuming uniaxial anisotropy, we get the anisotropic energy of the system:

$$\begin{aligned} E_a &= K_1 \sin^2(\phi - \alpha_1) / 2 + K_1 \sin^2(\phi - \alpha_2) / 2 \\ &= K_1 \{1 + \cos(2\alpha_1 - 2\alpha_2)\}^{1/2} \sin^2(\phi - \theta) / \sqrt{2} + \text{constant} \end{aligned} \quad (9.24)$$

which also implies uniaxial magnetic anisotropy.

If there are N crystalline particles in L_{ex}^3 , we get, from analogy of the 2 particle system,

Fig. 9.29 Volume L_{ex}^3 **Fig. 9.30** Two grains with different direction of easy axes

$$E_a = (K_1/N) \sum \sin^2 (\phi - \alpha_i), \quad (9.25)$$

$$E_a \approx K_1 / \sqrt{N} \sin^2 (\phi - \theta). \quad (9.26)$$

Transforming (9.26) leads to (9.27),

$$K_1 \rightarrow \langle K \rangle = K_1 / \sqrt{N} = K_1 (D/L_{\text{ex}})^{3/2} \quad (9.27)$$

Though effective anisotropy decreases like this with a decrease of particle size, L_{ex} or L_{ex}^3 will be changed. Then, putting K_1 to $\langle K \rangle$ in (9.22),

$$L_{\text{ex}} = (A / \langle K \rangle)^{1/2} \quad (9.28)$$

which means that L_{ex} or L_{ex}^3 increases with a decrease in $\langle K \rangle$. Then, when the number of crystal grain included in it increases and it follows the (9.23), it becomes further smaller because area grows. Consequentially by substituting the (9.28) for (9.27)

$$\langle K \rangle = K_1^4 D^6 / A^3. \quad (9.29)$$

Assuming that the magnetic wall energy γ has changed sinusoidally for position x of the domain wall by the magnetic wall displacement, an initial permeability may be expressed:

$$\mu_i \approx \frac{\mu_0 M_s^2 \ell}{\pi^2 (AK_1)^{1/2}} \quad (9.30)$$

where γ is wavelength and $(AK_1)^{1/2}$ corresponds to amplitude.

Replacing K_1 for $\langle K \rangle$ in (9.30) and ℓ for L_{ex} in the fine crystalline grains,

$$\mu_i \approx \frac{\mu_0 M_s^2 A^3}{K_1^4 D^6} \left(H_c = \frac{K_1^4 D^6}{\mu_0 M_s A^3} \right), \quad (9.31)$$

where it is inversely proportional to the sixth power of the particle size of the crystal, and accordingly the grain diameter becomes small, and initial permeability rapidly increases. On the other hand, if the magnetization advances by the rotation, permeability

$$\mu_i \approx \frac{\mu_0 M_s^2}{3 \langle K \rangle} = \frac{\mu_0 M_s^2 A^3}{3 K_1^4 D^6} \left(H_c = \frac{3 K_1^4 D^6}{\mu_0 M_s A^3} \right). \quad (9.32)$$

The discussion mentioned so far is on three-dimensional (bulk or thick film) material. When the film thickness becomes thin (about 500 Å), we get:

$$N = (L_{\text{ex}} / D)^2 \quad (9.33)$$

$$\langle K \rangle = K_1^2 D^2 / A \quad (9.34)$$

Then, initial permeability

$$\mu_i \approx \frac{\mu_0 M_s^2 A}{2 K_1^2 D^2} \left(H_c = \frac{2 K_1^2 D^2}{\mu_0 M_s A} \right) \quad (9.35)$$

is reversely proportional to the second power of D .

(ii) Large particle size of the crystal ($D > L_{\text{ex}}$)

In this case, permeability does not depend on the particle size if the magnetization displaces by the rotation.

$$\mu_i \approx \mu_0 M_s^2 / 3K_1. \quad (9.36)$$

If the magnetization advances by the domain wall movement, $\ell = D$. Therefore, initial permeability will be expressed as

$$\mu_i \approx \frac{\mu_0 M_s^2 D}{(AK_1)^{1/2}} \left(H_c = \frac{(AK_1)^{1/2}}{\mu_0 M_s D} \right). \quad (9.37)$$

It may be shown that initial permeability is proportional to the particle size.

In the various alloy systems described mainly in the thesis of Herzer [27, 28] the relation between the particle size of the crystal and the coercive force is shown in Fig. 9.31. It is understood to satisfy the discussion about the particle size dependence of coercive force overall.

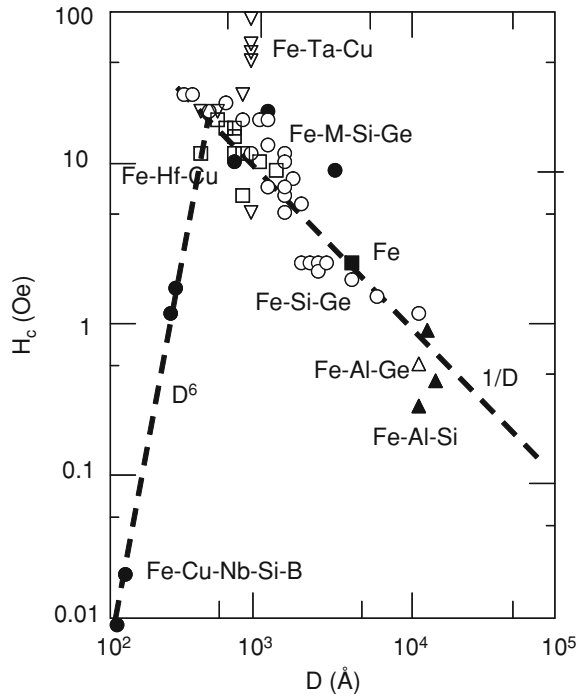
9.2.2.6 Grain-Oriented Silicon Steel

Permalloy, Sendust alloy, and Fe–Co–Ni alloy mentioned above are soft magnetic materials using the point where standing up of the magnetization in a weak magnetic field of mOe (initial permeability) is large with a high frequency, while there is a soft magnetic material using a full loop of the hysteresis curve with a comparatively low frequency. A recent major application of the former is in electronic equipment including the recording head in a magnetic recorder, while the latter one is core material of heavy electrical equipments such as transformers and electric motors. As this material, the large-scale one is a grain-oriented silicon steel (Hereafter, Grain-Oriented Silicon Steel is abbreviated as G.O.) though no oriented silicon steel of various grades is used according to the usage in the small one. G.O. is an iron alloy which may have 3%Si–Fe. It is processed with cold rolling and heat treatment. In the material, the rolling direction is parallel to magnetic easy axis [001] and polycrystalline aggregate of fine particle with several 10 μm and rolling plane (100).

To cause an equal tension on the surface of the steel board, several μm glass film has been courted of which thermal expansion coefficient is smaller than that of Si–Fe. A magnetic characteristic of causing same direction uniaxial anisotropy is improved in [001] directions of tension material by (110)[001] orientation through magnetostriction ($\lambda_{100} = 26 \times 10^{-6}$). A different point from the high permeability material of Permalloy, Fe–Co–Ni alloys, and Sendust is that G.O. has a large saturation magnetic induction, large magnetostriction, and also large crystalline magnetic anisotropy ($B_s 2.04 \text{ T}$, $K_1 = 4\text{--}4.5 \times 10^4 \text{ J/m}^3$).

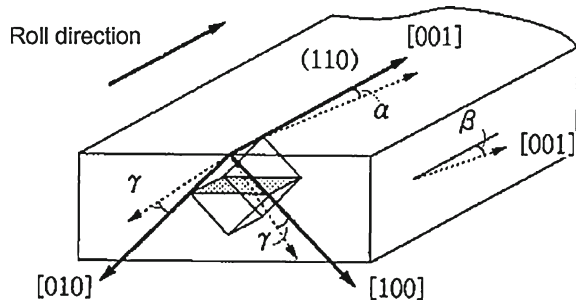
A magnetic characteristic required for the material G.O. is that iron loss (hysteresis loss and eddy current loss) should be small. Iron loss of G.O. decreased rapidly after the invention by Goss in 1934, and W_{15/50} (15: the excitation magnetic induction, 50:50 Hz) was less than 1.0 W/kg. However, there was no substantial change since about 1960, and it was thought that it had been saturated technically. However, a low loss G.O. was invented by a name of (Orientocore HI-B) in 1964.

Fig. 9.31 Coercive force as a function of grain diameter for various kind of alloy systems



After that RGH was sold in 1974, the research for a low loss is continued again [29], and today the minimum $W_{15/50}$ is attained 0.2 W/kg. HI-B and RGH are the (110)[001] oriented materials which were improved by using AlN and SbSe, respectively as a recrystallization control materials in the manufacturing process. As the key technology to decrease iron loss, improvements of (110)[001] oriented integration and the subdivision at 180° magnetic wall intervals were researched actively in the 1980s. A problem on making the (110)[001] oriented material may be solved if single crystalline material were made. The profit cannot be, however, industrially taken. As producing process of G.O., the second re-crystallization and annealing of the first crystallized board were taken. Highly oriented particle is distributed on the board like points in this process, which becomes the nucleus, and grows up. However, it takes time by the enough growth of grain and becomes large crystal grain. As a result, the remaining low-oriented nucleus is generated and grows up in the first re-crystallized area, resulting in deterioration in (110)[001] orientation. To prevent this problem, the method of developing only sharp (110)[001]-oriented particle is taken, for the second re-crystallization nucleus not by heating at the same temperature of the entire steel board but by putting the temperature gradient [30, 31]. Though B_8 increases by raising (110)[001]-oriented integration, the loss does not decrease. The integration must be raised to decrease the loss, and, in addition, it is necessary to subdivide the domain width.

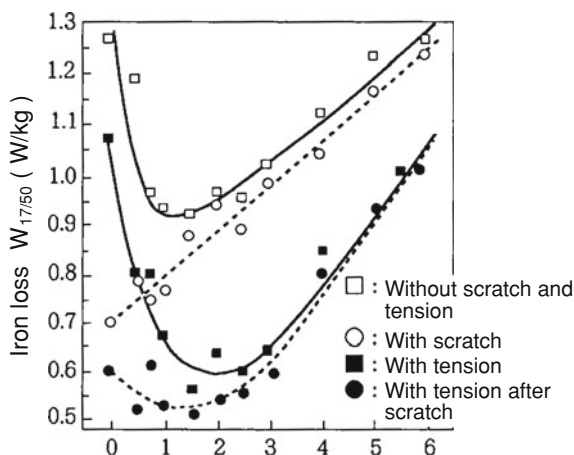
Fig. 9.32 Definition of the misorientation angles α , β and γ of 3%Si-Fe single crystal with (110)[001] orientation



To examine the effect of subdivision on a loss decrease, the experiment in 3%Si-Fe single crystal was carried out [31]. Figure 9.32 shows the sample used schematically.

A solid line indicates the case where the rolling direction completely coincides with [001] axes and the sample side is (110) in an ideal case. The gap from an ideal direction is shown by three angles of α , β , and γ . Here, α is an angle between the direction of the length hand of the sample (roll in case of the rolling sample) and the [001] axes projected to the sample surface. β is an inclination in [001] directions on both surfaces of the sample (roll side). Moreover, γ shows the rotation angle around [001] axes on the surface of the sample. Therefore, the case that $\alpha \neq 0$, $\beta = 0$, and $\gamma = 0$ means shifts of [001] axis from the direction of length hand of the sample, while the case that $\alpha = 0$, $\gamma = 0$, and $\beta \neq 0$ means the shifts from the sample surface. In any case the tension σ of the sample with 0 or $\sigma = 1.5 \text{ kg/mm}^2$, $W_{17/50}$ did not depend on α in $0 \leq \alpha \leq 3^\circ$ according to the experiment. Similarly, $W_{17/50}$ did not depend on γ in $0 \leq \gamma \leq 9^\circ$ irrespective to σ value. On the other hand, when β is changed within the range from 0 to 6° , $W_{17/50}$ strongly depends on β and shows the minimum with $\beta = 1 \sim 2^\circ$ (Fig. 9.33). In the case where scratch, tension, or both are added to the sample, $W_{17/50}$ is also shown in the figure. First of all, the β dependence of $W_{17/50}$ can be understood qualitatively when neither scratch nor tension is added. The domain width increases if β is brought close to 0 . The loss increases so that this may increase in the magnetostatic energy because of the increase of the magnetic pole of both ends of the sample. On the other hand, if β is increased, a part of 180° magnetic domain takes a ring style magnetic district (Lancent domain) which prevents the magnetic pole from going out to both surfaces of the sample. The ratio of which this ring style magnetic district structure (Lancent domain) is taken increases with an increase in β . The effect is larger with a decrease of β though iron loss decreases with any value of β if scratch (depth $0.5\text{--}1 \mu\text{m}$ of the ditch) is put in vertically to [001] of single rystalline sample. The mechanism of decrease of an iron loss by scratch may be due to pulling stress in the vertical direction (direction of length of the sample), which causes making miniaturization of 180° magnetic domain and a decrease in a ring style magnetic district. When β is small as seen in the figure, the effect is small though similar effect can be expected even if the tension is added directly, and iron loss decreases.

Fig. 9.33 Total loss as a function of the misorientation angle β



The ratio of a ring style magnetic district to erase the surface magnetic pole decreases at the point where β is small. In the steel board of practical use, decrease of iron loss is caused by giving tool (kegaki) by steel ball, giving scratch by the Laser light irradiation, or by giving the tension by coating the glass film on the surface. In G.O. made under temperature gradient, with miniaturization of interval of domain wall subdivision added, we can get nearly of the value of 0.3 W/kg as $W_{17/50}$.

Researches mentioned above were mainly carried out in 1980s. Afterwards, the researches have been continued about roughness of surface and iron loss of G.O., ultra thin films under $100\mu\text{m}$ with high crystallographic orientation, and structure of domain wall and magnetostriction in double-oriented cube texture. The development of soft magnetic material and making method and the main characteristic for representative materials were described. It is interesting that there are two extremes for how to bring the material close to single crystal with specific crystal face, on the other hand how to make aggregates of very uniform, fine crystals.

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Chapter 10

Hard Magnetism

This chapter briefly introduces hard magnetism. It contains the sections of Requirement on permanent magnetic properties; Coercivity mechanisms; and Permanent magnetic materials.

10.1 Requirements on Permanent Magnetic Properties

A most important application of permanent magnet is to provide a static magnetic field of specified strength in a designated space such as in magnet motor, magnet generator, magnetic resonance imaging, loudspeaker, actuator, magnetic separator, traveling wave tube, eddy current brake, etc.

Consider the magnetic field energy produced by a magnet and stored in the space outside the magnet. Since it holds

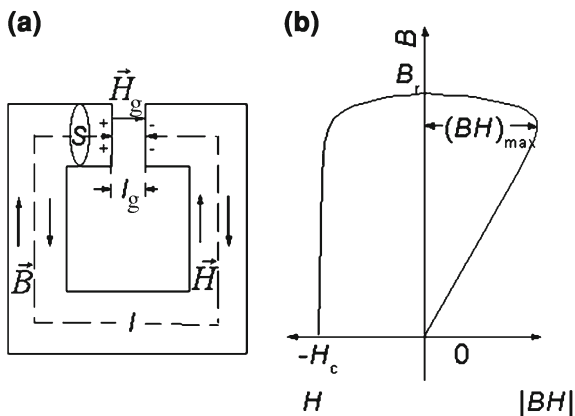
$$\int_{\infty} \vec{B} \cdot \vec{H} dv = 0, \quad (1.72) \quad (10.1)$$

the field energy stored outside a permanent magnet is

$$\frac{1}{2} \int_{\text{space}} \mu_0 H^2 dv = -\frac{1}{2} \int_{\text{magnet}} \vec{B} \cdot \vec{H} dv. \quad (10.2)$$

The signs of B and H in a magnet are opposite and $\vec{B} \cdot \vec{H} = BH < 0$. The energy stored in the space is proportional to the product of the volume v and $|BH|$, a function of B , of the magnet. The relation of the function can be obtained from the demagnetization curve (Fig. 10.1b). The maximum value of $|BH|$ is called maximum energy product or tersely energy product and is denoted by $(BH)_{\max}$.

Fig. 10.1 Magnetic circuit of permanent magnet (a) and energy product (b)



Consider the magnetic circuit of Fig. 10.1a. The length and cross-sectional area of the magnet are l and S , the distance between the pole faces is l_g , the magnetic induction and magnetic field in the magnet are B and H , and the field in the space region between the pole faces is H_g .

According to (10.2) the following relation holds roughly

$$\mu_0 H_g^2 l_g S = -BHS. \quad (10.3)$$

Select the value of l to make $-HB = (BH)_{\max}$, then the minimum volume of the magnet necessary to produce the field H_g is $lS = \mu_0 H_g^2 l_g S / (BH)_{\max}$. The theoretical upper limit of $(BH)_{\max}$ is $B_r^2 / 4\mu_0$. Apparently, the permanent magnet material should have a large $(BH)_{\max}$, that is, large B_r , H_c and a convex demagnetization curve (Fig. 10.1b).

For good temperature stability, the temperature coefficient of B_r and H_c , α_{B_r} and α_{H_c} , should be small. B_r can be increased by aligning the easy axes of the grains parallel. Its upper limit is $B_s \equiv J_s$. The alignment also improves the convexity of the demagnetization curve. H_c being proportional to the anisotropy constant of the material, large magnetocrystalline or shape anisotropy is necessary. High Curie or Néel temperature is advantageous for small temperature coefficients and is necessary for use in a wide range of temperature.

Large B_s is essential for the magnet used for strong magnetic attraction, such as magnetic separation and magnetic lifting.

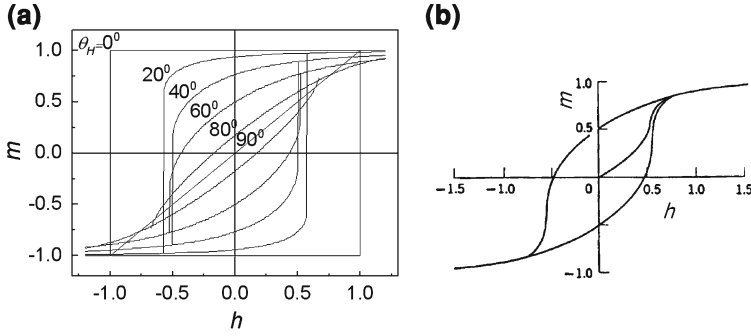


Fig. 10.2 Hysteresis loops calculated for **a** a single domain grain and **b** assembly of randomly oriented single domain grains. $m \equiv M/M_s$, $h \equiv H/H_K$, θ_H : angle between $\vec{H}$ and easy direction

10.2 Coercivity Mechanisms

10.2.1 Coercivity of Rotation Process

If a magnet is consisted of completely aligned non-interacting single domain uniaxial grains of anisotropy constant $K > 0$, and the demagnetization processes through coherent rotation, the hysteresis loop can be calculated from minimum condition of the thermal potential. Figure 10.2 demonstrates the calculated hysteresis loops [1].

The coercivity in the easy direction is the largest which is

$$iH_c = \frac{2K}{J_s} = H_K. \quad (10.4)$$

If the grains are randomly oriented in a magnet,

$$iH_c = 0.48H_K. \quad (10.5)$$

The coercivity of non-coherent rotation processes never exceeds that of (10.4) (Fig. 8.2), and (10.4) of coherent rotation process in the easy direction is the upper limit for the permanent magnetic material.

10.2.2 Characteristics of Coercivity Dominated by Nucleation of Reversed Domain

As was analyzed in Sect. 8.1.2, the nucleation of magnetization reversal in a uniform infinite long cylindrical crystal develops in the whole medium at the negative nucleation field $-H_n$ (Fig. 8.1). Real magnets are nonuniform, and at near-remanent state

dispersed spike-like reverse domains can be observed at grain boundaries, magnet surfaces, impurities, etc, which reveal that a nucleus of reverse domain forms at such inhomogeneous regions of small magnetocrystalline anisotropy and exchange constants and large demagnetizing field overcoming the energy barrier of the anisotropy and exchange energies. The nucleus develops to a spike-like domain extending into the main phase region of larger anisotropy and exchange constants at the field of $-H_g$, which becomes larger with further decrease of the field and transforms to a normal reverse domain reaching the grain boundary at the field of $-H_w$. The normal reverse domain irreversibly expands at the negative pinning field of domain wall movement $-H_p$.

If H_p is not larger than all of H_n , H_g , and H_w , the coercivity of the grain is characterized by the processes of generation and growth of the nucleus and spike-like reverse domain, and the coercivity of the grain is the largest among H_n , H_g , and H_w .

Figure 10.3 demonstrates the hysteresis curves for NdFeB. The magnets consist of aligned grains much larger than the critical size for single-domain. At thermally demagnetized state most of the grains are multidomains. H_p being small the domain wall moves easily within each grain but it is hard to cross across the grain boundary for the majority of grains. The magnetization curve rises sharply around H_p , and essentially saturates at a not very large maximum field H_{mx} . The coercivity increases with further increase of H_{mx} . The characteristic can be explained as follows by taking the simplest case of $H_n > (H_g, H_w) > H_p$ as an example. At the saturation most domains of opposite magnetization are wiped out and the remainders are compressed to spike-like domains and/or nuclei of reverse domain. The coercivity of the grain is H_p if the grain contains at least one spike-like reverse domain or nucleus of reverse domain, and is H_n if the grain contains neither of them. Each of the above critical fields for the magnetization reversal is the coercivity of the grain, and iH_c of the magnet is the average of them. With increase of H_{mx} the number of the grains containing spike-like reverse domains and/or nuclei of reverse domain decreases resulting in successive increase of iH_c to the largest value (Fig. 10.3).

Figure 10.4 demonstrates $\mu_0 iH_c$ as a function of $\mu_0 H_K$ for sintered NdFeB and (NdDy)FeB magnet. It demonstrates that the empirical relation

$$iH_c = \alpha H_K - N_{\text{eff}} M_s \quad (10.6)$$

holds for them. Here α is a coefficient smaller than 1 and N_{eff} is the effective demagnetizing factor. The parameters are sensitive to the microstructure of the magnet.

Fig. 10.3 Magnetization and hysteresis curves of a sintered NdFeB magnet for different H_{mx} [2]

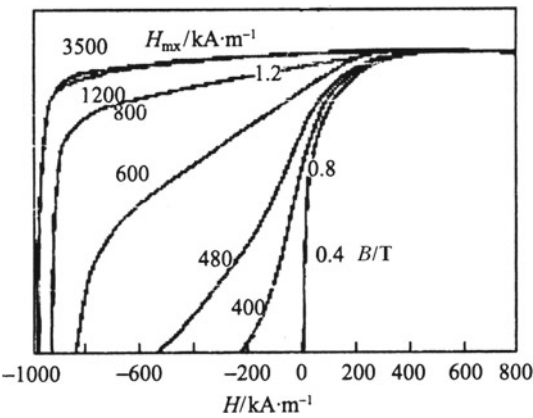
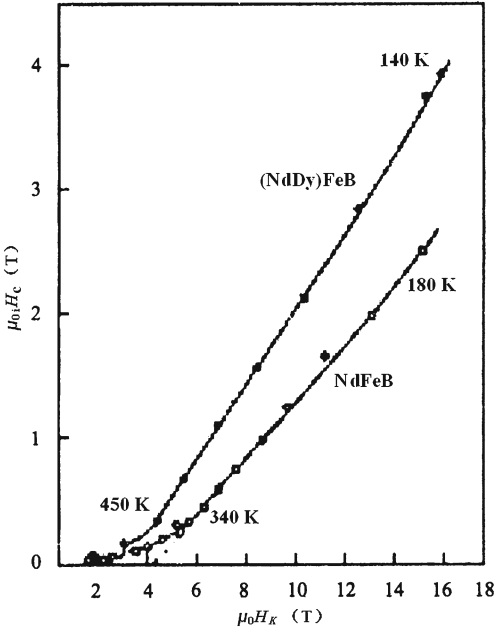


Fig. 10.4 $\mu_{0i}H_c$ versus μ_0H_K for NdFeB and (NdDy)FeB magnets [3]



10.2.3 Characteristics of Coercivity Dominated by Domain Wall Pinning

If H_p is larger than all of H_n , H_g , and H_w , the coercivity of the magnetic material is controlled by the domain wall pinning mechanism. Such magnets have the magnetization curve and minor hysteresis loops like those of SmCoCuFeZr magnets (Fig. 10.5). The B of magnetization curve increases slowly with increase of H and sharply increases around $iH_c = H_p$. After saturation iH_c does not change with H_{mx} .

Fig. 10.5 Magnetization and a part of hysteresis curves of $\text{Sm}(\text{Co}_{0.80}\text{Cu}_{0.14}\text{Fe}_{0.06})_{6.8}$ magnet for different H_{mx} [4]

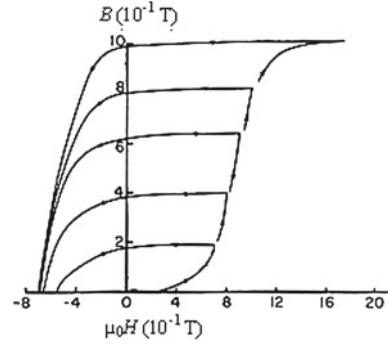
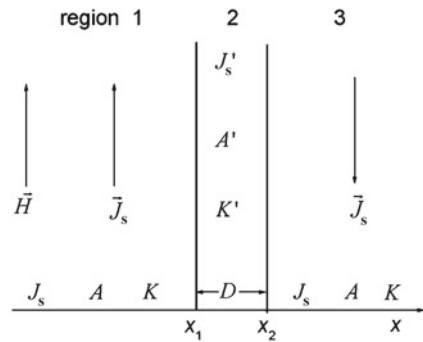


Fig. 10.6 Planar defect model



10.2.4 Coercivity of Domain Wall Pinning at Planar Defect

Consider an infinite magnetic crystal consisting of a major phase and a minor phase [5]. The minor phase of width $D = x_2 - x_1$ occupies region 2 of $x_1 < x < x_2$ and the major phase region 1 of $-\infty < x \leq x_1$ and region 3 of $x_2 \leq x < \infty$ (Fig. 10.6). Both of the phases are uniaxial with easy axes along z axis. The saturation magnetic polarizations, exchange constants and magnetocrystalline anisotropy constants K_1 ($K_{i>1} = 0$) for the major and minor phases are

$$J_s, A, K \ (x \leq x_1, x \geq x_2) \quad \text{and} \quad J'_s, A', K' \ (x_1 < x < x_2). \quad (10.7)$$

Consider a 180° domain wall. The angle between $\vec{J}_s$ and the z direction is θ ,

$$\theta(-\infty) = \frac{d\theta(\pm\infty)}{dx} = 0, \quad \theta(\infty) = \pi. \quad (10.8)$$

The thermal potential density of the wall is

$$G = \int_{-\infty}^{\infty} \left[A_i \left(\frac{d\theta(x)}{dx} \right)^2 + K_i \sin^2 \theta(x) - J_{si} H \cos \theta(x) \right] dx. \quad (i: 1, 2, 3) \quad (10.9)$$

From minimum condition of G we get the boundary conditions at x_1 and x_2

$$A \frac{d\theta(x_{1-})}{dx} = A' \frac{d\theta(x_{1+})}{dx}, \quad A' \frac{d\theta(x_{2-})}{dx} = A \frac{d\theta(x_{2+})}{dx} \quad (10.10)$$

and the Euler equation in each region (Note 1 of this section)

$$-2A_i \frac{d^2\theta(x)}{dx^2} + 2K_i \sin \theta(x) \cos \theta(x) + J_{si} H \sin \theta(x) = 0. \quad (i = 1, 2, 3) \quad (10.11)$$

Integrating (10.11) under the boundary conditions of (10.8) we get

$$-A \left[\frac{d\theta(x)}{dx} \right]^2 + K \sin^2 \theta(x) + J_s H [1 - \cos \theta(x)] = 0, \quad (\text{region1}) \quad (10.12)$$

$$-A \left[\frac{d\theta(x)}{dx} \right]^2 + K \sin^2 \theta(x) - J_s H [1 + \cos \theta(x)] = 0, \quad (\text{region3}) \quad (10.13)$$

$$-A' \left[\frac{d\theta(x)}{dx} \right]^2 + K' \sin^2 \theta(x) - J'_s H \cos \theta(x) = C, \quad (\text{region2}) \quad (10.14)$$

where C is a constant to be determined. Let

$$\theta_1 \equiv \theta(x_1), \quad \theta_2 \equiv \theta(x_2), \quad h \equiv \frac{J_s H}{K}, \quad a \equiv 1 - \frac{A' J'_s}{A J_s}, \quad b \equiv 1 - \frac{A' K'}{A K}. \quad (10.15)$$

Insert $x = x_{1-}$ into (10.12) and $x = x_{2+}$ into (10.13), and multiply each equation by A . Exploiting (10.10) we get

$$\left(A \frac{d\theta}{dx} \Big|_{x_{1-}} \right)^2 = A K \sin^2 \theta_1 + A J_s H (1 - \cos \theta_1) = \left(A' \frac{d\theta}{dx} \Big|_{x_{1+}} \right)^2, \quad (10.16)$$

$$\left(A \frac{d\theta}{dx} \Big|_{x_{2+}} \right)^2 = A K \sin^2 \theta_2 - A J_s H (1 + \cos \theta_2) = \left(A' \frac{d\theta}{dx} \Big|_{x_{2-}} \right)^2. \quad (10.17)$$

Inserting $x = x_{1+}$ and $x = x_{2-}$ into (10.14), respectively, we get

$$\begin{aligned}
C &= -A' \left(\frac{d\theta}{dx} \Big|_{x_1+} \right)^2 + K' \sin^2 \theta_1 - J'_s H \cos \theta_1 \\
&= -A' \left(\frac{d\theta}{dx} \Big|_{x_2-} \right)^2 + K' \sin^2 \theta_2 - J'_s H \cos \theta_2.
\end{aligned} \tag{10.18}$$

Inserting the second relation of (10.16) into the first relation of (10.18) we get

$$C = \left(K' - \frac{AK}{A'} \right) \sin^2 \theta_1 - \left(J'_s - \frac{AJ_s}{A'} \right) H \cos \theta_1 - \frac{AJ_s}{A'} H. \tag{10.19}$$

Inserting the second relations of (10.16) and (10.17) into the second relation of (10.18) we get

$$\begin{aligned}
&-AK \sin^2 \theta_1 - AJ_s H (1 - \cos \theta_1) + (A' K' \sin^2 \theta_1 - A' J'_s H \cos \theta_1) \\
&= -AK \sin^2 \theta_2 + AJ_s H (1 + \cos \theta_2) + (A' K' \sin^2 \theta_2 - A' J'_s H \cos \theta_2),
\end{aligned}$$

i.e.,

$$\left(\cos \theta_1 + \frac{ah}{2b} \right)^2 - \left(\cos \theta_2 + \frac{ah}{2b} \right)^2 = \frac{2h}{b}. \tag{10.20}$$

If the wall spans the minor phase region,

$$A' \left(\frac{d\theta}{dx} \right)^2 = K' \sin^2 \theta - J'_s H \cos \theta - C \neq 0, \tag{10.14} \tag{10.21}$$

and from (10.14) and (10.19) we get

$$\begin{aligned}
D &= \int_{x_1}^{x_2} dx = \int_{\theta_1}^{\theta_2} \left(\frac{K' \sin^2 \theta - J'_s H \cos \theta - C}{A'} \right)^{-\frac{1}{2}} d\theta \\
&= \int_{\theta_1}^{\theta_2} \left[\frac{K' \sin^2 \theta - J'_s H \cos \theta - \left(K' - \frac{AK}{A'} \right) \sin^2 \theta_1 + \left(J'_s H - \frac{AJ_s H}{A'} \right) \cos \theta_1 + \frac{AJ_s H}{A'}}{A'} \right]^{-\frac{1}{2}} d\theta \\
&= \frac{A'}{\sqrt{AK}} \int_{\theta_1}^{\theta_2} [(1-b) \sin^2 \theta - h(1-a) \cos \theta + b \sin^2 \theta_1 - ha \cos \theta_1 + h]^{-1/2} d\theta.
\end{aligned} \tag{10.22}$$

When $H = 0$,

$$\cos \theta_1^2 - \cos \theta_2^2 = 0. \tag{10.20} \tag{10.23}$$

This equation has two kinds of solution:

(1)

$$\theta_1 = \theta_2. \quad (10.24)$$

$\theta(x)$ being a monotonous function of x , it holds (10.18)

$$\left(\frac{d\theta}{dx} \Big|_{x_{1+}} \right)^2 = \left(\frac{d\theta}{dx} \Big|_{x_{2-}} \right)^2 = \frac{d\theta(x)}{dx} = 0, \quad (x_1 < x < x_2) \quad (10.25)$$

that is $\theta_1 = \theta_2 = \theta(x) = 0$ or $=\pi$ ($x_1 < x < x_2$), and the wall is in the major phase.

(2)

$$\theta_1 = \pi - \theta_2, \quad (10.26)$$

that is the center of the wall is at the center of the minor phase.

Assume that initially the wall is at the state of (10.26). If a small H is applied in the $-z$ direction, the wall moves toward $-x$ direction and is pinned at the phase boundary at x_1 . When H is increased to iH_c the wall breaks out of the boundary irreversibly. In general cases iH_c cannot be solved analytically. Two special cases which can be solved analytically will be analyzed below.

① The case of $h \ll 1$ and $\delta_0 (\equiv \sqrt{A/K}) \gg D$.

Equations (10.20) and (10.22) become

$$\cos^2 \theta_1 - \cos^2 \theta_2 = \frac{2h}{b}, \quad (10.27)$$

$$\begin{aligned} D &= \frac{A'}{\sqrt{AK}} \int_{\theta_1}^{\theta_2} [(1-b) \sin^2 \theta + b \sin^2 \theta_1]^{-1/2} d\theta \\ &\approx \frac{A'}{\sqrt{AK}} \int_{\cos^2 \theta_1}^{\cos^2 \theta_2} \frac{1}{\sin \theta_1} \frac{d(-\cos^2 \theta)}{\sin(2\theta)} \left(\theta \approx \theta_1, \quad d\theta = \frac{d(-\cos^2 \theta)}{\sin(2\theta)} \right) \\ &\approx \frac{A'}{\sqrt{AK}} \frac{1}{\sin \theta_1 \sin(2\theta_1)} \frac{2h}{b}. \end{aligned} \quad (10.27) \quad (10.28)$$

Inserting the third and last relations of (10.15) into (10.28) we get

$$h = \frac{J_s H}{K} = \frac{D\sqrt{AK} \left(1 - \frac{A'K'}{AK} \right) \sin \theta_1 \sin(2\theta_1)}{2A'}, \quad (10.29)$$

$$\begin{aligned}
{}_iH_c = H_{\max} &= \frac{K}{J_s} \frac{\sqrt{\frac{A}{K}} D \sqrt{AK} \left(1 - \frac{A'K'}{AK}\right)}{\delta_0 2A'} [\sin \theta_1 \sin(2\theta_1)]_{\max} \\
&= \frac{2K}{3^{3/2} J_s} \frac{D}{\delta_0} \left(\frac{A}{A'} - \frac{K'}{K}\right). \tag{10.30}
\end{aligned}$$

② The case of $\delta_0 \ll D$.

Assume that the wall is pinned at x_1 and the right part of the wall satisfies the condition of $\theta = \pi$ within the region 2. Thus $C = J'_s H$ (10.14) and the region 3 can be taken out of consideration. Multiply (10.12) by A and (10.14) by A' , then subtract the former by the latter at $x = x_1$. By exploiting the first boundary condition of (10.10) we get

$$(AK - A'K') \sin^2 \theta_1 - H(AJ_s - A'J'_s) \cos \theta_1 + H(AJ_s + A'J'_s) = 0,$$

i.e.,

$$h = \frac{b \sin^2 \theta_1}{a \cos \theta_1 - 2 + a}. \tag{10.31}$$

From the maximum condition of $dh/d\theta_1 = 0$ we get

$$\cos \theta_1 = \frac{2 - a - 2\sqrt{1-a}}{a}, \tag{10.32}$$

therefore,

$$\sin^2 \theta_1 = \frac{a^2 - (2 - a - 2\sqrt{1-a})^2}{a^2}. \tag{10.33}$$

Inserting the above relations into (10.31) we get

$$\begin{aligned}
{}_iH_c &= \frac{2K}{J_s} \left(1 - \frac{A'K'}{AK}\right) \left(\frac{1 - \sqrt{A'J'_s/AJ_s}}{1 - A'J'_s/AJ_s}\right)^2 \\
&= H_K \left[1 - \left(\frac{\gamma'_w}{\gamma_w}\right)^2\right] \left(\frac{1 - \sqrt{A'J'_s/AJ_s}}{1 - A'J'_s/AJ_s}\right)^2. \\
&\quad \left(H_K = 2K/J_s, \gamma_w = 4\sqrt{AK}, \gamma'_w = 4\sqrt{A'K'}\right) \tag{10.34}
\end{aligned}$$

Note 1

Consider a general case. Suppose $\theta(x)$ is continuous in the region of $x_a \leq x \leq x_c$, a parameter of medium μ changes discontinuously at x_b within the region, the values of $\theta(x_a)$, $\theta(x_c)$, $\theta_x(x_a) \equiv d\theta/dx|_{x_a}$, and $\theta_x(x_c)$ are fixed, and I is a function of x , $\theta(x)$, $\theta_x(x)$, and μ . Solve the minimum condition of

$$G = \int_{x_a}^{x_c} I [x, \theta(x), \theta_x(x)] dx. \quad (10.35)$$

$$\begin{aligned} \delta G = 0 &= \int_{x_a}^{x_c} \left(\frac{\partial I}{\partial \theta} \delta \theta + \frac{\partial I}{\partial \theta_x} \delta \theta_x \right) dx \\ &= \int_{x_a}^{x_{b-}} \left(\frac{\partial I}{\partial \theta} \delta \theta + \frac{\partial I}{\partial \theta_x} \frac{d}{dx} \delta \theta \right) dx + \int_{x_{b+}}^{x_c} \left(\frac{\partial I}{\partial \theta} \delta \theta + \frac{\partial I}{\partial \theta_x} \frac{d}{dx} \delta \theta \right) dx \\ &= \int_{x_a}^{x_{b-}} \left(\frac{\partial I}{\partial \theta} - \frac{d}{dx} \frac{\partial I}{\partial \theta_x} \right) \delta \theta dx + \left(\frac{\partial I}{\partial \theta_x} \delta \theta \right) \Big|_{x_a}^{x_{b-}} \\ &\quad + \int_{x_{b+}}^{x_c} \left(\frac{\partial I}{\partial \theta} - \frac{d}{dx} \frac{\partial I}{\partial \theta_x} \right) \delta \theta dx + \left(\frac{\partial I}{\partial \theta_x} \delta \theta \right) \Big|_{x_{b+}}^{x_c}. \end{aligned} \quad (10.36)$$

By inserting the relations of $\delta \theta(x_a) = \delta \theta(x_c) = 0$ and $\delta \theta(x_{b-}) = \delta \theta(x_{b+})$ into the above equation we get the boundary condition

$$\frac{\partial I}{\partial \theta_x} \Big|_{x_{b-}} = \frac{\partial I}{\partial \theta_x} \Big|_{x_{b+}} \quad (10.37)$$

and Euler equation

$$\frac{\partial I}{\partial \theta} - \frac{d}{dx} \frac{\partial I}{\partial \theta_x} = 0. \quad (x_a < x < x_b, \quad x_b < x < x_c) \quad (10.38)$$

(10.10 and 10.11) are (10.37 and 10.38) for $x_b = x_1, x_2$ and

$$I = A_i \left(\frac{d\theta(x)}{dx} \right)^2 + K_i \sin^2 \theta(x) - J_{si} H \cos \theta(x). \quad (10.39)$$

10.3 Permanent Magnetic Materials

The percentage of composition in this section is % by weight for crystalline alloys and % in atom for ferrites, compounds and amorphous alloys unless otherwise mentioned.

10.3.1 Survey of Permanent Magnets and Their Properties

Steels alloyed with W, Cr, Mn, Co, etc of $(BH)_{\max} < 10 \text{ kJ/m}^3$ used to be typical magnets applied in the early 1900s. Nowadays Ba(Sr) ferrite, Alnico, and rare earth magnets are the three most important and widely applied permanent magnets. Table 10.1 and Fig. 10.7 shows typical magnetic parameters and demagnetization curves of the permanent magnet series, respectively.

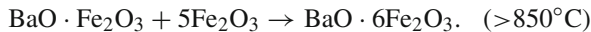
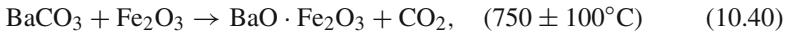
10.3.2 Ba(Sr) Ferrites

The hexagonal Ba and Sr magnets, developed since 1952, are also called M-type ferrites and denoted by BaM and SrM. The large coercivity arises from the large magnetocrystalline anisotropy constants of the main phases Ba(or Sr)O·6Fe₂O₃ (Fig. 3.13, Table 5.1).

10.3.2.1 Manufacture Process and Microstructure

The magnets are prepared mainly by powder metallurgy method as follows.

- ① Ball mill the mixture of powders of BaCO₃ and Fe₂O₃ in the water.
- ② Press the dried powders.
- ③ Presinter the pressed block to form BaO·6Fe₂O₃ phase at $\sim 1, 300^\circ\text{C}$.



- ④ Pulverize the ferrite into powder of around $0.9 \mu\text{m}$ of critical size for single domain (Table 7.2) by coarse crushing and ball milling in the water in sequence. Each particle is a disk parallel to the c plane thickness of which is about one-fourth of the diameter. The pulverized particle contains serious crystal defects and iH_c is small (The defects can be eliminated and iH_c can be increased by annealing at $\sim 1,000^\circ\text{C}$ at which temperature no noticeable sintering takes place [6]).
- ⑤ Dry press in the absence of magnetic field to produce isotropic magnets, or wet press in a strong magnetic field to align the easy c axes to produce anisotropic magnets.
- ⑥ Sinter at $\sim 1, 200^\circ\text{C}$ for hours. Higher the sinter temperature, smaller the amount of void, defects, and iH_c , and larger the grain size and B_s . During the sintering mis-oriented grains of anisotropic ferrite are preferentially removed thus improving the alignment of the grains.

Figure 10.8 Demonstrates a metallographic micrograph of an anisotropic Ba ferrite [6].

Table 10.1 Magnetic properties of major permanent magnets

Material (is. ≡isotropic) (anis. ≡anisotropic)	B_s /T	B_r /T	H_K /(10 ² kA/m)	iH_c /(10 ² kA/m)	$B_s^2/4\mu_0$ /(kJ/m ³)	$(BH)_{max}$ /(kJ/m ³)	T_C or T_N / °C	α_{Br} /(10 ⁻² %/°C)	α_{H_c} /(10 ⁻² %/°C)
Ba ferrite (is.)	0.48	0.2	14	1.5	46	~9	450	20	20
(anis.)	0.48	0.4	14	1.6	46	~29	450	20	40
Sr ferrite (anis.)	0.47	0.4	16	2.7	42	~34	460	20	40
AlNiCoCu (anis.)		1.3		0.5		~40	860	-2	3
(columnar anis.)		1.4		0.6		~60			
AlNiCoFeZr (anis.)		0.8		1.2		~40	800	-2	3
(columnar anis.)		1.2		1.2		~80			
SmCo ₅ (anis.)	1.1	1.0	~290	17	240	150~200	720	-4	-25
SmCoCuFeZr (anis.)	1.2	1.1		8		~240	800	-3	-25
NdFeB (anis.)	1.6	1.4	~55	10	510	~360	310	-10	-70

Fig. 10.7 Typical demagnetization curves of major permanent magnets

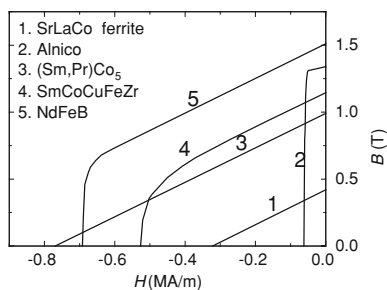
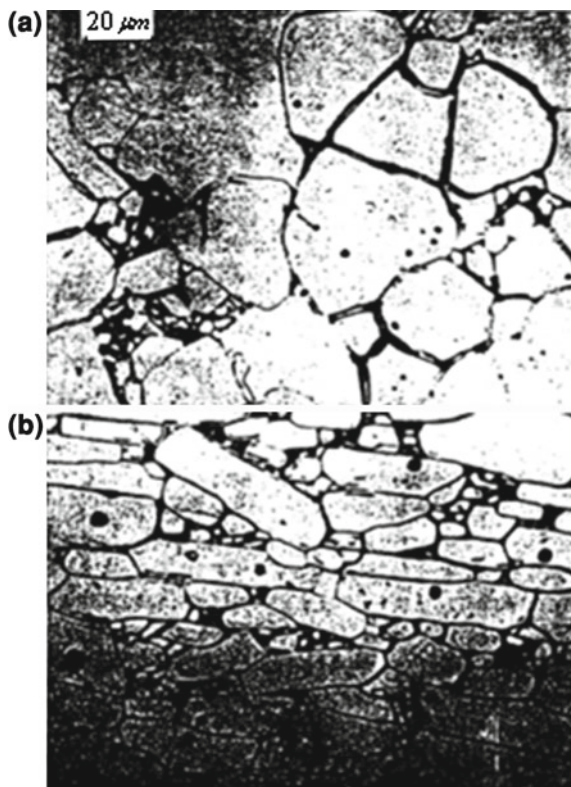


Fig. 10.8 Metallographic micrographs of anisotropic Ba ferrite. Aligned direction: **a** normal to the picture **b** up and down in the picture



Based on the experiences, the additives of 1–5% Bi_2O_3 ($<860^\circ\text{C}$), SiO_2 ($>1,600^\circ\text{C}$), PbO (888°C), CaSiO_3 ($1,540^\circ\text{C}$), $\text{Na}_2\text{B}_4\text{O}_7$ (743°C), H_2BO_3 (117°C), NaF_2 ($>68^\circ\text{C}$), BaAlO_4 , BaSiO_3 , BaB_2O_4 etc are added in BaM, and SrSO_4 , SiO_2 , Al_2O_3 ($2,050^\circ\text{C}$), CaF_2 ($1,418^\circ\text{C}$), CaO ($2,572^\circ\text{C}$), etc in SrM. Here the temperatures in the parentheses are the melting points. The mechanisms of the additives are not very clear. In general, the additives of low melting point are advantageous in lower-

ing sintering temperature, and those of high melting point can obstruct grain growth, thus enhancing iH_c .

10.3.2.2 Magnetic Properties

Being ferrimagnetism B_s is small and hence $(BH)_{\max}$ cannot be large (Table 10.1). The superiorities of the magnets are low prices due to the abundant and cheap raw materials, simple manufacture process, and high electric resistance and chemical stability due to absence of oxidizing Fe^{+2} ion.

The magnetic properties have been improved by doping and adjusting manufacture process. One example is Co–La-substituted Sr ferrite of $Sr_{0.7}La_{0.3}Fe_{11.7}Co_{0.3}O_{19}$ which has $H_K = 18 \times 10^2$ kA/m ($\mu_0 H_K = 2.26$ T), $iH_c = 3.5 \times 10^2$ kA/m ($\mu_{0i} H_c = 0.44$ T), and $B_r = 0.42$ T [7]. Co^{+2} can provide a large magnetocrystalline anisotropy at least at some crystal sites (Sect. 5.2.3.2) and La^{+3} neutralizes the electric charge of the compound arising from partial substitution of three valence Fe^{+3} by two valence Co^{+2} .

They are most widely used in motors and loudspeakers.

The large magnetocrystalline anisotropy of BaM and SrM should arise from the only magnetic ion $Fe^{+3}(3d^5)$. The ground term of Fe^{+3} ion ^6S with $L = 0$ cannot produce a large single ion magnetic anisotropy (Sect. 5.2.3), and the excited terms of $L \neq 0$ should play an important role. A difficulty met in explaining the anisotropy is lack of knowledge about the intensities of the CEF interactions [8].

The grain size of the ferrite is one order larger than the critical size for single domain (Fig. 10.8, Table 7.2). It has been observed by Lorentz microscope and electron holography that the demagnetization of an anisotropic magnet on the demagnetization curve proceeds by domain wall movement, and the wall is pinned at the grain boundaries [9].

10.3.3 Alnico

The development of Alnico magnets began since it was found that an alloy of 58 Fe–30 Ni–12Al had a $\mu_{0i} H_c$ of 0.04 T in 1931, double that of the best magnet steels of the time. Different from ferrite and rare earth permanent magnets, the large magnetic anisotropy of Alnico arises from the shape anisotropy of the $\alpha_1 + \alpha_2$ phase structure (Sect. 5.4.5).

10.3.3.1 Manufacture Process

Alnico magnets are manufactured by either casting or sintering process. A typical process is

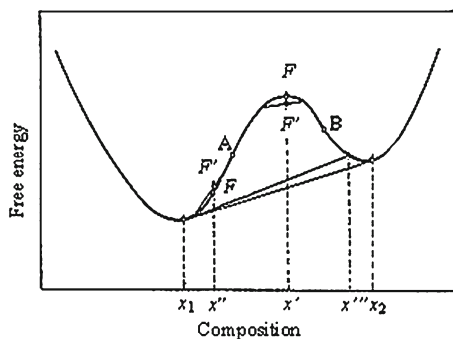
- ① Induction melt in air. Usual casting produces equigranular ingot. An ingot of columnar crystallites for production of anisotropic magnet is produced by casting into a high temperature crucible bottom of which is open and placed on a copper plate cooled by flowing water beneath the plate. The melt solidifies from bottom upward and forms large columnar grains along the solidification direction with $<100>$ axis in the same direction.
- ② Alnico alloy is very hard and brittle. Machining or drilling cannot be accomplished by ordinary methods. If the magnet is very small, or very thin, or the shape is complicated, sinter processing (sintered Alnico) replaces the casting process (cast Alnico). Here the mixture of powders of Fe, Ni, Fe–Co alloy, etc or Alnico alloy of dozens micrometer size is pressed into the magnet shape and sintered at $\sim 1,260^\circ\text{C}$ in a hydrogen atmosphere.
- ③ Solution treatment at $\sim 1,250^\circ\text{C}$ to form the single bcc α phase.
- ④ Dissolution treatment at $\sim 600^\circ\text{C}$ for hours. The α phase dissolves to coherent $\alpha_1 + \alpha_2$ phases. The differences in compositions and M_s between the two phases develop during the treatment. Higher treatment temperature gives rise to coarser $\alpha_1 + \alpha_2$ structure. The temperature and treatment time are adjusted to produce the best composition distribution and fineness of the structure.
- ⑤ For high T_C Alnico of high Co content a magnetic field is applied during the dissolution treatment to produce anisotropic micro structure (Fig. 5.12). If the columnar crystallite alloy magnet is magnetic heat treated in the columnar direction, the effect of the treatment is more effective and the permanent magnetic properties can be enhanced further.

10.3.3.2 Spinodal Decomposition

The characteristic of $\alpha \rightarrow \alpha_1 + \alpha_2$ dissolution is quite different from conventional nucleation and growth processes. Consider a general case [10]. Suppose composition dependence of the free energy $F(x)$ for a single phase binary alloy at a temperature is given by the curve in Fig. 10.9. A and B on the curve are the inflection points so that $\partial^2 F / \partial x^2$ is negative between A and B and positive outside the inflection points. A homogeneous solid solution of composition x' lying between A and B is unstable. In fact any small fluctuations in composition results in lowering of the free energy $F(x')$ to $F'(x')$ and the dissolution proceeds to decompose to two phases compositions of which deviate from x' toward x_1 and x_2 if other energies arising from the decomposition, such as the stress energy arising from different lattice constants of the phases, are neglected. There is no nucleation process and the decomposition proceeds in the whole crystal, and the lattices of the two phases are coherent. This type of dissolution is called spinodal decomposition.

For an alloy of composition x'' outside the composition region between the inflection points small fluctuation in composition causes increase of the free energy from $F(x'')$ to $F'(x'')$ and hence no decomposition occurs. But when the fluctuation produces a nucleus of a fairly different composition such as x''' the free energy of the system decreases making the nucleus grow to decrease the energy further. The com-

Fig. 10.9 Free energy diagram for a binary system



position of the precipitation approaches x_2 and that of the matrix x_1 . This kind of dissolution is the conventional nucleation and growth process.

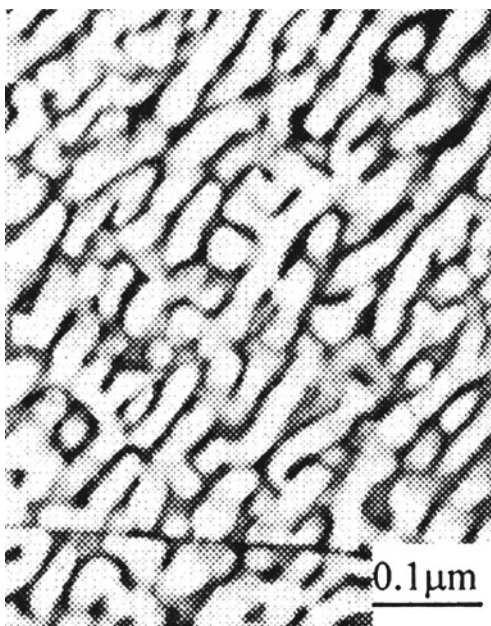
In Alnico Fe, Ni, and Al are basic components and form a single α phase at high temperatures, which spinodally decomposes to $\alpha_1 + \alpha_2$ phases during cooling. Co metal has a very high T_C , and addition of Co can increase T_C for many materials. Alnico belongs to this category, and T_C increases with increase of Co content by accompanying decrease of spinodal decomposition temperature. If both of the temperatures are high enough and T_C is higher than the dissolution temperature, the ferromagnetic precipitate phase α_1 senses the action of magnetic field and precipitates in the form of rods stretched in or near the $\langle 100 \rangle$ axis direction nearest to the field direction to reduce the shape anisotropy energy. Addition of $\sim 5\%$ Ti enhances the ratio of the length to width of the rod (Fig. 5.12) causing increase in the shape anisotropy.

10.3.3.3 Magnetic Properties

Alnico series have large B_r and T_C , small magnetic temperature coefficients and excellent temperature stability. But iH_c are relatively small compared to Ba(Sr) ferrites and rare earth magnets and contain large amount of precious Co. The values of $(BH)_{\max}$ are between those of Ba(Sr) ferrites and rare-earth magnets (Table 10.1, Fig. 10.7). Corrosion resistance is excellent. The magnets are applied in the field of precise instruments, etc which require high temperature stability.

It has been observed by means of electron holography and Lorentz microscope that the demagnetization of Alnico proceeds through entire magnetization reversal in each α_1 grain [11]. iH_c being much smaller than that of coherent rotation, the process should be non-coherent rotation.

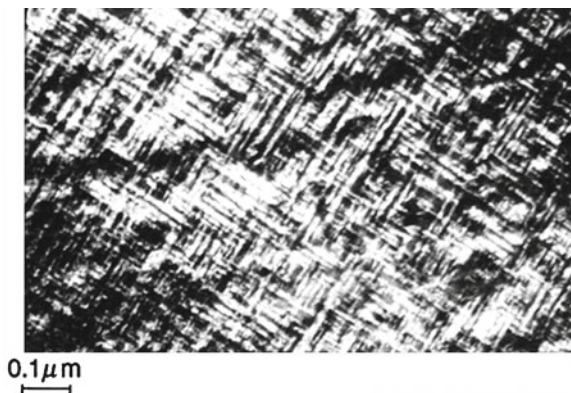
Fig. 10.10 Electron micrograph of Fe–24Cr–15Co–3Mo magnet [13]



10.3.4 FeCrCo

FeCrCo magnet has been developed since early 1970s. It contains small amount of additives Al, Mo, Ti, V, or Nb to improve magnetic properties. The magnets have good ductility and are machinable. The magnetic properties, microstructure, and coercivity mechanism are similar to those of Alnico, but are much sensitive to thermal treatment conditions. The optimal heat treatment cycle for a Fe–28Cr–15Co–3.5Mo–1.8Ti magnet, for example, begins from solution treatment in the temperature range 1,000–1,300°C. The high temperature single bcc α phase breaks down to coherent bcc $\alpha_1 + \alpha_2$ phases by spinodal decomposition during dissolution treatment in the temperature range 630–650°C for 40 min and then in the range 605–625°C for 1–5 h all in a magnetic field, which is followed by tempering at 600°C for 3 h and cooled down to 490°C at the rate of 3°C per hr and hold for 7 h and finally furnace cooled. The α_1 particles (Fe–7.1Cr–15Co–1.3 Mo–3.6Ti) rich in Fe, Co, and Ti are elongated in the magnetic field direction applied during the treatments (Fig. 10.10). α_2 (Fe–26.1Cr–6Co–4.4Mo–0.7Ti) is rich in Cr and Mo. A typical properties of large $(BH)_{\max}$ are $B_r = 1.35$ T, $iH_c = 49$ kA/m, and $(BH)_{\max} = 52$ kJ/m³ and that of large iH_c are $B_r \geq 0.9$ T, $H_c \geq 80$ kA/m and $(BH)_{\max} \geq 28$ kJ/m³ [12]. The magnets are suitable for making small and thin elements of accurate dimensions and complicated shapes.

Fig. 10.11 Microstructure of PtCo magnet in its optimum condition. The streaks are parallel to (110) plane [14]



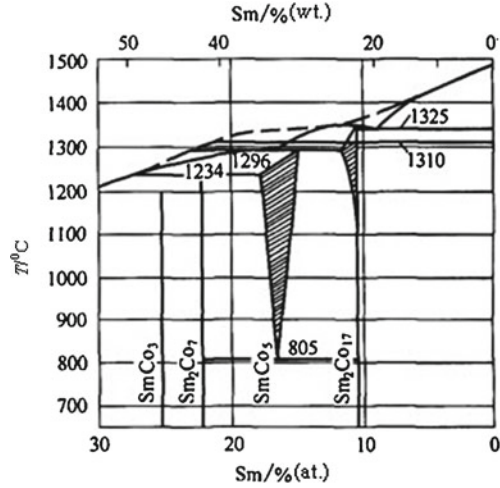
10.3.5 PtCo

The most precious permanent magnet PtCo was developed since early 1970s. It has excellent mechanical and corrosion resistant properties and is used in special cases as a small size magnet.

Pt_{~0.5}Co_{1-~0.5} (atomic %) ingot is solution treated at 1,000–1,100°C for ~2 h to form single disordered fcc A1 phase. Dissolution treatment at ~690°C gives rise to coherent precipitation of fine grains of partially ordered face-centered tetragonal L1₀ phase in the disordered matrix phase through spinodal decomposition. The degree of order enhances with time. The ratio of the lattice constants of fully ordered L1₀ phase is $c/a = 0.97$ in which Pt occupies (0, 0, 0) and (1/2, 1/2, 0) sites and Co (1/2, 0, 1/2) and (0, 1/2, 1/2) sites. The magnetocrystalline anisotropy of the phase is very large ($\mu_0 H_K \approx 13$ T at R.T.) with the easy axis along the c axis. In contrast, the anisotropy of the fcc matrix phase is small. The disorder-order transition also takes place in the matrix phase but much slowly. The c axes of the L1₀ grains are distributed along the [100], [010], and [001] axes to decrease the strain energy of the material. The grains grow to fine lamellae (Fig. 10.11). The last treatment at ~600°C for ~1 h increases the degree of order of both phases and increases iH_c remaining the microscopic structure essentially unchanged. iH_c rises to a peak when about half the material is ordered.

The magnetization vector of the fine fcc matrix phase of softer magnetic properties coupled with the fine hard magnetic L1₀ phase is aligned parallel to the magnetization direction of the latter. Thus PtCo is a two-phase nanocrystalline exchange-coupled composite permanent magnet. The typical magnetic properties of the magnets available in market are $B_r \sim 0.65$ T, $iH_c \sim 500$ kA/m, and $(BH)_{\max} \sim 70$ kJ/m³.

Fig. 10.12 Sm-Co diagram [15]



10.3.6 Foundation of Rare Earth Magnets

The term “rare earth” is misleading. In fact some of these metals are not particularly rare or precious.

The 4f transition element R and 3d transition element T form a series of compounds such as R_mT_n and Sm and Co form Sm_mCo_n (m, n : integer or near integer) compounds of $(m, n) = (1, 2), (1, 3), (2, 7), (1, 5),$ and $(2, 17)$ (Fig. 10.12). In solids 4f ions except Ce are usually in the +3 valence state and preserve the values of magnetic moments of free ions (Fig. 3.8).

Experiments show that the 3d and 4f ion spins in 3d–4f compounds are coupled antiparallel. The orbital moment being quenched, the magnetic moment of 3d ion comes mainly from the spins. Therefore the magnetic moments of the 3d and 4f ions are aligned parallel in the light rare earth 3d compounds and antiparallel in the heavy rare earth 3d compounds.

The request of large B_s makes light rare earth-3d metal compounds only the candidate for rare earth permanent magnetic materials. Fortunately resources of light rare earths are much abundant and prices are much cheaper than heavy rare earths. Among light rare earths the total angular momenta of La^{+3} , Ce^{+4} , and Eu^{+3} are zero and have no magnetic moment. Pm^{+3} being radioactive is out of consideration. Thus the remaining Nd^{+3} , Pr^{+3} , and Sm^{+3} of atomic magnetic polarization moments $g_J J \mu_B = 3.27, 3.20,$ and $0.71 \mu_B$ (Table 2.3) constitute the major 4f constituents. Their main role is to provide large magnetocrystalline anisotropy. The request of large B_s and high T_C makes Fe ($B_s = 2.16 \text{ T}$, $T_C = 770^{\circ}\text{C}$) and Co ($B_s = 1.79 \text{ T}$, $T_C = 1,115^{\circ}\text{C}$) the major 3d components, while Ni ($B_s = 0.61 \text{ T}$, $T_C = 358^{\circ}\text{C}$) of small B_s and low T_C is excluded as the component.

Rare earth magnets have largest $(BH)_{\max}$ (Table 10.1, Fig. 10.7). There are mainly three magnet series of $(\text{Sm}, \text{Pr})\text{Co}_5$, SmCoCuFeZr , and NdFeB .

The rare earth metals being easily oxidized, the melting, milling, sintering, and annealing are processed in vacuum or shielded atmosphere.

10.3.7 SmCo_5

SmCo_5 is the first-generation rare earth magnets exploited around 1970. SmCo_5 has hexagonal crystal structure (Fig. 5.3). The magnetocrystalline anisotropy constant at R.T. is the largest among all magnetic materials (Table 5.1).

10.3.7.1 Manufacture Process and Microstructure

A typical manufacturing process of sintered SmCo_5 is

- ① Induction melt $\text{Sm}_{1+x}\text{Co}_5$ alloy in vacuum. An additional Sm is added to cover the loss of Sm caused by preferential oxidization during the melting and following processes. As SmCo_5 is produced through peritectic reaction during solidification it is difficult to avoid precipitation of Sm_2Co_7 , $\text{Sm}_5\text{Co}_{19}$, and even Co phases (Fig. 10.12). The precipitations are very difficult to eliminate through homogenization treatment at high temperature.
- ② Pulverize with a coarse grind and jet mill in sequence to obtain powder of 3–5 μm mean particle size in an inertial atmosphere. Most of the particles are monocrystals. On contrary if it is milled to 1.3 μm of the critical size for single domain, the iH_c of the magnet decreases. An important cause of the decrease is the partial oxidization of Sm on the surface of each particle during the subsequent processes under the influence of the oxygen absorbed on the surface during the milling which makes the effective composition of the compound on the surface Sm poor [16].
- ③ Press in a magnetic field to align the c axes of the grain particles followed by isostatic press for densification.
- ④ Sinter at 1,100–1,200°C for ~ 0.5 h. The crystallites grow $\sim 10 \mu\text{m}$ in size.
- ⑤ Slowly cool to 850–900°C (1–2°C/min), hold for 1–4 h at the temperature to refine the grain boundary texture.
- ⑥ Quickly cool ($\sim 200^\circ\text{C}/\text{min}$) to R.T..

The composition of the SmCo_5 magnets are slightly hyperstoichiometric with small excess of Sm. Except the hard magnetic matrix SmCo_5 grains, the magnets contain major second phase formed by layers of phases of Sm_2Co_7 , $\text{Sm}_5\text{Co}_{19}$, etc and minor Sm_2O_3 , Sm-rich phase and pores (Fig. 10.13).

SmCo_5 alloy can also be prepared by reduction-diffusion method:

- ① The mixture of powders of Sm_2O_3 , Co metal, and Ca grains or CaH_2 is loaded into a steel can fully filled with Ar.

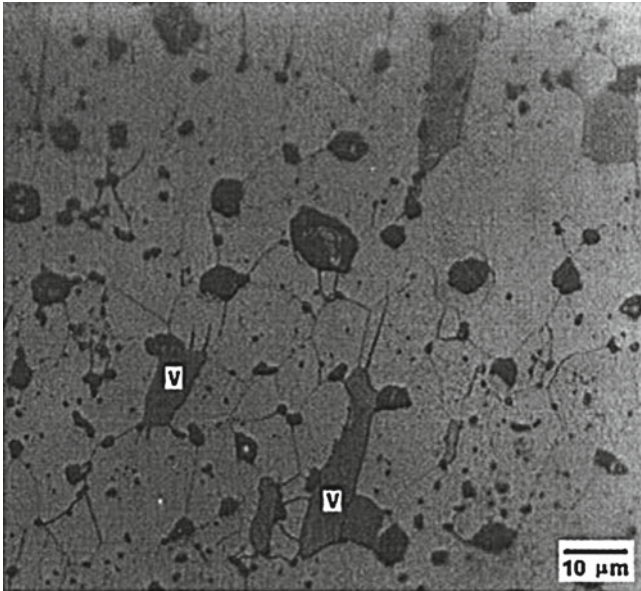


Fig. 10.13 Microstructure of sintered SmCo₅ magnet. Gray regions: SmCo₅; Darker grains two of them labeled by V: main second phase consisting of Sm₂Co₁₇, Sm₅Co₁₉, etc. The other dark regions of small size: Sm₂O₃ and pores [17]

- ② By heating the can, the SmCo₅ alloy gobbets form through an intense exothermic reaction



The gobbets do not contain Sm₂Co₇, Sm₅Co₁₉, etc precipitations.

- ③ The crushed gobbets are put into water. They disintegrate into powder emitting heat.
 ④ Wash away the impurities of CaO, Ca(OH)₂, CaCO₃, etc.

10.3.7.2 Magnetic Properties

iH_c of as-sintered magnet is small. High iH_c develops after the heat treatment at 850–900°C. At thermally demagnetized state most of the grains are multi domains. In most cases the domain structure within grains is independent of their neighbors, but in some cases the domain walls were observed to extend through the grain boundaries caused by the magnetostatic interaction between neighboring grains. The domain walls move easily within the grains. In most cases the magnetization reversal processes in individual grains proceed independently. Nevertheless, in some cases (not so rare), group wise magnetization reversal of adjacent grains takes place,

Table 10.2 Lattice constants of the main phase and coercivity after different heat treatments [17]

	Sintered	Normally heat treated	Annealed at 750°C for 25 days after normal heat treatment
c (10^{-1} nm)	3.962	3.967–3.968	3.960–3.961
a (10^{-1} nm)	5.004	5.001–5.002	5.006–5.007
$\mu_{0i}H_c$ (T)	0.17	2.54–2.90	0.05–0.48

an unfavorable effect for high- iH_c magnets. The magnetization reversal mechanism is mainly related to the nucleation and growth of reversed domains [18].

If the magnet is heat treated at 700–750°C for a short time or cooled slowly in this temperature range after the heat treatment at 850–900°C, iH_c decreases dramatically. The grains remain strikingly free of defects such as dislocations or stacking faults and no second phases precipitate at grain boundaries. The nucleation of reversed domains takes place in regions with low magnetocrystalline anisotropy. Some authors report that the SmCo_5 phase decomposes into $\text{Sm}_2\text{Co}_{17}$ and Sm_2Co_7 phases under the treatment at 700–750°C, while other authors did not observe such decomposition even after 25 days treatment. The magnet of large iH_c state has slightly smaller value of lattice constant a and larger c than smaller iH_c states (Table 10.2).

Though it is generally accepted that the coercivity mechanism is nucleation of reverse domains, the reverse domain nucleation center remains under discussion. Some authors suspect that structural defects induce a severe reduction of iH_c and the elimination of defects at the atomic level is responsible for the increase of iH_c due to the heat treatment at 850–900 °C [17]. Some calculations demonstrate that many kinds of nearest and second nearest Sm vacancies change the easy direction of the central Sm ion from c axis to c plane [19].

The resources of Sm being much less abundant than Pr and Nd and the magnet containing large amount of precious Co, SmCo_5 magnet is precious. It is hard and brittle. T_C is high and iH_c is large (Table 10.1) and hence the temperature stability is good. It has an excellent corrosion resistance. The magnet is well suited for high temperature applications.

10.3.8 SmCoCuFeZr

This family is the second-generation rare earth magnets exploited in the end of 1970s. A typical composition is $\text{Sm}_{25}\text{Co}_{50}\text{Cu}_8\text{Fe}_{15}\text{Zr}_2$.

10.3.8.1 Manufacture Process and Microstructure

A typical manufacture process is

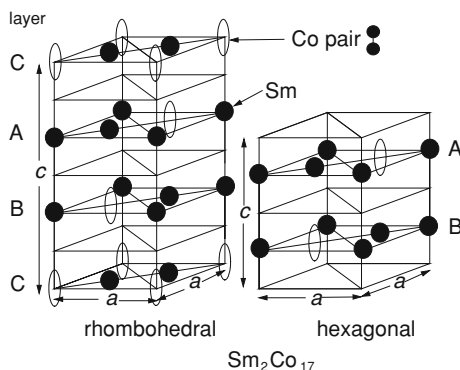


Fig. 10.14 Distribution of Sm ion and Co pair in rhombohedral and hexagonal $\text{Sm}_2\text{Co}_{17}$

- ① Induction melt in vacuum.
- ② Homogenize at $\sim 1,200^\circ\text{C}$ for 5–20 h followed by pulverization to obtain powder of 5–8 μm in size.
- ③ Press in a magnetic field. The c axes of the grain particles are aligned.
- ④ Sinter at $\sim 1,200^\circ\text{C}$ for ~ 1 h and solution treat at $\sim 1,180^\circ\text{C}$ for ~ 1 h.
- ⑤ Dissolution treatment at $\sim 800^\circ\text{C}$ for ~ 30 h.
- ⑥ Slowly cool ($0.7^\circ\text{C}/\text{min}$) to $\sim 400^\circ\text{C}$.

The magnets are closely related with the phases of $\text{Sm}_2\text{Co}_{17}$ crystal structure. The structure is rhombohedral or hexagonal. They are formed by stacking the SmCo_5 unit cells (Fig. 5.3) along the c axis in which one-third of Sm is replaced by Co–Co pairs. According to the position of the pair on the c plane the plane encompassing both Sm and the pair can be assorted to A, B, and C planes. In the rhombohedral structure the planes are accumulated in sequence of ABCABC, and in the hexagonal structure in ABAB (Fig. 10.14).

At the solution temperature, the 2:17 phase has an off-stoichiometric disordered hexagonal structure. During the dissolution treatment the phase spinodal decomposes into (Fe, Co)-rich and (Cu, Zr)-poor ordered stoichiometric rhombohedral 2:17 phase of cellular-type structure and Cu-rich and (Fe, Zr)-poor ordered hexagonal 1:5 phase network. The 1:5 phase precipitates coherently on the $\{01\bar{1}1\}$ plane of the rhombohedral 2:17 matrix. In addition to a coarser cellular structure formed during the first minutes, the fine lamellas normal to the c axis called z-phase precipitate rather slowly in the matrix 2:17 cell which is Sm-poor and Zr-rich (Fig. 10.15). These thin lamellas are thought to function as diffusion paths for Cu and Fe atoms to segregate to the 1:5 and 2:17 phases. The composition and microstructure depend on the thermal treatment conditions.

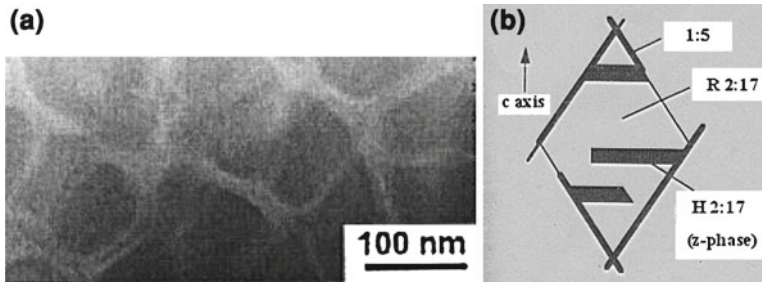
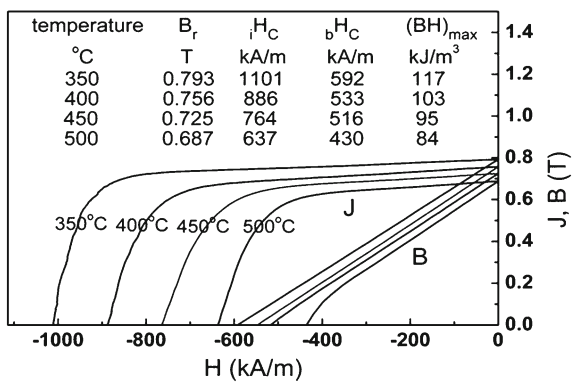


Fig. 10.15 Microstructure of $\text{Sm}(\text{Co}_{0.74}\text{Fe}_{0.14}\text{Cu}_{0.08}\text{Zr}_{0.04})_{7.6}$ [20] (a) and schematic of grain size microstructure (R and H are the shortening of rhombohedral and hexagonal) [21] (b)

Fig. 10.16 Demagnetization curves of $\text{Sm}(\text{Co}_{\text{bas}}\text{Fe}_{0.07}\text{Cu}_{0.08}\text{Zr}_{0.025})_{7.5}$ magnet at different temperatures [12]



10.3.8.2 Magnetic Properties

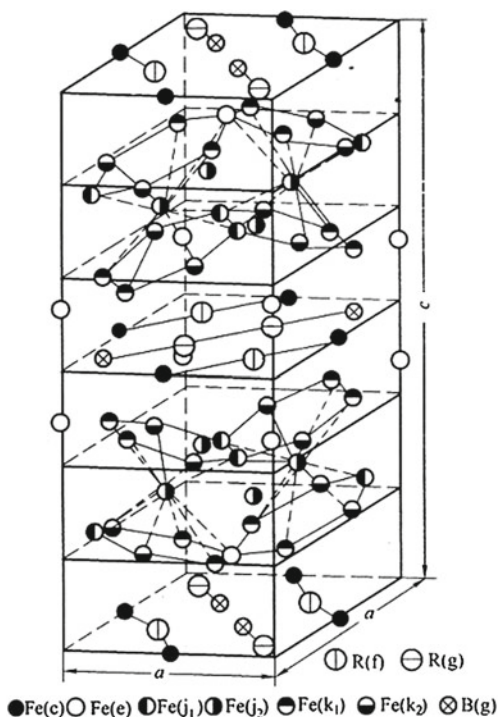
SmCoCuFeZr magnets have magnetization and minor hysteresis curves like those shown in Fig. 10.5 and the coercivity mechanism is of domain wall pinning. Major pinning site is the 1:5 phase boundaries, where serrated domain walls stay in the absence of magnetic field or in a weak magnetic field [21, 22]. iH_c is related mainly to the difference between the domain wall energies of the 2:17 and 1:5 phases (10.34).

Compared with SmCo_5 $(BH)_{\text{max}}$ is larger, T_C is higher, and the content of Sm is lower. The weakness is that the processing conditions are complicated and onerous. T_C being high iH_c preserves large at high temperature (Fig. 10.16) such that it can be applied at relatively high temperatures.

10.3.9 NdFeB

NdFeB is the third-generation rare earth magnets exploited in 1983. Principal phase is the high magnetocrystalline anisotropy $\text{Nd}_2\text{Fe}_4\text{B}$ (Fig. 10.17, Table 5.1). This family

Fig. 10.17 Crystal structure of $\text{Nd}_2\text{Fe}_{14}\text{B}$ [2]



includes sintered, rapid quenched, HDDR, and nanocrystalline exchange-coupled composite magnets.

10.3.9.1 Sintered NdFeB

A typical manufacture process is

- ① Induction melt $\text{Nd}_{\sim 2.4}\text{Fe}_{14}\text{B}$ alloy in vacuum. Strip cast (cast onto a copper roller of speed ~ 1 m/s) to rapidly solidify to avoid the formation of a high quantity of peritectic precipitation α -Fe and large Nd-rich regions.
- ② Pulverize with a coarse grind and jet mill in sequence to powder of ~ 5 μm mean particle size in an inert gas. Most of the particles are monocrystals.
- ③ Press in a magnetic field ($1 \sim 2$ T) to align the c axes.
- ④ Sinter at $\sim 1,100^\circ\text{C}$ for $1 \sim 2$ h.
- ⑤ Temper at $\sim 600^\circ\text{C}$ for ~ 1 h to refine the grain boundary texture and relieve internal stresses.

The magnet mainly consists of $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains surrounded by non-magnetic Nd-rich network phase. The grain size is $5\text{--}20$ μm which is much larger than 200 nm of the critical size for single domain (Fig. 10.18).

Fig. 10.18 Microstructure of NdFeB magnet. A, B and C: $\text{Nd}_2\text{Fe}_{14}\text{B}$, D: Nd-rich phase, thin light region: Nd-rich network [2]



The magnets have the largest energy product. The products of $(BH)_{\text{max}} \sim 400\text{--}440 \text{ kJ/m}^3$, which are not far from the theoretical upper limit of $J_s^2/4\mu_0 = 510 \text{ kJ/m}^3$ are available on the market.

The coercivity mechanism is nucleation of reverse domains (Fig. 10.3).

10.3.9.2 Rapid Quenched NdFeB

Melt spinning molten alloy onto a rapidly rotating ($\sim 40 \text{ m/s}$) copper wheel produces several micrometer thick thin slices. The grain size is $30\text{--}100 \text{ nm}$. The grains of $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase are surrounded by thin Nd-rich boundary phases. The magnetic property is isotropic.

The grain size being smaller than $\sim 200 \text{ nm}$ of critical size for single domain (Table 7.2) and the grains being under strong intergrain exchange interactions, the magnetic moments of the grains are deviated more or less from their easy directions and aligned parallel to some extent resulting in larger than 0.5 value of B_r/B_s for non-interacting grain system. The slices are crushed into the powder of $\sim 200 \mu\text{m}$ size for use in bond magnets. Typical magnetic properties of the powder are listed in Table 10.3.

The magnetic properties of rapid quenched magnet can be simulated fairly well by finite element calculations of micromagnetism (Sect. 8.2).

10.3.9.3 HDDR NdFeB

Rare earth compounds including NdFeB alloys absorb great amount of hydrogen. Exploiting this characteristic the manufacture process of NdFeB powder by HDDR (hydrogenation-disproportionation-desorption-recombination) method was developed since 1989. Typical manufacture process is

- ① Hydrogenation. The ingot is crushed to several millimeter size pieces which are annealed at $\sim 400^\circ\text{C}$ in a flowing hydrogen gas. Through hydrogen absorption (H is first absorbed at crystal defects and Nd-rich grain boundaries) the pieces swell, release heat, and self-crush to powder. The main resultants are $\text{Nd}_2\text{Fe}_{14}\text{BH}_x$ and NdH_x . Under one atmospheric pressure of hydrogen $x = 2.2\text{--}2.7$.
- ② Decomposition. The hydrogenized powder is annealed at $\sim 800^\circ\text{C}$ in the H atmosphere to decompose $\text{Nd}_2\text{Fe}_{14}\text{BH}_x$ to NdH_x , Fe, and Fe_2B .
- ③ Desorption and recombination. The decomposers recombine to $\text{Nd}_2\text{Fe}_{14}\text{B}$ by extracting H. Originally large grain transforms to an aggregation of fine grains of $\sim 300\text{ nm}$ size surrounded by a uniform Nd-rich layer resulting in greatly enhanced iH_c [23].
- ④ Powder of $\sim 100\text{ }\mu\text{m}$ size can be obtained through light milling. The powder is isotropic polycrystals.
- ⑤ Anisotropic powder can be obtained by the d-HDDR method which slowly processes the decomposition and desorption. This method makes the crystal direction of the fine grains preserve the original direction of the initial large grain. Additive of Co and Ga can enhance the anisotropy. At the initial stage of decomposition $\alpha\text{-Fe}$ and NdH_2 have definite crystal orientation relations of $(100)\text{NdH}_2// (100)_{\text{Fe}}$ and $<100>\text{NdH}_2// (100)_{\text{Fe}}$ [24]. But the mechanism of the alignment of the fine crystals along the original crystal direction remains unclear.

Typical magnetic properties of isotropic powder are $B_r = \sim 0.8\text{ T}$, $iH_c = 800\text{ kA/m}$ and $(BH)_{\text{max}} = 100\text{ kJ/m}^3$. Those of anisotropic powder are $B_r = \sim 1.4\text{ T}$, $iH_c = 1070\text{ kA/m}$ and $(BH)_{\text{max}} = 358\text{ kJ/m}^3$ [25].

10.3.9.4 Nanocrystalline Exchange-Coupled Composite NdFeB/ $(\alpha\text{-Fe or Fe}_3\text{B})$

Two-phase nanocrystalline exchange-coupled composite magnet based on NdFeB has been developed in the early 1990s. Fe-rich amorphous NdFeB ribbon is produced by melt-spinning. The isotropic alloy is obtained through crystallization at $\sim 650^\circ\text{C}$. The material is rich in Fe and is composed of even mixture of $\sim 20\text{ nm}$ size $\text{Nd}_2\text{Fe}_{14}\text{B}$ (or $(\text{Nd, Pr})_2\text{Fe}_{14}\text{B}$) and $\alpha\text{-Fe}$ or Fe_3B crystallites. The sizes of the crystallites are smaller than the critical sizes for single domains (Table 7.2). Under the strong exchange interactions through the grain boundaries with the $\text{Nd}_2\text{Fe}_{14}\text{B}$ crystallite the magnetization moment of the soft magnetic phase is aligned toward the magnetic moment direction of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ crystallite. The B_s of the soft phase being large B of the demagnetization curve is enhanced at the expense of decreased

Table 10.3 Typical magnetic properties of permanent magnet powders

	B_r (T)	iH_c (kA/m)	$(BH)_{\max}$ (kJ/m ³)	Powder size (μm)
Sr ferrite*	0.41	240	32	3–12
Alnico*	0.8	120	38	10–200
SmCo ₅ *	0.8	1600	120	
SmCoCuFeZr*	0.9	1200	140	
NdFeB**	0.8	700	100	50–200

* Obtained from sinter magnet. ** Obtained from rapid quenched NdFeB

iH_c so that $(BH)_{\max}$ remains large. $(BH)_{\max}$ of this kind of magnets reaches up to 180 kJ/m³.

Not containing precious Co and Nd being much cheaper than Sm, the prices of NdFeB magnets are much cheaper and the output is overwhelmingly larger than the Sm-Co series. The magnetic moment of Fe and Nd is the largest among the ferromagnetic 3d metals and light rare earths, respectively, and hence B_s of the magnets is large. The weakness of the magnets is low T_C of 310°C. iH_c decreases rapidly with increase of temperature and the application temperature is low. Application temperature is increased to above 180°C for use as magnet of motors by adding Co, Dy, or Tb. Co enhances T_C and Dy and Tb increases magnetocrystalline anisotropy (5.57, Table 5.2) resulting in larger iH_c . The magnetic properties of $B_r = 0.95$ T, $\mu_0 iH_c = 1.1$ T and $(BH)_{\max} = 167$ kJ/m³ can be obtained at 190°C for long period application [12].

10.3.10 Interstitial $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ and $\text{NdFe}_{10.5}\text{Mo}_{1.5}\text{N}_x$

The magnetocrystalline anisotropy being easy plane and T_C as low as $-30\sim 200^\circ\text{C}$, R_2Fe_{17} (R: rare earth) compounds have no intrinsic magnetic properties necessary for permanent magnet. After absorbing nitrogen, N atoms diffuse into the interstitial positions resulting in the increase of the volume, Fe–Fe distances, Fe–Fe and R–Fe exchange coupling, and change in the CEF interactions, which lead to apparent change in magnetocrystalline anisotropy, B_s , and T_C .

When $\text{Sm}_2\text{Fe}_{17}$ is transformed to $\text{Sm}_2\text{Fe}_{17}\text{N}_3$, the easy plane anisotropy changes to easy axis anisotropy of $\mu_0 H_K = 21$ T, T_C increases from 116°C to 476°C, and J_s from 0.94 to 1.54 T [2, 26]. $\text{Sm}_{9.2}\text{Fe}_{90.8}\text{N}_x$ bond magnet of $(BH)_{\max} = 106$ kJ/m³ has been reported by a Japanese group, and Sumitomo metal mining Co. has produced 100 t $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ bond magnet in 2002 [27].

$\text{NdFe}_{10.5}\text{Mo}_{1.5}$ transforming to $\text{NdFe}_{10.5}\text{Mo}_{1.5}\text{N}_x$ T_C increases from 197°C to 392°C, B_s increases from 1.02 T to 1.21 T, and K_1 from 300 kJ/m³ to 6400 kJ/m³, and magnetic properties of $B_r = 1.0$ T, $iH_c = 480$ kA/m, and $(BH)_{\max} = 170$ kJ/m³ have been obtained [28].

Table 10.4 Typical magnetic properties of bond magnets

	B_r (T)	iH_c (kA/m)	$(BH)_{\max}$ (kJ/m ³)
Sr ferrite	0.25	200	12
Alnico(isotropic)	0.35	90	7
SmCo ₅	0.5	800	60
SmCoCuFeZr	0.7	800	80
NdFeB (isotropic)	0.7	700	90

10.3.11 Bond Magnets

Bond magnets are manufactured by molding the mixture of the powder of permanent magnet and binder. The binder is resin, plastic, or rubber. The amount of binder is typically 2 wt% in compression molded magnets and 8–15 wt% in injection molded magnets. The magnetic powder is the mixture of a finer and coarser powder.

Typical magnetic properties of permanent magnet powders and bond magnets available in the market are listed in Tables 10.3 and 10.4, respectively.

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Part III

Spintronics

Chapter 11

Magnetoresistance Effect

The history of the research on magnetoresistance effect is described first and then the basis of electron conduction is explained. Classification of the magnetoresistance effect is done. Among them, experiment on anisotropic magnetoresistance and its origin based on the model by Campbell et al. are explained. Further, it is shown that the measurement of magnetoresistance and magnetization curves is useful to investigate the magnetization states. Finally, the finding of giant magnetoresistance effect (GMR) and its further development are described.

11.1 History of research

The word “magneto-resistance” (magnetic resistance) is seen when we open a textbook to learn about electromagnetism. Here, the magnetic circuit may be considered to be corresponding to the electric circuit. Magnetoresistance is a value in which the magneto-motive force is divided by magnetic flux N (product of the sectional area S of the circuit and the magnetic flux density B). The magneto-motive force can be shown with nI . Here, I is electric current in the coil that surrounds the magnetic circuit and n is the number of wounded coils (Fig. 11.1b). The magnetoresistance in this case is proportional to the magnetic path length but inversely proportional to the product of permeability μ and the cross area S of the material that composes the circuit. On the other hand, the explanations on magnetoresistance effect in this section on electric current magnetic effect (galvanomagnetic effect) are shown in the last pages of several technical books on magnetism. This is considered as an associated phenomenon of magnetization [1]. When the magnetic field is applied from the outside in this case, generically the phenomenon of the change of electric resistance of the material is called the magnetoresistance effect.

The research on the magnetoresistance effect is very old [2], and that on electromagnetism was completed as early as 1857. The anisotropic magnetoresistance effect (AMR) of the 3d transition metal and the alloy were researched by 1960 and

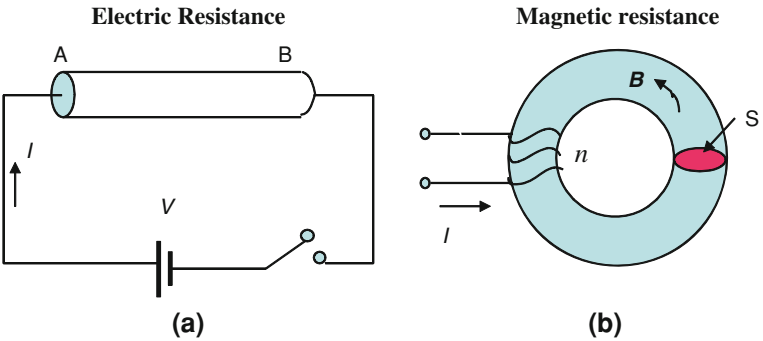


Fig. 11.1 Comparison between electric resistance (a) and magnetic resistance (b). In the case of electric resistance R_{AB} , $V = IR_{AB}$, where V is applied voltage, I is current. While in the case of magnetic resistance R_{AB} , $F = NR_{AB}$, where F is magnetomotive force and N is magnetic flux. Here, R_{AB} is given by $\oint dr/\mu S$, where μ is permeability and S is a cross area of material

Table 11.1 History of magnetoresistance effect research

1857	Effects of magnetization on the electric conductivity of nickel and of iron, William Thomson, Proc. Roy. Soc. (London) 8(1857) 546–550
1930–1960	Anisotropic magnetoresistance effect in 3d transition metal and alloys (AMR Effect)
1960–1970	AMR effect in metal and alloys and its interpretation (two current model, $\rho_{\uparrow}$, $\rho_{\downarrow}$). These are mainly carried out by Campbell and Fert Giant magnetoresistance effect in magnetic semiconductors ($\text{CdCr}_2\text{Se}_4 \cdots$)
1975	First report of related to tunnel magnetoresistance effect See the following papers Anisotropic magnetoresistance in ferromagnetic 3d alloys, T. R. McGuire and R. I. Potter, IEEE Trans. Magn. MAG-11 (1975) 1018. Thin film magnetoresistors in memory, storage and related applications, D. A. Thompson et al., IEEE Trans. Magn. MAG-11 (1975) 1039
1988	Giant magnetoresistance in Fe/Cr super-lattices

beyond [3]. Discussions based on the two current models to interpret the effect of AMR and GMR [4] of the magnetic semiconductor were researched in 1960–1970 [5]. The recent research on GMR and tunnel magnetoresistance effect (TMR) effect is the object of the artificial thin film or the junction, and the results achieved after a technological idea though a research was, in the past, the one intended for metals, alloys, or compounds. The historical details of the research on the magnetoresistance effect are roughly put together in Table 11.1. The root of TMR will be explained in detail in the Introduction of Chap. 12.

11.2 Basis of Electrical Conduction

The knowledge of the extent of thinning or reducing the thickness of a magnetic substance with a large resistivity to reduce the eddy current loss when the material was used in high frequency by the person who had been researching on magnetic materials. Therefore, there is not much knowledge of electrical conduction in general. Few experimental studies concerning magnetoresistance were done. Correspondingly, there are few reference books concerning conduction that become the basis as described in the previous section. Then, the author will explain some basic problems on conduction.

11.2.1 Drift Velocity and Fermi Velocity

It is important to understand, at first, the terms Fermi velocity, relaxation time, and mean free paths when thinking about the conductivity of a material. If we do not understand these words and phrases, the behavior of the electron will not be well understood. Thus, the author first explains them though they are often described in textbooks. It is assumed that one electron is put in electric field $\mathbf{E}$.

Because the electron receives the power of $-e\mathbf{E}$, the movement is given by the following equation:

$$m \frac{d^2 \mathbf{r}}{dt^2} = m \frac{d\mathbf{v}}{dt} = -e\mathbf{E}. \quad (11.1)$$

Here, m is the mass of the electron and $-e$ the electric charge. Solving this equation, we have the relation $\mathbf{v} = -(e\mathbf{E}/t)t$, in which current density is expressed as $\mathbf{i} = n(-e)\mathbf{v}$. Hence, $\mathbf{v} = (ne^2\mathbf{E}/m)t$, which implies that the increase of electric current will increase with time. However, this behavior cannot be observed if the electric field is applied to an actual material, and the electric current shows the definite value only instantaneously. This is because the resistance force acts on the electron and the balance between them is maintained, becoming the constant speed. Let us assume resistance force is proportional to velocity, then the equation of motion is described as

$$m \frac{d\mathbf{v}_D}{dt} = -e\mathbf{E} + c\mathbf{v}_D. \quad (11.2)$$

It can be understood intuitively that this is the same as the motion equation of a raindrop that falls from the sky. We can describe $\mathbf{v}_D$ for the velocity in (11.2) because we treat the material as a many-electron system. It means the average velocity of the electron or drift velocity. Putting $c/m = -1/\tau$, (τ : relaxation time), and solving (11.2), we have

$$\mathbf{v}_D = -\frac{e\tau}{m}\mathbf{E}. \quad (11.3)$$

where τ is the average time from the collision of the electron with the ion, etc., to the next collision. Equation (11.3) shows that the velocity of the electron (crowd) is proportional to the electric field, and the proportional coefficient $e\tau/m \equiv \mu$ depends on the following factors:

- Thermal motion of crystal lattice and ions.
- Defects such as grain boundary, dislocations, and voids in crystal.

For thin films, surface etc. cannot be disregarded. The electric current density is

$$i = -nev_D = \frac{ne^2\tau}{m}E \equiv \sigma E. \quad (11.4)$$

Thus, we have

$$\sigma = \frac{ne^2\tau}{m}, \quad \text{or} \quad \rho = \frac{m}{ne^2\tau}. \quad (11.5)$$

Here, n is the number of electrons per unit volume that contributes to conduction. The symbol σ is called the rate of electric conductivity, and the reciprocal ρ is called the resistivity or a specific resistance. If the value ρ of the material is determined in (11.5), the relaxation time can be obtained. For instance, $\rho = 1.5 \times 10^{-8} \Omega\text{m}$, $n = 8.5 \times 10^{28}/\text{m}^3$, $e = 1.6 \times 10^{-19}\text{C}$, and $m = 9.1 \times 10^{-31}\text{kg}$ in Cu, thus, $\tau = 3.8 \times 10^{-14}\text{s}$. By the way, the movement of the electron when the electric field is applied to the material has been described till now. When the electric field is not applied, are the electrons in a stationary state? To tell the truth, the electron does a random movement even though the electric field is not applied. The density of states is used to describe the energy state of the electron. The electrons are packed from the lowest energy state, to the highest energy level, so-called Fermi level. When we assume the Fermi energy (see Fig. 11.2) at the speed of the electron that exists in the Fermi level to be E_F , it can be shown as

$$\frac{1}{2}mv_F^2 = E_F. \quad (11.6)$$

For instance, in $E_F = 7\text{eV}$ ($7 \times 1.6 \times 10^{-19}\text{J}$) of Cu it becomes $v_F = 1.3 \times 10^6\text{m/s}$ ($= 470 \times 10^4\text{km/h}$), and is 10^4 times further as fast as the fastest train developing in the world now. By the way, when the distance between the collision (scatter) and the next collision is assumed to be ℓ , we have $\ell = 350\text{\AA}$ from $\ell = v_F \cdot \tau$. The length ℓ is called the mean free path of the electron. Drift velocity previously described becomes $v_D = 5\text{mm/sec}$, assuming $E = 1\text{V/m}$ and is far smaller compared with v_F . The movements of the particles (water molecules) are violent and random in volcanic smoke that occurs from a volcano. The velocity corresponds to the Fermi ones. The entire volcanic smoke will move sideways if the wind blows from the side against this volcanic smoke. We are able to understand intuitively that this is one-sided velocity.

Fig. 11.2 Scheme for intuitive understanding both **a** Fermi velocity and **b** drift velocity

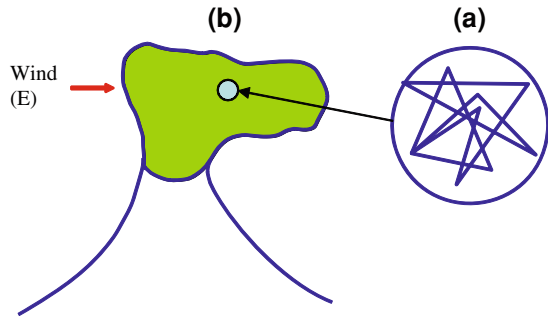
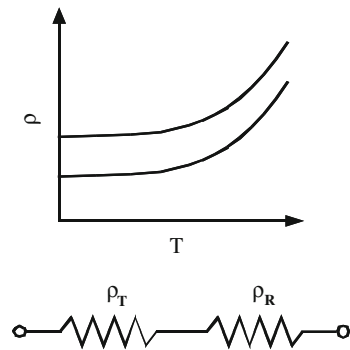


Fig. 11.3 Matthiessen's law, ρ_R , ρ_T are the resistivities due to impurity and phonons, respectively



11.2.2 Matthiessen's Law

There are two kinds of $1/\tau$, if there are two factors for scattering of the electrons. Thus, the rate of resistance is given by

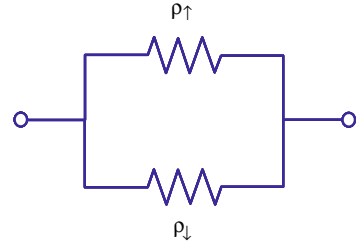
$$\rho = \frac{m}{ne^2} \left(\frac{1}{\tau_1} + \frac{1}{\tau_2} \right) = \rho_1 + \rho_2. \quad (11.7)$$

For instance, two kinds of scattering may be considered to be caused from impurities and lattice vibrations (ρ_T). Thus, we have the resistivity as $\rho = \rho_R + \rho_T$. The total resistance is shown by the sum of ρ_R and ρ_T of individual resistance, which is called Matthiessen's law. Figure 11.3 shows this law schematically ρ_R .

11.2.3 Two-Current Model

How can we observe phenomena that in the kind of medium where the electron moves in case of the above-mentioned, etc., two kinds of scattered ones (electron) exist? These cannot be distinguished, because e is an elementary charge and any

Fig. 11.4 Two-current model, $\rho_{\uparrow}$ and $\rho_{\downarrow}$ are the resistivities of $\uparrow$ and $\downarrow$ electrons, respectively



electron is the same as the mass in m , even if two kinds of electrons are assumed. However, two kinds of electrons with different spins may be considered because there are electrons of $\uparrow$ (up spin) and $\downarrow$ (down spin) in the ferromagnetic substance. That is, we can consider about the two kinds of relaxation times, and assume both the electron numbers to be equal. Then, we have (11.8) as follows:

$$\sigma = \frac{ne^2}{m}(\tau_{\uparrow} + \tau_{\downarrow}) = \sigma_{\uparrow} + \sigma_{\downarrow} \quad \text{or} \quad \rho = \frac{\rho_{\uparrow}\rho_{\downarrow}}{\rho_{\uparrow} + \rho_{\downarrow}} \quad (11.8)$$

That is, the equivalent circuit is shown as in Fig. 11.4.

11.2.4 Resistance Due to Spin Flip

It was considered that the spins of $\uparrow$ and $\downarrow$ are maintained in the case of scattering in the current discussion. That is, the scattering by the magnon or the phonon can be disregarded at low temperature [6, 7]. Then, how does it occur with rising temperature? It is thought that the change (spin flip) in $\uparrow \leftrightarrow \downarrow$ occurs because of scattering by the magnon and the spin flip because of the phonon, even though the extent is small. How can the resistance for that case be shown? Figure 11.5 shows this model schematically.

The rate of a decrease in the momentum is a product of the change in the scattering probability and the momentum. Since $d\mathbf{p}/dt = \mathbf{F}$,

for the spin $\uparrow$,

$$-eE = \frac{1}{\tau_{\uparrow}}mv_{\uparrow} + \frac{1}{\tau_{\uparrow\downarrow}}m(v_{\uparrow} - v_{\downarrow}).$$

For $\downarrow$ spin,

$$-eE = \frac{1}{\tau_{\downarrow}}mv_{\downarrow} + \frac{1}{\tau_{\downarrow\uparrow}}m(v_{\downarrow} - v_{\uparrow}). \quad (11.9)$$

It is assumed here that $\tau_{\uparrow\downarrow}$ and $\tau_{\downarrow\uparrow}$ are equal. Each of $\uparrow$ and $\downarrow$ spins,

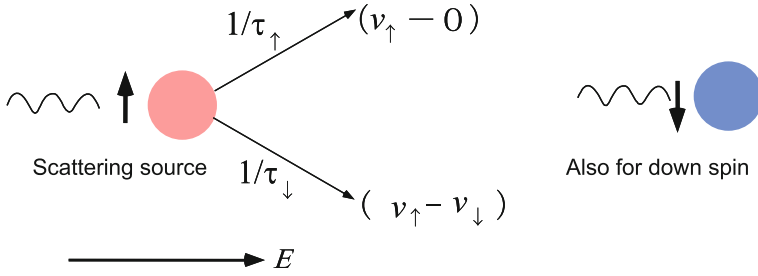


Fig. 11.5 In the model chart, each of $\tau_{\uparrow}$ and $\tau_{\downarrow}$ is relaxation time, while spin flip occurs, each of $v_{\uparrow}$ and $v_{\downarrow}$ is corresponding to each velocity

$$i_{\uparrow(\downarrow)} = nev_{\uparrow(\downarrow)}, \quad \rho = m/ne^2\tau_{\uparrow(\downarrow)}, \quad (11.10)$$

then,

$$\frac{1}{\tau_{\uparrow}} = \frac{ne^2}{m}\rho_{\uparrow} = \frac{ne^2}{m}[\rho_{\uparrow}(0) + \rho'_{\uparrow}(T)]. \quad (11.11)$$

Here, $\rho_{\uparrow}(T)$ is an increment of resistance with the temperature. That is, it is resistance by an electronic phonon scattering. Similarly,

$$\frac{1}{\tau_{\downarrow}} = \frac{ne^2}{m}\rho_{\downarrow} = \frac{ne^2}{m}[\rho_{\downarrow}(0) + \rho'_{\downarrow}(T)]. \quad (11.12)$$

In addition,

$$\rho_{\uparrow\downarrow}(T) = \frac{m}{ne^2\tau_{\uparrow\downarrow}}. \quad (11.13)$$

Therefore, resistance at temperature T is given by

$$\rho(T) = \frac{E}{i_{\uparrow} + i_{\downarrow}} = \frac{E}{ne} \cdot \frac{1}{v_{\uparrow} + v_{\downarrow}} \quad (11.14)$$

First obtaining $v_{\uparrow}$ and $v_{\downarrow}$ from (11.9), next substituting them into (11.14) and finally using (11.11–11.13),

$$\rho(T) = \frac{[\rho_{\uparrow}(0) + \rho'_{\uparrow}(T)][\rho_{\downarrow}(0) + \rho'_{\downarrow}(T)] + \rho_{\uparrow\downarrow}(T)[\rho_{\downarrow}(0) + \rho_{\uparrow}(0) + \rho'_{\uparrow}(T) + \rho'_{\downarrow}(T)]}{\rho_{\downarrow}(0) + \rho_{\uparrow}(0) + \rho'_{\uparrow}(T) + \rho'_{\downarrow}(T) + 4\rho_{\uparrow\downarrow}(T)} \quad (11.15)$$

In the special case of scattering, let us consider that the spin flip by the magnon scattering occurs but the scattering by the phonon can be disregarded. From (11.15),

$$\rho = \frac{\rho_{\uparrow}\rho_{\downarrow} + \rho_{\uparrow\downarrow}(\rho_{\uparrow} + \rho_{\downarrow})}{\rho_{\uparrow} + \rho_{\downarrow} + 4\rho_{\uparrow\downarrow}}. \quad (11.16)$$

We can see the representation often in such published papers as Fert et al. [7] published.

11.2.5 Temperature Dependence of ρ

In (11.7), $\rho_{\uparrow}(0), \rho_{\downarrow}(0) \gg \rho'_{\uparrow}(T), \rho'_{\downarrow}(T), \rho'_{\uparrow\downarrow}(T)$ and $\rho'_{\uparrow}(T) = \rho'_{\downarrow}(T) \equiv \rho'_i(T)$ ($i = \uparrow, \downarrow$), further we put $\rho_{\uparrow}(0) = a, \rho_{\downarrow}(0) = b, \rho_i(T) = c, \rho_{\uparrow\downarrow}(T) = d$. Then, (11.16) is expressed as

$$\begin{aligned} \rho &= \frac{(a+b)(b+c) + d(a+b+2c)}{a+b+2c+4d} \\ &= \frac{1}{a+b} \left[\{ab + c(a+b) + d(a+b+2c)\} \left\{ 1 - \frac{4(c+d)}{a+b} \right\} \right] \\ &\approx \frac{ab}{a+b} + \frac{(a-b)^2}{(a+b)^2}c + \frac{(a-b)^2}{(a+b)^2}d, \end{aligned} \quad (11.17)$$

$$\rho(T) = \frac{\rho_{\uparrow}(0)\rho_{\downarrow}(0)}{\rho_{\uparrow}(0) + \rho_{\downarrow}(0)} + \left[\frac{\rho_{\uparrow}(0) - \rho_{\downarrow}(0)}{\rho_{\uparrow}(0) + \rho_{\downarrow}(0)} \right]^2 \rho_i(T) + \left[\frac{\rho_{\uparrow}(0) - \rho_{\downarrow}(0)}{\rho_{\uparrow}(0) + \rho_{\downarrow}(0)} \right]^2 \rho_{\uparrow\downarrow}(T). \quad (11.18)$$

If the relations are set in Fert's article as follows:

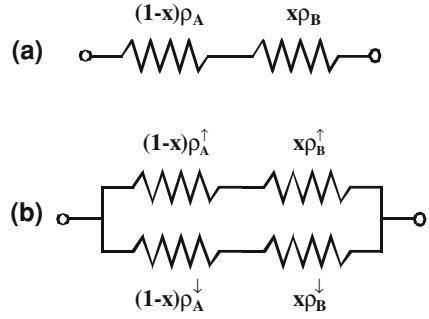
$$\frac{\rho_{\downarrow}(0)}{\rho_{\uparrow}(0)} \equiv \alpha, \quad \frac{\rho_{\uparrow}(0)\rho_{\downarrow}(0)}{\rho_{\uparrow}(0) + \rho_{\downarrow}(0)} \equiv \rho_0$$

the following relation is introduced:

$$\rho(T) = \rho_0 + \left[\frac{\alpha - 1}{\alpha + 1} \right]^2 \rho_i(T) + \left[\frac{\alpha - 1}{\alpha + 1} \right]^2 \rho_{\uparrow\downarrow}(T). \quad (11.19)$$

Here, $(\alpha - 1)^2 / (\alpha + 1)^2$ is independent of the temperature, which is, however, determined by $\rho_{\uparrow}(0)$ and $\rho_{\downarrow}(0)$. Moreover, the first term of (11.19) corresponds to the residual resistivity, and the second and third terms to the scattering by the phonon and the magnon (the gap from the Matthiessen's law).

Fig. 11.6 **a** Matthiessen's law and **b** two-current model in $A_{1-x}B_x$ alloy



11.2.6 How to Obtain $\rho_\uparrow$, $\rho_\downarrow$, and $\alpha = \rho_\downarrow/\rho_\uparrow$

The author explains how to obtain $\rho_\uparrow$ and $\rho_\downarrow$ next, following the points of an argument in papers such as Fert and Campbell [8, 9]. The resistance of the $MA_{1-x}B_x$ alloy will be discussed. It is assumed either of magnetic elements of M such as Fe, Co, and Ni here, and A and B are the 3d transition metal elements other than Ni such as Fe, Co, Mn, Cr, and V. Resistance (residual resistivity) is expressed as

$$\rho_1 = \rho_0 + (1-x)\rho_A + x\rho_B, \quad (11.20)$$

when a resistance changes according to Matthiessen's law (Fig. 11.6a). where, ρ_0 is resistivity without A and B elements and ρ_A and ρ_B are resistivity per atom for A and B elements, respectively. On the other hand, $\uparrow$ and $\downarrow$ spins become parallel connection in two-current model as shown in Fig. 11.6b. That is, the total resistance is given by

$$\rho_2 = \rho_0 + \frac{\left[(1-x)\rho_A^\uparrow + x\rho_B^\uparrow \right] \left[(1-x)\rho_A^\downarrow + x\rho_B^\downarrow \right]}{(1-x)\rho_A^\uparrow + x\rho_B^\uparrow + (1-x)\rho_A^\downarrow + x\rho_B^\downarrow}, \quad (11.21)$$

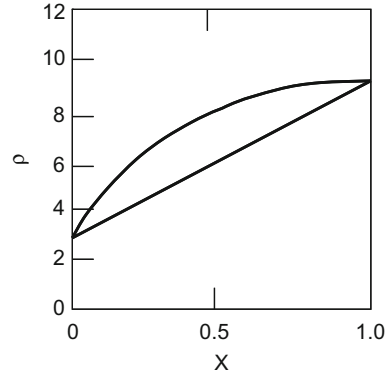
$$\Delta\rho = \rho_2 - \rho_1 = \frac{(\alpha_A - \alpha_B)^2 (1-x)\rho_A x\rho_B}{(1 + \alpha_A)^2 \alpha_B (1-x)\rho_A + (1 + \alpha_B)^2 \alpha_A x\rho_B}, \quad (11.22)$$

where,

$$\rho_A = \frac{\rho_A^\uparrow \rho_A^\downarrow}{\rho_A^\uparrow + \rho_A^\downarrow}, \quad \rho_B = \frac{\rho_B^\uparrow \rho_B^\downarrow}{\rho_B^\uparrow + \rho_B^\downarrow} \quad (11.23)$$

$$\alpha_A \equiv \frac{\rho_A^\downarrow}{\rho_A^\uparrow}, \quad \alpha_B \equiv \frac{\rho_B^\downarrow}{\rho_B^\uparrow} \quad (11.24)$$

Fig. 11.7 Residual resistivity of $MA_{1-x}B_x$ alloys (schematic). The two-current model in the curved line and the Matthiessen's law in the straight line are shown, respectively



or,

$$\rho_A^\uparrow = \frac{(1 + \alpha_A)}{\alpha_A} \rho_A, \quad \rho_A^\downarrow = (1 + \alpha_A) \rho_A \quad (11.25)$$

$$\rho_B^\uparrow = \frac{(1 + \alpha_B)}{\alpha_B} \rho_B, \quad \rho_B^\downarrow = (1 + \alpha_B) \rho_B. \quad (11.26)$$

Here, $\alpha_{A(B)}$ is an important value to discuss the magnetoresistance, so the concrete example will be shown later. The ratio of $\rho_\downarrow$ to $\rho_\uparrow$ is physically significant but not only parameter though some persons call it parameter α . For $\alpha_{A(B)}$, the following experiments only have to be analyzed. First of all, residual resistivity $\rho_{A(B)}$ ($\mu\Omega \cdot cm/at\%$) is necessary to obtain from the experiment on the electric resistance of dual alloy MA(B) that puts the A(B) atom, respectively, as impurities in M. Next, the residual resistivity of the ternary alloy $MA_{1-x}B_x$ is measured. In general, one data (curved line) may be obtained as shown in Fig. 11.7. From this data, $\rho_2 - \rho_1$ may be obtained. Equation (11.22) is best fitted to the experimental value of $\rho_2 - \rho_1$. From (11.22), the following are obtained:

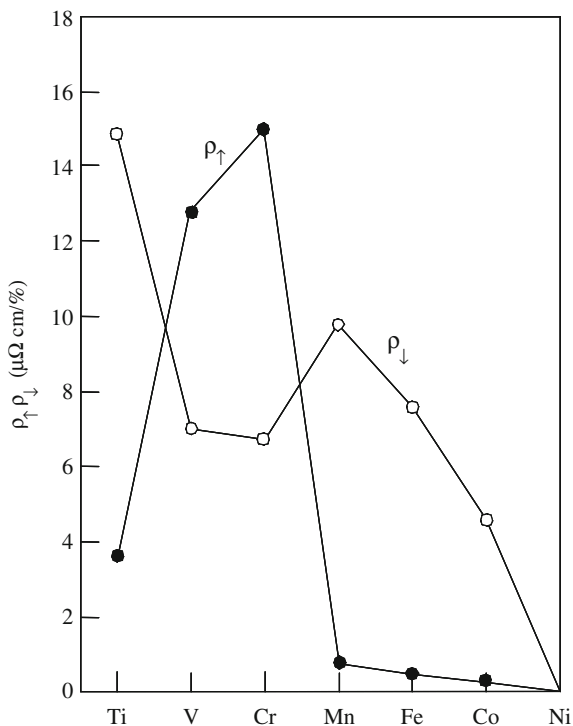
$$\frac{1}{a} \cdot \frac{\Delta \rho}{\rho_B x} + \frac{1}{b} \cdot \frac{\Delta \rho}{\rho_A (1 - x)} = 1 \quad (11.27)$$

$$a = (\alpha_A - \alpha_B)^2 / (1 + \alpha_A)^2 \alpha_B.$$

$$b = (\alpha_A - \alpha_B)^2 / (1 + \alpha_B)^2 \alpha_A \quad (11.28)$$

Therefore, we have a straight line when $\Delta \rho / \rho_B x$ is plotted with respect to $\Delta \rho / \rho_A (1 - x)$ and then α may be obtained from the intersection of the axis with the straight line. This value is substituted into (11.28), and we can solve these equations

Fig. 11.8 Values of $\rho_{\uparrow}$ and $\rho_{\downarrow}$ put in various 3d impurities of Ni



simultaneously with respect to α_A and α_B . If $\alpha_{A(B)}$ is obtained, $\rho_{A(B)}^{\uparrow}$ from (11.25), $\rho_{A(B)}^{\downarrow}$ from (11.24). Figure 11.8 shows the value of $\rho_A^{\uparrow}$, $\rho_A^{\downarrow}$ to examine the ternary alloy with M = Ni (A or B = Co, Fe, Mn, Cr, V, and Ti).

11.3 Classification of Magnetoresistance Effects

The phenomenon of the change of conductivity by the applied magnetic field is generically called a magnetoresistance effect. The contents are divided into the variable case. The resistivity changes even if the magnetic field is applied not to the ferromagnetic substance but to the non-magnetic substance. This is called ordinary magnetoresistance effect. The lower the temperature, the stronger the magnetic field, and the more remarkable the effect. On the other hand, the magnetic field is applied to the material that has spontaneous magnetization, the ferromagnetic substance, and the phenomenon of the change of resistivity, corresponding to the magnetized state, is called anomalous magnetoresistance effect. The change of resistivity in ferromagnetic films such as Permalloy often examined depends on the direction of the spontaneous magnetization. These are called anisotropic magnetoresistance

Table 11.2 Classification of magnetoresistance effects

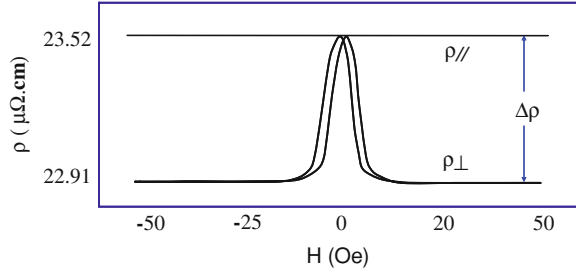
(1) Nomal magnetoresistance effect
(2) Effect of anomalous magnetoresistance
(i) Anisotropic magnetoresistance effect (orientation effect)
(ii) Giant magnetoresistance effect (The spin valve is included)
(iii) Tunnel magnetoresistance effect
(iv) Forced magnetoresistance effect

(AMR effect) or orientation effect. The multilayered thin film that repeats the metallic lattice or this accumulates of F/N/F is as described in Sect. 5.2. In the case, a negative exchange interaction works at interface of ferromagnetic layer. As a result, the magnetization is in the state of the antiparallel. In this case, the magnetic field is applied so that the magnetization can be in a parallel state and then, the resistance decreases. Because the ratio of changes is larger than AMR, this effect is called a GMR effect. Moreover, the change of tunneling current depends on a relative angle of the magnetization of both ferromagnetic substances between which the insulator is inserted. This is called a TMR effect. In both the GMR effect and the TMR effect, the change of resistivity may be observed depending on the relative angle of the magnetization of the ferromagnetic layers. In the former, there are two types of situations in the directions of current. One is the case of the parallel electric current in plane (CIP) and the other is perpendicular to the accumulating side, or current perpendicular to plane (CPP).

However, only CPP is in the TMR. Details of GMR and the effect of TMR will be mentioned in Sect. 11.7 and Chap. 12, respectively. In addition, there is an effect of the Perovskite type Mn oxide described for a super huge magnetoresistance (Colossal magnetoresistance: CMR for short), too. The magnetoresistance effect is brought together above, as shown in Table 11.2.

11.4 Anisotropic Magnetoresistance Effect

Let us consider the physical meaning of α that implies the degree of the spin-dependent condition. Here, α is defined as $\alpha_{\downarrow}/\alpha_{\uparrow}$. So, the equation $\alpha = 1$ means that $\rho_{\uparrow}$ and $\rho_{\downarrow}$ are equal, and the resistivity is equal in $\uparrow$ and $\downarrow$ electrons. That is, there is no scattering depending on a spin. Therefore, the magnetoresistance effect does not occur for this case. In contrast, the scattering depending on the spin may be remarkable in the case $\alpha \gg 1$ or $\alpha \ll 1$. That is, the GMR is sure to appear. Let us think how it is possible to show by the magnetoresistance effects using α of the effect of AMR. Figure 11.9 shows one example of the magnetoresistance curve of the Permalloy thin film. The $\rho_{//}$ shows the specific resistance when the magnetic field is applied in the same direction as the electric current and $\rho_{\perp}$ in the perpendicular situation. The magnetoresistance ratio is defined as

Fig. 11.9 Magnetoresistance curve of permalloy thin film

$$\frac{\Delta\rho}{\rho_0} = \frac{\rho_{//} - \rho_{\perp}}{\frac{1}{3}\rho_{//} + \frac{2}{3}\rho_{\perp}} \times 100 \approx \frac{\rho_{//} - \rho_{\perp}}{\rho_{\perp}} \times 100 \approx \frac{\rho_{//} - \rho_{\perp}}{\rho_{//}} \times 100, \quad (11.29)$$

where ρ_0 is a resistivity ratio in the demagnetized state, and may be shown by using $\rho_{//}$ and $\rho_{\perp}$ like in (11.29). The approximation may be supported by the justification that $\rho_{//} \approx \rho_{\perp}$, since $\rho_{//}$ and $\rho_{\perp}$ are resistivities with $\uparrow$ and $\downarrow$ electrons, respectively.

$$\rho_{//(\perp)} = \frac{\rho_{//(\perp)}^{\uparrow} \rho_{//(\perp)}^{\downarrow}}{\rho_{//(\perp)}^{\uparrow} + \rho_{//(\perp)}^{\downarrow}}. \quad (11.30)$$

Further, $\rho_{//}^{\uparrow}$ is not independent of $\rho_{\perp}^{\uparrow}$ and also $\rho_{//}^{\downarrow}$ is not independent of $\rho_{\perp}^{\downarrow}$, and the following relations are led:

$$\rho_{//}^{\uparrow} = \rho_{\perp}^{\uparrow} + \gamma \rho_{\perp}^{\downarrow},$$

$$\rho_{//}^{\downarrow} = \rho_{\perp}^{\downarrow} - \gamma \rho_{\perp}^{\uparrow}. \quad (11.31)$$

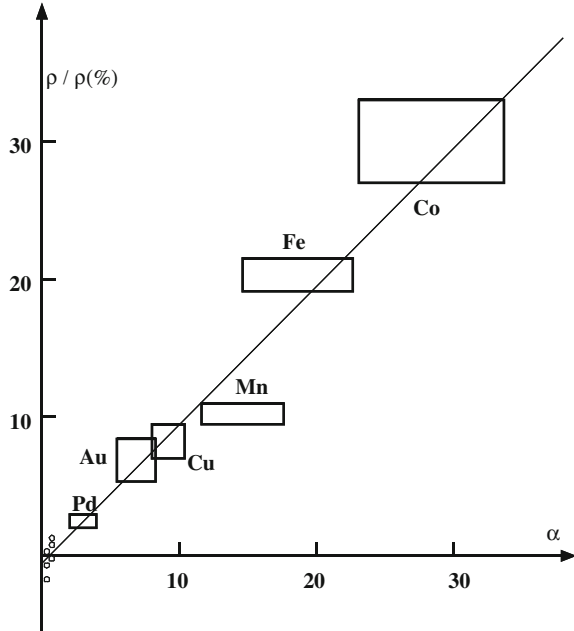
Leading (11.31) is a little troublesome exercise level of quantum mechanics which the author will explain in the next section.

In these equations, $\gamma = (\lambda/H_{\text{ex}})^2$ and λ is spin-orbital interaction coefficient and H_{ex} is exchange interaction energy. In Fe, Ni, Co, and the alloys, γ is of the order of 0.01. When we transform (11.29) by using (11.30) and (11.31),

$$\frac{\Delta\rho}{\rho_0} = (1 + \alpha\gamma)(1 - \gamma) - 1 \approx \gamma(\alpha - 1), \quad (11.32)$$

where $\alpha \equiv \rho_{\perp}^{\downarrow}/\rho_{\perp}^{\uparrow}$. It is understood to satisfy (11.32) though the arranged experimental results of α are shown in Fig. 11.10. The first report of the AMR was in the 1800s. However, the effect has been in the spotlight since the latter half of the 1980s. The recording density of the hard disk went up, and the tendency to use the

Fig. 11.10 $\alpha = \rho_{\downarrow}/\rho_{\uparrow}$ dependence compared with AMR when various 3d impurities are introduced in Ni. The straight line shows $\Delta\rho/\rho_0 = 0.01(\alpha - 1)$



magnetoresistance effect as a magnetic head of high sensitivity was on the rise. The composition dependence of Ni–Fe–Co ternary alloy films (chemical composition) is shown in Fig. 11.11 [10, 11].

At 7 % Fe and 10–20 %Co of chemical composition, $\Delta\rho/\rho_0$ is understood to indicate the large value. Calculating the composition dependence of the α of Ni–Fe–Co referring to the discussion about the above-mentioned behavior, we show the result in the contour line in Fig. 11.12. In this case, we have the value of α using the value estimated by the proportion distribution in the bulk value of Ni–Fe and Ni–Co. When Figs. 11.11 and 11.12 are compared, it is understood that the composition dependence of α is almost corresponding to that of $\Delta\rho/\rho_0$.

11.5 Origin of Anisotropic Magnetoresistance Effect

Why is the AMR caused? It is not a phenomenon intuitively understood easily [12]. Thus, the author explains how the relation of (11.31) of the previous section is to be derived.

Resistivity is given by

$$\rho = \frac{m}{ne^2} \frac{1}{\tau}, \quad (11.33)$$

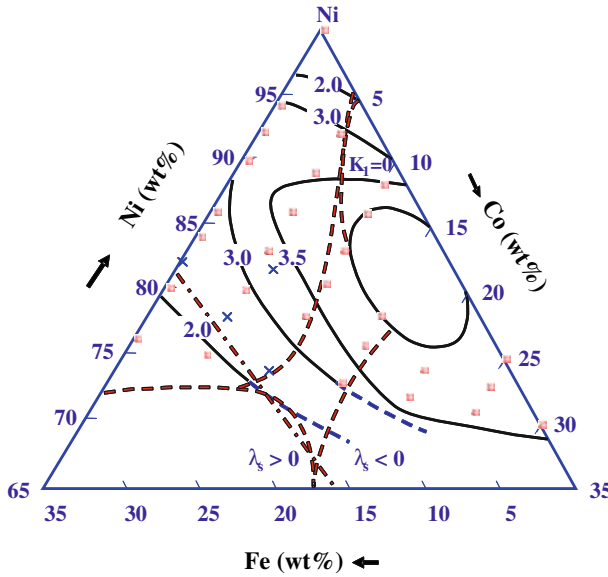


Fig. 11.11 Composition dependence of MR ratio of Ni–Fe–Co ternary alloy thin film

though the author has already discussed the resistivity in Sect. 11.2, where τ is a relaxation time and $1/\tau$ shows the probability of the electron scattering. It is assumed that the electron of the wave of Ψ_1 is scattered by potential $V(r)$ and changed to the wave of Ψ_2 . $1/\tau$ is given by

$$\frac{1}{\tau} \propto \left| \int \Psi_2^* V(r) \Psi_1 dv \right|^2. \quad (11.34)$$

The discussion will be in more detail about Ni now. In view of the electronic structure of Ni, leading parts of conduction are 4s electrons. However, the anisotropy does not come out, taking considerations only to 4s electrons. If the scheme of scattering may be expressed concretely in consideration of this, it becomes as shown in Fig. 11.13. Assuming that Ψ_s and Ψ_d are electron wave functions in s and d states, respectively, and that the spin flip may not be occurred by the spin scattering, the transition of the electron from 1 to 2 is

$$\int \Psi_s^{*\uparrow} V(r) \Psi_s^\uparrow dv \quad (11.35)$$

$$\int \Psi_d^{*\uparrow} V(r) \Psi_s^\uparrow dv \quad (11.36)$$

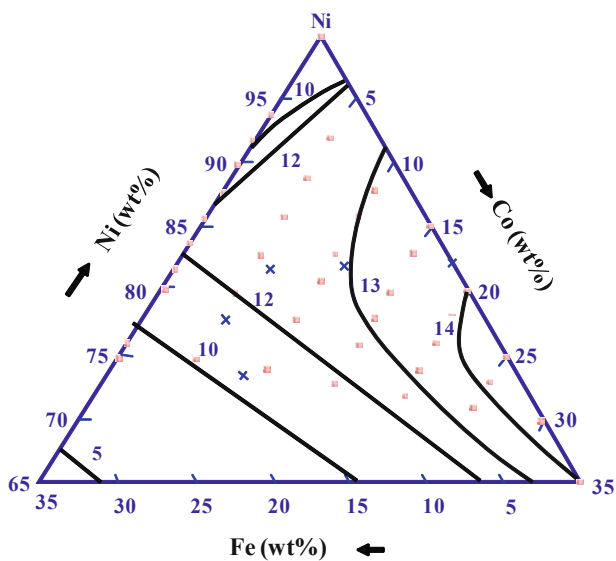
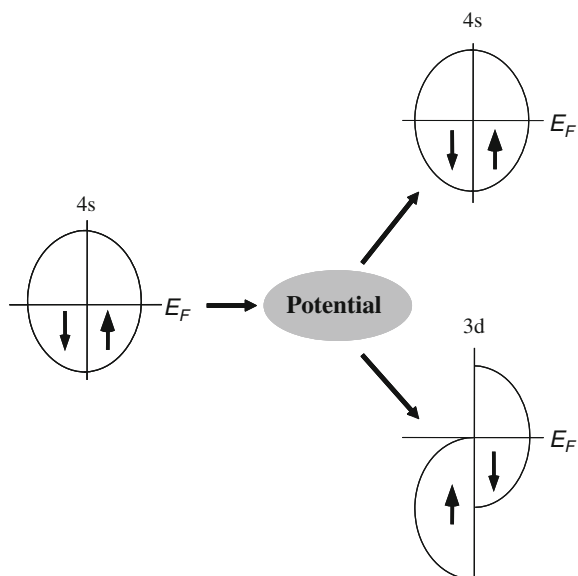


Fig. 11.12 Composition dependence of α ($\rho_{\downarrow}/\rho_{\uparrow}$) of Ni-Fe-Co ternary alloy thin film

Fig. 11.13 Scattering process and $1/\tau$ of 4s electrons are given



$$\int \Psi_s^{*\downarrow} V(r) \Psi_s^{\downarrow} dv \quad (11.37)$$

$$\int \Psi_d^{*\downarrow} V(r) \Psi_s^\downarrow d\nu. \quad (11.38)$$

Four transitions described above may be considered. However, neither (11.35) nor (11.37) (with transition from s to s) contributes to the AMR. Moreover, the transition (11.36), $s^\uparrow \rightarrow d^\uparrow$ vanishes, since there is no density of state $\uparrow$ at the Fermi energy, as shown in Fig. 11.13. After all, we only have to consider the transition of $s^\downarrow \Rightarrow d^\downarrow$ in (11.38). When the plane wave is assumed to be $\Psi_s^\downarrow = e^{ik \cdot r}$, the normal state of the d electron is described by five wave functions of $\ell = 2, m = 2, 1, 0, -1$, and -2 . It is assumed that the Ψ of (11.38) is a product of the orbit and the spin here and the part in the orbit is in the form of the variable separation. Thus we have

$$\lambda L \cdot S \Psi |2 \downarrow\rangle = \left(1 - \frac{1}{2}\varepsilon^2\right) \phi |2 \downarrow\rangle + \varepsilon \phi |1 \uparrow\rangle \quad (11.39)$$

$$\lambda L \cdot S \Psi |1 \downarrow\rangle = \left(1 + \frac{3}{4}\varepsilon^2\right) \phi |1 \downarrow\rangle + \left(\frac{3}{2}\right)^{1/2} \varepsilon \phi |0 \uparrow\rangle \quad (11.40)$$

$$\lambda L \cdot S \Psi |0 \downarrow\rangle = \left(1 - \frac{3}{4}\varepsilon^2\right) \phi |0 \downarrow\rangle + \left(\frac{3}{2}\right)^{1/2} \varepsilon \phi |-1 \uparrow\rangle \quad (11.41)$$

$$\lambda L \cdot S \Psi |-1 \downarrow\rangle = \left(1 - \frac{1}{2}\varepsilon^2\right) \phi |-1 \downarrow\rangle + \varepsilon \phi |-2 \uparrow\rangle \quad (11.42)$$

$$\lambda L \cdot S \Psi |-2 \downarrow\rangle = \phi |-2 \downarrow\rangle. \quad (11.43)$$

Here, $\varepsilon = \lambda/H_{\text{ex}}$. In (11.38), $\Psi_d^\downarrow$ is expressed by the product of orbit and spin (χ). Further, the orbital part is expressed by the product of functions $R_{n\ell}(r)$ and ϕ_ℓ^n .

$$\Psi_d^\downarrow = R_{n\ell}(r) \phi_\ell^m \cdot \chi. \quad (11.44)$$

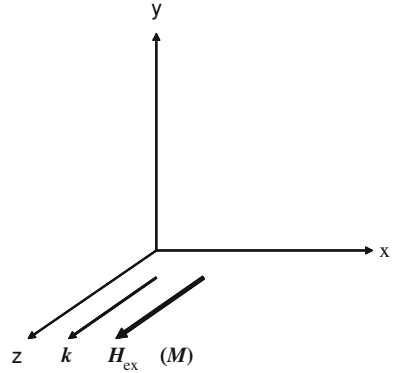
Here, n, ℓ, m are principal, azimuth, and magnetic quantum numbers, respectively and in this case $n = 3, m = \pm 2, \pm 1, 0$. Therefore, ϕ_2^m is given by

$$m = \pm 2 \quad \phi_2^{\pm 2} \propto \frac{1}{2\sqrt{2}} (x \pm iy)^2 \quad (11.45)$$

$$m = \pm 1 \quad \phi_2^{\pm 1} \propto \mp \frac{1}{\sqrt{2}} z (x \pm iy) \quad (11.46)$$

$$m = 0 \quad \phi_2^0 \propto \frac{1}{2\sqrt{3}} (r^2 - 3z^2). \quad (11.47)$$

Fig. 11.14 Wave number of electron and relation to external magnetic field



We choose the coordinate system as shown in Fig. 11.14 and discuss for two cases.
 ① $\mathbf{k} = (0, 0, k_z)$ case. This corresponds to the electric current that is parallel to magnetization, namely corresponding to $\rho_{//}$. In (11.33), ρ is divided by m/ne^2 and put as ρ .

$$\rho_{sd}^{\uparrow}(k_z) = \left| \int [\text{sum.of.right.side} \cdot \text{term} \cdot \text{in} \cdot (11.39) - (11.42)] * V(r) e^{ik_z z} dv \right|^2 \quad (11.48)$$

In (11.45), (11.46), the term corresponding to $m = \pm 2, \pm 1$ becomes zero and only the term of (11.8) remains. Then,

$$\begin{aligned} \rho_{sd}^{\uparrow}(k_z) &= \left| \int e^{ik_z z} V(r) \left(\frac{3}{2}\right)^{1/2} \varepsilon R(r) \frac{1}{\sqrt{12}} (r^2 - 3z^2) dv \right|^2 \\ &= \frac{3}{2} \varepsilon^2 \cdot \frac{4}{12} \left| \int e^{ik_z z} V(r) R(r) z^2 dv \right|^2. \end{aligned} \quad (11.49)$$

Similarly,

$$\rho_{sd}^{\downarrow}(k_z) = \left(1 - \frac{3}{4} \varepsilon^2\right)^2 \cdot \frac{4}{12} \left| \int e^{ik_z z} V(r) R(r) z^2 dv \right|^2. \quad (11.50)$$

② $\mathbf{k} = (k_x, 0, 0)$ case. The electric current is perpendicular to the magnetization which corresponds to $\rho_{\perp}$. Since at $M/m = \pm 2$ and 0 , $1/\tau \neq 0$ and at $m = \pm 1$, $1/\tau = 0$

$$\begin{aligned}
\rho_{\text{sd}}^{\uparrow}(k_x) &= \frac{3}{2}\varepsilon^2 \left| \int e^{ik_x x} V(r) R(r) \frac{1}{\sqrt{12}} x^2 dv \right|^2 + \varepsilon^2 \left| \int e^{ik_x x} V(r) R(r) \frac{1}{2\sqrt{2}} x^2 dv \right|^2 \\
&= \frac{3}{4}\varepsilon^2 \frac{4}{12} \left| \int e^{ik_x x} V(r) R(r) x^2 dv \right|^2.
\end{aligned} \tag{11.51}$$

Also,

$$\begin{aligned}
\rho_{\text{sd}}^{\downarrow}(k_x) &= \left(1 - \frac{1}{2}\varepsilon^2\right)^2 \left| \int e^{ik_x x} V(r) R(r) \frac{1}{2\sqrt{2}} x^2 dv \right|^2 \\
&\quad + \left(1 - \frac{3}{4}\varepsilon^2\right)^2 \left| \int e^{ik_x x} V(r) R(r) \frac{1}{\sqrt{12}} x^2 dv \right|^2 \\
&\quad + \left| \int e^{ik_x x} V(r) R(r) \frac{1}{\sqrt{12}} x^2 dv \right|^2 \\
&= \left(1 - \frac{3}{4}\varepsilon^2\right) \left| \int e^{ik_x x} V(r) R(r) x^2 dv \right|^2.
\end{aligned} \tag{11.52}$$

Therefore,

$$\frac{4}{12} \left| \int e^{ik_x x} V(r) R(r) x^2 dv \right|^2 = \frac{4}{12} \left| \int e^{ik_x x} V(r) R(r) z^2 dv \right|^2 \equiv \rho'.$$

Then,

$$\begin{aligned}
\rho_{\text{sd}}^{\uparrow}(k_z) &= \rho_{//}^{\uparrow} = \frac{3}{2}\varepsilon^2 \rho' \\
\rho_{\text{sd}}^{\downarrow}(k_z) &= \rho_{//}^{\downarrow} = \left(1 - \frac{3}{2}\varepsilon^2\right) \rho' \\
\rho_{\text{sd}}^{\uparrow}(k_x) &= \rho_{\perp}^{\uparrow} = \frac{3}{4}\varepsilon^2 \rho' \\
\rho_{\text{sd}}^{\downarrow}(k_x) &= \rho_{\perp}^{\downarrow} = \left(1 - \frac{3}{4}\varepsilon^2\right) \rho'.
\end{aligned} \tag{11.53}$$

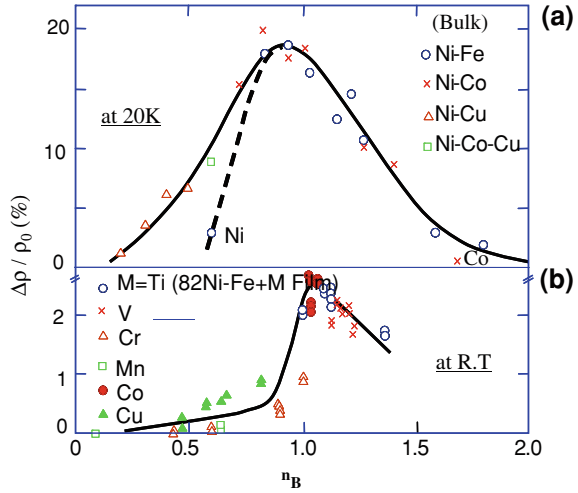
From these equations,

$$\begin{aligned}
\rho_{//}^{\uparrow} &\approx \rho_{\perp}^{\uparrow} + \gamma \rho_{\perp}^{\downarrow} \\
\rho_{//}^{\downarrow} &\approx \rho_{\perp}^{\downarrow} - \gamma \rho_{\perp}^{\uparrow}.
\end{aligned} \tag{11.54}$$

Here, $\gamma \approx 3\varepsilon^2/4$. When the spin-orbit interaction is negligibly small, we can set $\gamma = 0$ in (11.54). Then, $\rho_{//}^{\uparrow} = \rho_{\perp}^{\uparrow}$, $\rho_{//}^{\downarrow} = \rho_{\perp}^{\downarrow}$, and $\rho_{//} = \rho_{\perp}$. Namely, no anisotropic magnetoresistance occurs.

It is quite difficult to explain that the spin-orbit interaction causes the AMR experimentally. As one method, the dependence of $\Delta\rho/\rho_0$ on the magnetic moment is discussed. Figure 11.15 shows $\Delta\rho/\rho_0$ as a function of magnetic moment (n_B) for various kinds of alloys. In both bulk and thin film [13] cases,

Fig. 11.15 $\Delta\rho/\rho_0$ versus magnetic moment n_B



$\Delta\rho/\rho_0$ exhibits a maximum at around $n_B = 1$. It is concluded that the spin–orbital interaction works as a cause of the magnetoresistance effect because it is the most effective at $n_B = 1$.

11.6 Magnetoresistance Curve Based on the Magnetization Rotation Model

The strange shape of the magnetoresistance curve can be explained by simple calculation [14]. Moreover, the result might act as a practical use. The author introduces two examples for this. The directions of applied magnetic field H , saturation magnetization M_s , and the electric current now are taken with respect to the direction of the uniaxial anisotropy as shown in Fig. 11.16. The total energy of this system is,

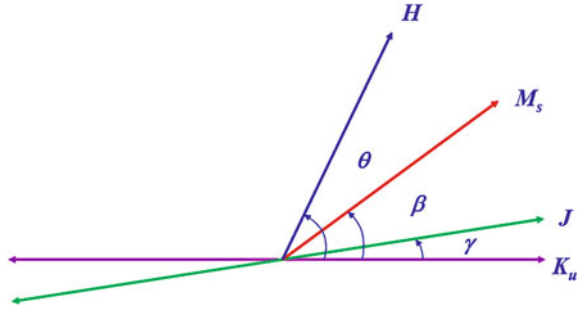
$$E = K_u \sin^2 \beta - \mu_0 M_s H \cos(\theta - \beta). \quad (11.55)$$

We only have to calculate a component of magnetization in the direction of the applied magnetic field to draw the magnetization curve.

$$M = M_s \cos(\theta - \beta) \quad (11.56)$$

On the other hand, the magnetoresistance curve may be obtained only by calculating (11.57). $\rho_{//}$ and $\rho_{\perp}$ are electrical resistivities here when the magnetic field is applied in a parallel and perpendicular direction to the electric current direction, respectively. Here, ρ_0 is the one in the demagnetized state.

Fig. 11.16 Coordinates when hysteresis curve and magnetoresistance curve are calculated



$$\frac{\rho_{//} - \rho_{\perp}}{\rho_0} = \frac{\rho_{//} - \rho_{\perp}}{\frac{\rho_{//}}{3} + \frac{2\rho_{\perp}}{3}} \left\{ \cos^2(\gamma - \beta) - \frac{1}{3} \right\}. \quad (11.57)$$

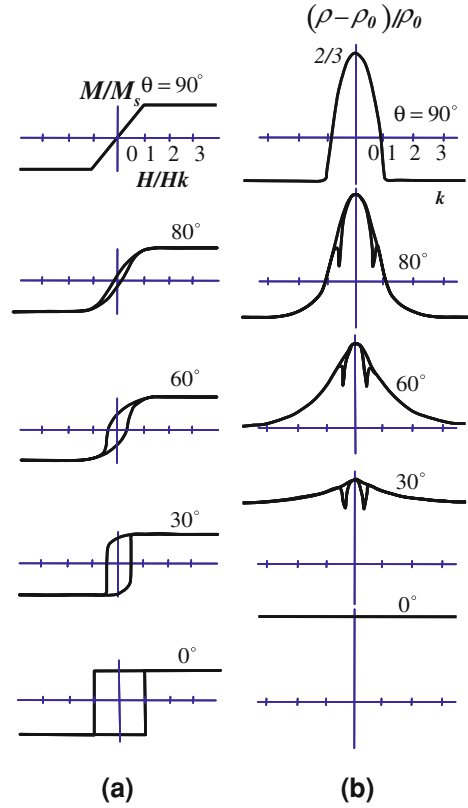
Setting $M_s = 1$, $(\rho_{//} - \rho_{\perp}) / (\rho_{//}/3 + 2\rho_{\perp}/3) = 1$ and $H_k = 2K_u/\mu_0 M_s$, we calculated the hysteresis curve and magnetoresistance curve (MR curve) when the direction of current is parallel to easy axis ($\gamma = 0$). The result is shown in Fig. 11.17.

If the direction of the applied field deviates from the hard axis, sharp dips appear. If the current direction deviates from easy axis, there appears hysteresis in the MR curve which is not shown in the figure. The dips and hysteresis mentioned above have been considered due to Bulkhausen noise. But they appear even in the uniform rotation of magnetization. Let us show another example of an MR curve for a film which has perpendicular magnetic anisotropy. Figure 11.18a shows MR curves reported by Velu et al. [15] for Co/Au multilayers. This resistance was measured in the film plane by applying magnetic field perpendicular to the film plane. The MR curve was calculated by (11.57) with $\theta = 0^\circ$ and $\gamma = 0^\circ$ in the coordinate system shown in Fig. 11.16. As a result, resistance was constant as a function of the applied field, which was quite different from the curve in Fig. 11.18a. Further, the MR curve was measured with the assumption that easy axis is declined from the normal to film. A very similar curve with Fig. 11.18a was obtained when $\theta = 40^\circ$, $\beta = 0^\circ$, $\gamma = 130^\circ$, $2K_u/M_s = 4$ (Oe) and combined with the case $\theta = 40^\circ$, $\beta = 0^\circ$, $\gamma = 50^\circ$, $2K_u/M_s = 6$ (Oe). The result is shown in Fig. 11.18b and the corresponding hysteresis curve in Fig. 11.18c. The calculated MR curve agrees well with that of experiment, supporting the propriety of the model described above. Although the measurement of magnetoresistance is very simple, we are able to investigate the magnetization process from the MR curves.

11.7 Giant Magnetoresistance Effect of Metallic Superlattices and Multilayer Films

The research on the metallic superlattice was from the end of 1970 to 1980. Judging from a historical point of view, the magnetic memory and the bubble magnetic memory, using the Permalloy thin film carried out ahead of this generation, were

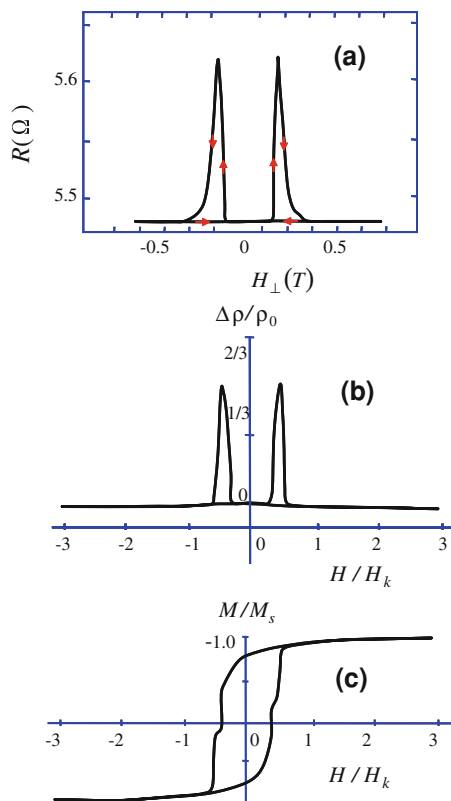
Fig. 11.17 Examples of hysteresis curve (a) and magnetoresistance curve (b)



researched. It can be said that thin film preparation technology, microfabricating technology, and the characterization technique cultivated there enabled this research though those researches did not develop greatly. Especially, the MBE (molecular beam epitaxy) technology is a suitable multilayer film-making technology for the metallic artificial superlattice, and contribution to the superlattice research was developed remarkably. As for the research on the metallic superlattice, especially initial research, reports such as multilayers effective for the generation of the perpendicular magnetic anisotropy or the high saturation magnetization thin film were eagerly performed. Moreover, such researches were chiefly done in Japan. However, it might be a report on GMR of the Fe/Cr artificial lattice, after all, that drew a lot of researchers (magnetic) in thin film study to the field of the metallic artificial superlattice.

Figure 11.19 shows MOKE hysteresis loops measured along easy and hard axes and corresponding MR curves for GaAs(100)/12nmFe/1nmCr/12nmFe sandwich junction [16]. If we start with parallel alignment in the positive field direction and reduce B_0 (see Fig. 11.19a), then at a certain field the magnetization of one film reverses via domain wall motion (①). Hence in small fields we have antiparallel alignment. In such fields the corresponding resistance is high state (see Fig. 11.19c).

Fig. 11.18 **a** Magnetoresistance curve for Au/Co(7.6Å)/Au(30Å)/Au measured at 4.2 K. **b** Calculated magnetoresistance curve and **c** corresponding hysteresis curve



In a negative field, at point ① in Fig. 11.19a, the other film also reverses and we have saturation. In this field, the corresponding resistance is low state (see Fig. 11.19c). In Fig. 11.19b MOKE loop measured along hard axis is shown and the corresponding resistance is shown in Fig. 11.19d. In this case we can also see that resistance is high at antiparallel state and low at parallel state. In Fig. 11.19d normal anisotropic magnetoresistance curve for a 250 Å thick film is also shown. The magnetoresistance ratio defined as $(R_{AP} - R_P)/R_P$ is one order larger than the anisotropic magnetoresistance of pure iron film.

Figure 11.20 shows the magnetoresistance curve of $(30\text{ÅFe}/9\text{ÅCr})_{40}$ superlattice [17]. The multilayered films can be made by MBE method for epitaxial growth on the GaAs(011).

Any of (a) and (b) in the curves of Fig. 11.20 are the magnetoresistance curves where the electric current is parallel and vertical to the applied magnetic field in plane of film, respectively. Curve (c) obtained in vertically applied magnetic field to the film plane corresponds to curves (a) and (b) corrected by the demagnetizing field. The point for which the shape of the magnetoresistance curve does not depend on the direction of the applied magnetic field is a feature of the GMR effect. When the mag-

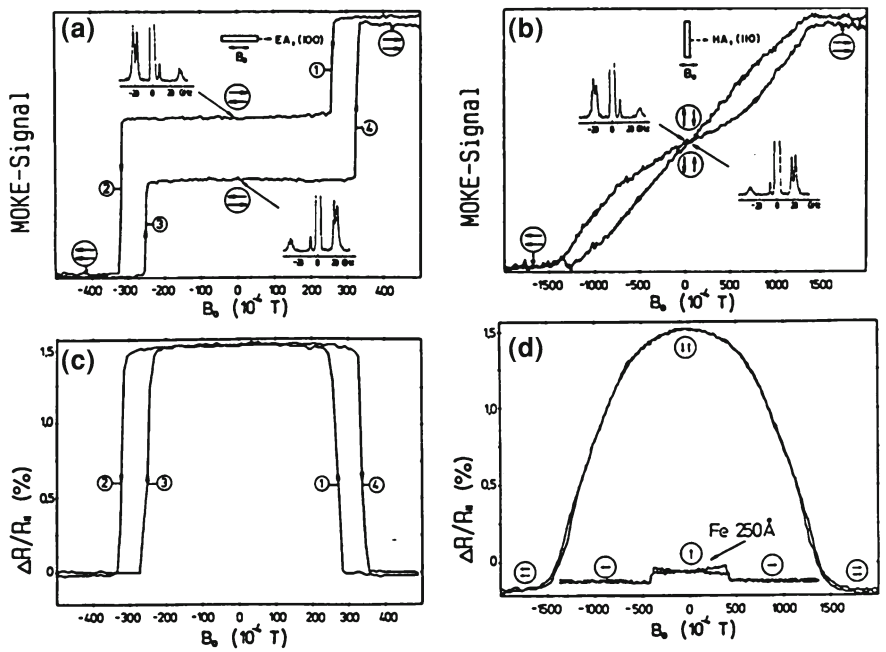
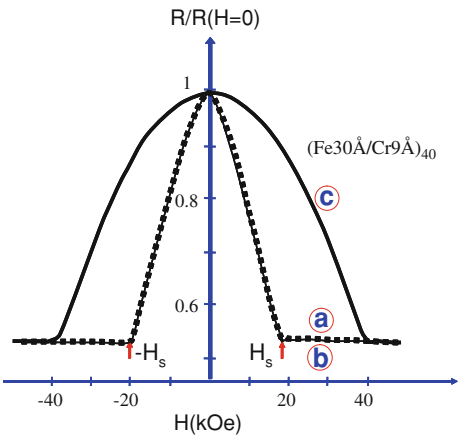


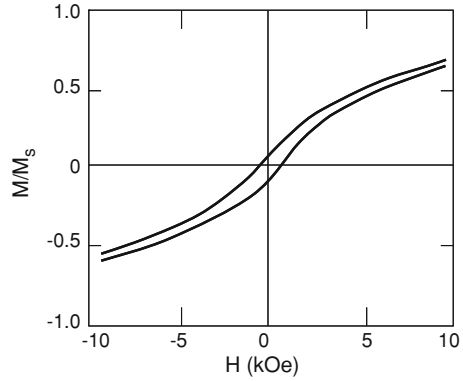
Fig. 11.19 MOKE hysteresis curves (a, b) and magnetoresistance $\Delta R/R_{//} = (R - R_{//}) / R_{//}$ from Fe layers with anti-ferromagnetic coupling (c, d). Also, (d) displays the anisotropic MR effect of a 250 Å thick Fe film

Fig.11.20 Magnetoresistance curve of superlattices (30 ÅFe/9 ÅCr)₄₀ (4.2 K)



netic field is strong enough as shown in this figure, the magnetization of the Fe layer is saturated in the direction of the applied magnetic field and the magnetization of the layer interface becomes complete in parallel. On the other hand, an antiferromagnetic interaction works at the Fe layer interface without magnetic field. Consequently, the

Fig. 11.21 Magnetization curve of superlattice in Fig. 11.20



magnetization is in the state of an antiparallel. That is, when the magnetization of the layer interface is parallel, the resistance is small, but when it is antiparallel, the resistance is large. The magnetization curve in Fig. 11.21 corresponds to the magnetoresistance curve in Fig. 11.20. The antiferromagnetic interaction works through Cr at the Fe layer interface. This is confirmed by the experiment such as neutron scatterings. Moreover, it was shown that the interaction between the layer interfaces and the value of MR are correspondent excellently. In Fig. 11.22 one example is shown. Both the ratio of MR and the value of H_s are corresponding to each other and, to be interesting, these oscillate with respect to the thickness of Cr [18]. Here, H_s is the magnetic field where the magnetization is saturated in the magnetization curve and proportional to the magnetic interlayer interaction.

Later, the GMR effect and the interaction between magnetic interlayers of the combination of a lot of ferromagnetic substances and the non-magnetic substance including the Co/Cu multilayer film were researched. A phenomenological explanation of GMR has been discussed as much as AMR, etc. by the spin-dependent scattering (two-current model). That is, the electric current is assumed to bear independently with $\uparrow$ and $\downarrow$ spin electrons, and, in addition, the scattering with a spin flip is disregarded for easiness. The resistance $\rho_{\uparrow}$ and $\rho_{\downarrow}$ in (F) parallel array of the magnetization of each ferromagnetic layer is given by $\rho_{\uparrow} = N\rho_{+}$ and $\rho_{\downarrow} = N\rho_{-}$, respectively. Here, $\rho_{\uparrow}$ and $\rho_{\downarrow}$ are resistance where 4s electrons are scattered, respectively by $\uparrow$ spin and $\downarrow$ spin of 3d band, and N denotes the total interfaces. The total resistance is given by $1/\rho_F = 1/\rho_{\uparrow} + 1/\rho_{\downarrow}$. As the resistance of $\uparrow$ spin and $\downarrow$ spin is the same, $\rho_{\uparrow} = \rho_{\downarrow} = N(\rho_{+} + \rho_{-})/2$. From $1/\rho_{AP} = 1/\rho_{\uparrow} + 1/\rho_{\downarrow} = 2/\rho_{\uparrow}$, $\rho_{AP} = N(\rho_{+} + \rho_{-})/4$.

When we define the MR ratio as $\Delta\rho/\rho = (\rho_{AP} - \rho_P)/\rho_P$,

$$\frac{\Delta\rho}{\rho_0} = \frac{(\rho_{+} - \rho_{-})}{4\rho_{+}\rho_{-}} = \frac{(\alpha - 1)^2}{4\alpha}. \quad (11.58)$$

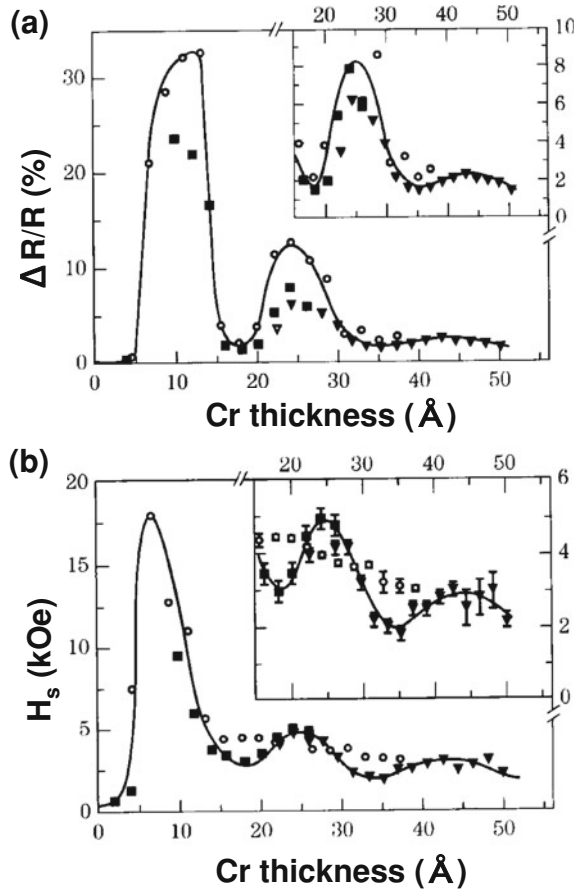


Fig. 11.22 Cr thickness dependence of (a) MR ratio and (b) saturation magnetic field in Fe/Cr artificial lattice

is given. Therefore, it can be understood that GMR vanishes at $\alpha = 1$, that is, $\rho_+ = \rho_-$. Then, why is the spin-dependent scattering microscopically caused? The theories are roughly divided into two groups. One is by Inoue and Maekawa [19–21]. According to their theory, an irregular exchange potential due to the atomic mixing of the region of 1 and 2 atomic layers is mainly responsible for the phenomenon. The result of calculation according to this idea seems to explain the experimental result to some degree in Fig. 11.23 [22].

The other theory is by Edwards [23] that the principal cause may be the bulk scattering. If d -band in the Fermi surface is remarkably different in $\uparrow$ spin and $\downarrow$ spins, it is expected that it is enough that scattering in the magnetic layer is different depending on the spin. When bands of Co and Ni are compared with that of Fe, the bulk scattering of the former is larger according to this idea. There are few examples

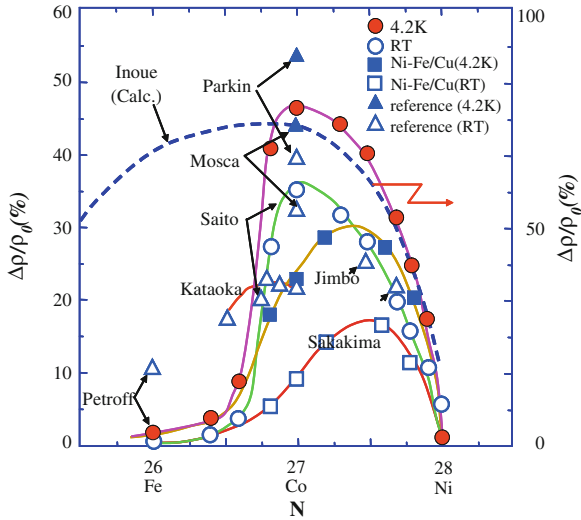
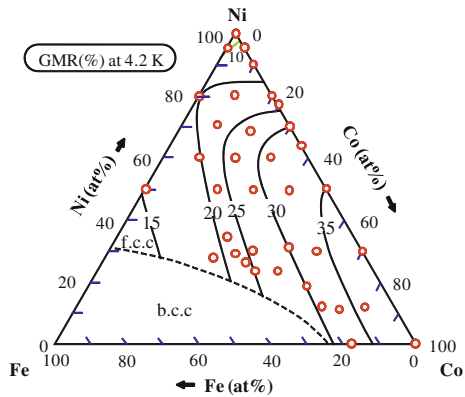


Fig. 11.23 Electron concentration dependence of MR ratio of various artificial lattices

Fig. 11.24 Composition dependence of GMR ratio of artificial lattice (15 Å Fe-Co-Ni/Cu)₃₀ (4.2 K)



of experimentally examining whether the interface scattering is effective or the bulk scattering is the main. The authors considered both the scatterings and explained the composition dependence of the GMR ratio of the Fe-Co-Ni/Cu multilayer film [24, 25]. One example is introduced here. In Fig. 11.24, the composition dependence of GMR ratio measured at 4.2 K of the multilayer films Fe-Co-Ni/Cu(15 Å)/Cu (18-25 Å) accumulated 30 times is shown in the contour line. The sample of the chemical composition of ○ sign in the figure is made. According to the two-current model, the GMR ratio is by the above-mentioned (11.58). In $\alpha \equiv \rho_+/\rho_-$ of (11.4), ρ_+ (ρ_-) is a resistivity of $\uparrow$ spin ($\downarrow$ spin) electrons that flow in the multilayer film. We assume it for the multilayer film as follows:

Fig. 11.25 Composition dependence of AMR ratio of Fe–Co–Ni alloy thin film (4.2 K)

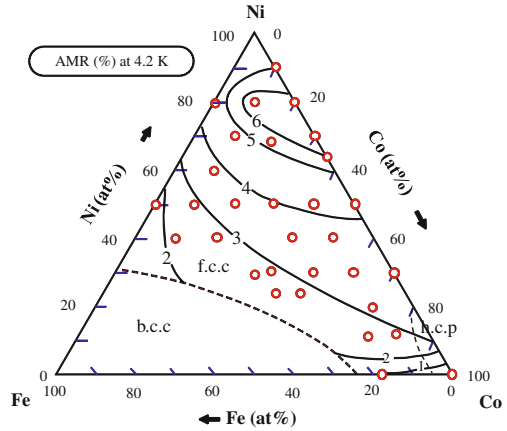
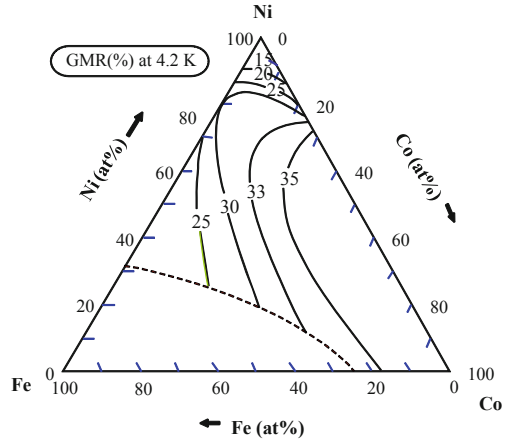


Fig. 11.26 Composition dependence of MR ratio of (Fe–Co–Ni/Cu)₃₀ artificial lattice (calculated value)



$$\rho_{\sigma} = \rho_{\text{int } \sigma} + \rho_{\text{bulk } \sigma} + \rho_0 \quad (\sigma = + \text{ or } -), \quad (11.59)$$

where $\rho_{\text{int } \sigma}$, $\rho_{\text{bulk } \sigma}$, and ρ_0 mean the residual resistivity of the spin-dependent interface or bulk scattering in the multilayer film, and ρ_0 shows the residual resistivity that does not depend on the spin. The term $\rho_{\text{int } \sigma}$ is assumed to be given by the linear combination of the concentration of the M(Fe, Co, Ni) atom in the magnetic layer and the state density of the Fermi level of each diffusive magnetic impurity atom to Cu layer (calculated value). We can obtain $\rho_{\text{bulk } \sigma}$ by analyzing the composition dependence of AMR ratio shown in Fig. 11.25. In addition, ρ_0 is assumed to be changeable in proportion to the concentration of Fe. These values are substituted for (11.59) and, in addition, it is substituted for (11.4). As a result, we can obtain the composition dependence of GMR and the ratio of the interface on the bulk scattering (Fig. 11.26).

Fig. 11.27 An interface scattering ratio of $\rho_{\downarrow}$

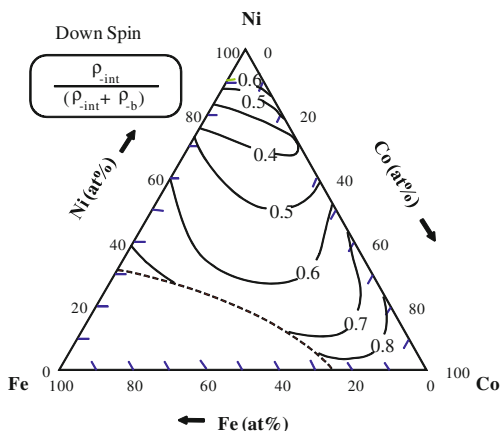


Figure 11.27 shows the interface scattering ratio of $\downarrow$ electron. As for $\uparrow$ electron, it is 0.4 in a core of the fcc region, and 0.6 in the circumference, and the composition dependence is not more remarkable than that of $\downarrow$ electrons. Moreover, when Figs. 11.26 and 11.27 are compared, it is understood that the magnetoresistance ratio is large in the chemical composition of rich Co where the interface scattering ratio of $\downarrow$ electron is large.

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Chapter 12

Tunnel Magnetoresistance Effect

First, both roots of tunnel effect in physics and magnetoresistance are described and then the birth of the term “tunnel magnetoresistance (TMR)” combining tunnel and magnetoresistance is explained. Then, the phenomenological theory of TMR based on Julliere is shown and the comparison among TMR, GMR, and Planer Hall Effect (PHE) is made. The trigger of magnesium oxide (MgO) barrier tunnel junction is described and typical data reported first are introduced. Further development of TMR study, especially the Heusler electrodes MTJ, is described.

12.1 Introduction

The discovery of giant magnetoresistance effect [1, 2] (GMR) of a metallic artificial lattice and TMR effect [3, 4] in the ferromagnetic tunnel junction which became a trigger for the field called “spin-electronics” or “spintronics” in the past 20 years has developed steadily. The point that this research is excellent is not only the object of basic research but also application. It has greatly contributed to the development of the industry, as the magnetoresistive reading heads, and nonvolatile random access memory (MRAM). First of all, the authors examine the root of TMR. Next, the development of the TMR effect using the Al_2O_3 barrier is described. Using the MgO barrier instead of the Al_2O_3 barrier, the TMR ratio rapidly increased. Also the TMR ratio increased, when the Heusler alloy is used for the electrodes. The situations of spin-RAM development and a few associated ongoing research are introduced in Chap. 13.

12.1.1 Root of Tunnel Effect

The term TMR consists of two words magnetoresistance and tunnel. Why does the physics of the tunnel phenomenon become interesting? As you know, the tunnel effect is a quantum-mechanical phenomenon which is impossible on the basis of

classical mechanics. G. Gamow explained the α particle (He-nuclei) decay on the basis of the tunnel effect in 1928. It may be said that the term tunnel effect was used, for the first time, by him. However, in around 1960, after about 30 years, it was popularly known as an electronic tunnel phenomenon in solids. Especially, the research of the diode p–n junction was developed into the device by Esaki [5] in 1958. Giaever and Megerle [6], early in the 1960s, began the research of the energy gap of the superconductor, using the junction consisting of superconductor/insulator/superconductor. The conduction electron can pass through the insulating layer by the tunnel effect even if the metal or the semiconductor is separated by a thin insulator or a potential barrier. Giaever and Megerle [6] paid attention to this respect, measured the energy gap of the superconductor for the I – V characteristics of various junctions, and clarified the density of state of superconductor. On the other hand, Tedrow and Meservey [7, 8] obtained the various ferromagnetic polarization including Ni by replacing the other superconductor of the junction by ferromagnetic material, and analyzing the I – V characteristics. These data of spin polarization were fine and very useful to investigate a high TMR junction. Julliere [9] (1975) reported on the applied voltage dependence of conductance of a tunnel junction in which both electrodes consist of a ferromagnetic substance. Moreover, they discussed the change of conductance with the change of magnetization direction in both magnetic layers using spin polarization. The term “magnetoresistance” is not used, though this paper is the first one to describe the TMR effect. The term magnetoresistance was not used though the researches using a ferromagnetic/insulator/ferromagnetic/ junction by 1990 were often reported. One of the double terms, “tunnel,” was often used in the papers. An interesting aspect is a point to approach to the term magnetoresistance. The term tunneling resistance by Maekawa and Gafvert [10] or magnetic valve by Slonczewski [11] was used in each of their papers. The typical junctions mentioned above are shown in Table 12.1, together with the fields of the research. By the way, tunneling junction with the vacuum instead of the insulator was reported by Binnig et al. [12] in 1982. It has been practically used as Scanning Tunneling Microscope (STM), which contributes much to research on the physics of surface phenomena.

12.1.2 Root of Magnetoresistance Effect

The first report of magnetoresistance effect in Ni and Fe was published by Thomson [13] in 1857. The term magnetoresistance was not used at that time even though the paper was published on the effect of an anisotropic resistance. By the way, the title is “Effects of magnetization on the electric conductivity of Nickel and of Iron”. He was later elevated to Lord Kelvin due to his contribution to fundamental science and engineering. However, one century was required for the contribution to engineering to work practically, since at that time it did not attract much practical attention. The term magnetoresistance was used by McKeehan [14] in 1930, though the first paper using magnetoresistance is not clear. An overview of anisotropic magnetoresistance up to 1975 was given by McGuire and Potter [15]. Moreover, the

Table 12.1 Historical details of research on junctions

Junction	Research targets
(1) p–n	Semiconductor
(2) $\text{Ag}^{(\text{N})}/\text{Al}_2\text{O}_3^{(\text{I})}/\text{Al}^{(\text{S})}$ $\text{Al}^{(\text{S})}/\text{Al}_2\text{O}_3^{(\text{I})}/\text{Sn}^{(\text{S})}$ $\text{Al}^{(\text{S})}/\text{Al}_2\text{O}_3^{(\text{I})}/\text{Pb}^{(\text{S})}$	Density of state for superconductors Josephson junction
(3) $\text{Fe}^{(\text{F})}/\text{Al}_2\text{O}_3^{(\text{I})}/\text{Al}^{(\text{S})}$	Spin polarization of ferromagnetic
(4) $\text{Fe}^{(\text{F})}/\text{GeO}^{(\text{I})}/\text{Co}^{(\text{F})}$ $\text{Ni}^{(\text{F})}/\text{NiO}^{(\text{I})}/\text{Co}^{(\text{F})}$	Bias dependence of G Field dependence of R
(5) $\text{Fe}^{(\text{F})}/\text{Cr}^{(\text{N})}/\text{Fe}^{(\text{F})}$ $\text{Fe}^{(\text{F})}/\text{Au}^{(\text{N})}/\text{Co}^{(\text{F})}$	Interlayer coupling Giant magnetoresistance
(6) $80\text{Ni}-\text{Fe}^{(\text{F})}/\text{Al}-\text{Al}_2\text{O}_3^{(\text{I})}/\text{Co}^{(\text{F})}$ $\text{Fe}^{(\text{F})}/\text{Al}_2\text{O}_3^{(\text{I})}/\text{Fe}^{(\text{F})}$ $\text{CoFe}^{(\text{F})}/\text{Al}_2\text{O}_3^{(\text{I})}/\text{Co}^{(\text{F})}$ $\text{Fe}^{(\text{F})}/\text{MgO}^{(\text{I})}/\text{Fe}^{(\text{F})}$ $\text{FeCo}^{(\text{F})}/\text{MgO}^{(\text{I})}/\text{FeCo}^{(\text{F})}$	Tunnel magnetoresistance

(N): Paramagnet, (I): Insulator, (S): Superconductor, (F): Ferromagnetic

review of the applied researches that came to be done extensively around 1960–1970 was given by Thompson et al. [16]. The first attempt to construct the theory of anisotropic magnetoresistance was made mainly in Europe in the 1950–1970s. Especially, Smit [17] took up this problem at early time. Moreover, both the theory and the experiment have been researched by Fert and Campbell [18–20] for a long time. These theoretical considerations [21] were based on the two-current model by Mott. The research on magnetoresistance is roughly summarized as shown in Table 11.1 in Chap. 11. Apparently, the term “tunnel magnetoresistance” was not used until the 1980s. Later in the 1990s several reports of magnetoresistance of the tunnel junction were published, besides GMR. It may be said, from the other point of view, that the research intended for application could link magnetoresistance with tunnel. The titles of the papers of tunnel junction quoted often until 1995 are shown in Table 12.2. The term TMR is not used, though the two terms of tunnel (tunneling) and magnetoresistance were used in the title. This kind of research increased gradually after 1995 and the term TMR came to be used. The author’s group used TMR for the first time in the latter half of the 1990s [27]. The root of TMR effect is summarized in Fig. 12.1. Moreover, the author’s group observed a large TMR ratio of about 18% at room temperature for the first time with the corresponding hysteresis curve shown in Fig. 12.3 [3].

12.2 Principle of TMR

The metallic superlattice described in Sect. 11.7 was a junction of ferromagnetic substance/non-magnetic metal/ferromagnetic substance. This non-magnetic metal is replaced with the insulator here. That is, ferromagnetic substance/insulator/

Table 12.2 Early research on tunnel magnetoresistance effect

• 1975 Julliere: tunneling between ferromagnetic films
• 1982 Maekawa and Gafvert: electron tunneling between ferromagnetic films
• 1987 Suezawa and Gongo: effect of spin-dependent tunneling on the magnetic properties of multilayered ferromagnetic thin films
• 1988 GMR reports
• 1989 Slonczewski: conductance and exchange coupling of two ferromagnets separated by tunneling barrier
• 1991 Miyazaki et al.: large, magnetoresistance effect in 82Ni-Fe/Al-Al ₂ O ₃ /Co magnetic tunneling junction
• 1991 Nakatani and Kitada: changes, in the electrical resistivity of Fe-C/Al ₂ O ₃ /Fe-Ru multilayered films due to a magnetic field
• 1992 Nowak and Rauluszkiewicz: spin dependent electron tunneling between ferromagnetic films
• 1993 Suezawa and Gondo: spin-polarized electrons and magnetoresistance in ferromagnetic tunnel junctions and multilayers
• 1995 Miyazaki and Tezuka: giant magnetic tunneling effect in Fe/Al ₂ O ₃ /Fe junction
• 1995 Moodera et al.: large, magnetoresistance at room temperature in ferromagnetic thin film tunnel junctions

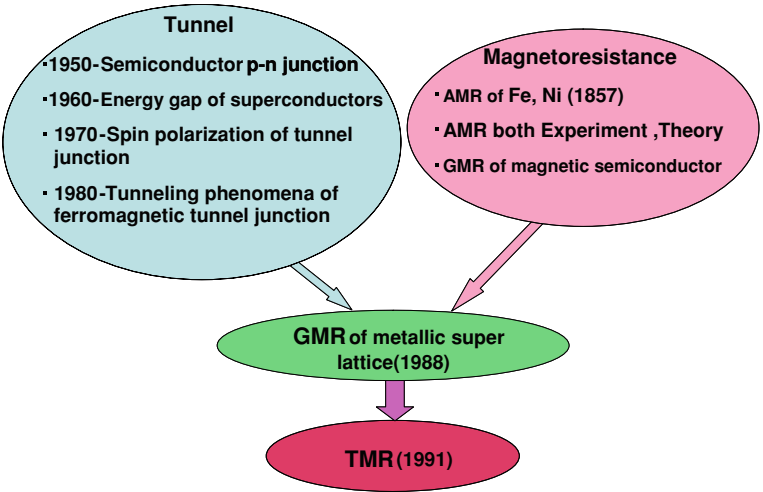


Fig. 12.1 TMR research combined with tunnel and magnetoresistance through GMR

ferromagnetic substance is called a tunnel junction. First of all, the principle of spin-dependent TMR effect and the history of the research are described here.

Pioneering research on the spin TMR effect was reported by Julliere [9] in 1975. He reported the magnetoresistance ratio at 4.2 K later described to be 14% in the Fe/GeO/Fe junction. The magnetoresistance effect in such a junction is explained theoretically as follows. The scheme to explain the cross-section of the junction, the density of states corresponding to each one, respectively, and the TMR effect

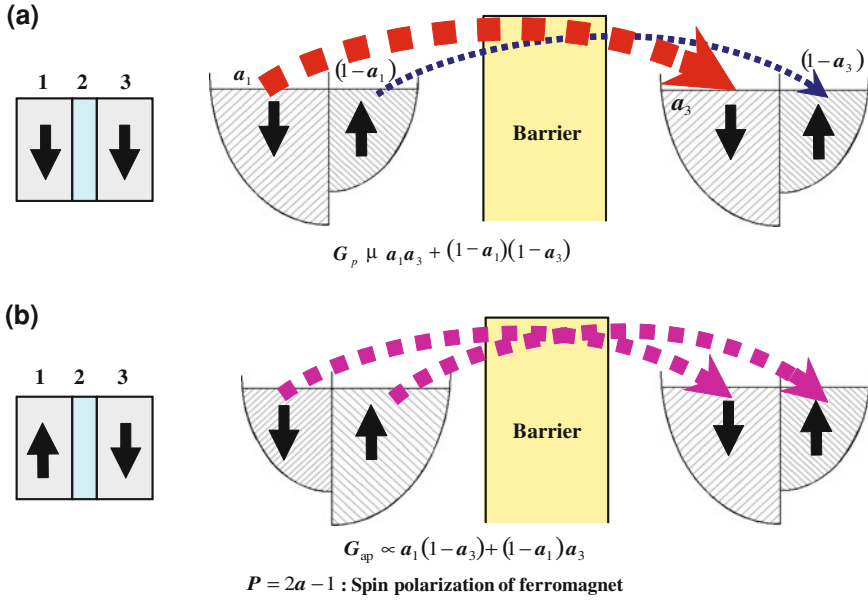


Fig. 12.2 Density of states of upward spin ($\uparrow$) electrons and downward spin ($\downarrow$) electrons in **a** parallel state and **b** antiparallel state in the magnetization of the magnetic layer. Each of a_1 or a_2 is existence probability of the electrons in the Fermi level

are shown in Fig. 12.2. The insulating layer in part 2 of Fig. 12.2 is assumed to be thin to the extent where the electron can do the tunneling. Coercive forces of the magnetic layers 1 and 3 are made different, and the magnetization of both layers can be achieved in parallel (above figure) and antiparallel (figure below). Moreover, the spin is assumed not to flip by the tunneling process of the electron. That is, $\uparrow$ spin electron and $\downarrow$ spin electron are assumed to move thoroughly, respectively, by the tunneling process of the spin from 1 to 3 layers.

When the magnetizations of both layers are in the parallel and antiparallel states under such assumption, the resistance is assumed to be R_p and R_{ap} , respectively. Hence, the magnetoresistance ratio $(R_{ap} - R_p) / R_p$ is given by

$$\frac{R_{ap} - R_p}{R_p} = \frac{2P_1 P_3}{1 - P_1 P_3}. \quad (12.1)$$

Both P_1 and P_3 are assumed to be a spin polarization of the magnetic substance in 1 and 3 layers. Moreover, the numbers of the majority spin and minority spin electron number are assumed to be N_M and N_m , respectively. Then, P is given by (12.2),

$$P = \frac{N_M - N_m}{N_M + N_m}. \quad (12.2)$$

And a_1 and a_3 in the figure correspond to $N_M/(N_M + N_m)$ of the 1 and 3 layers, respectively, and $P_{1(3)} = 2a_{1(3)} - 1$. Maekawa and Gafvert [10] replaced the tunneling electron ratio a_1 and a_3 of Fig. 12.2 with state density, D_σ ($\sigma = \uparrow, \downarrow$), of the Fermi surface, to discuss the magnetoresistance effect. We only have to replace $N_M(N_m)$ of (12.2) in that case with $D_{\uparrow(\downarrow)}$. Moreover, the polarization dependence of the magnetoresistance is shown in 12.1. In addition, Slonczewski [11, 28] assumed the potential of the frame as a barrier. Moreover, he took the smooth connection of the wave function in the interface of the ferromagnetic and the insulating layer. He showed that the polarization may be modulated as a result. Expressing the magnetoresistance as well as 12.1 of his representation (Conductance G is discussed in his theory)

$$\frac{R_{\text{ap}} - R_{\text{p}}}{R_{\text{p}}} = \frac{2P_1 A_{12} A_{32} P_3}{1 - P_1 A_{12} A_{32} P_3}, \quad (12.3)$$

$$A_{12(32)} = \frac{\kappa - k_{1(3)\downarrow}}{\kappa^2 + k_{1(3)\uparrow} k_{1(3)\downarrow}}. \quad (12.4)$$

Here, $k_{1(3)\sigma}$ ($\sigma = \uparrow, \downarrow$) is a Fermi wave number of both $\uparrow$ and $\downarrow$ spins, and κ is a wave number in the barrier, and given by

$$\kappa^2 = 2m^*(U_0 - E_F)/\hbar \equiv \Phi. \quad (12.5)$$

Moreover, m^* is an effective mass of the electron, U_0 potential energy of the barrier, Φ the barrier height, E_F Fermi energy of the ferromagnetic substance, $\hbar$ Planck's constant divided by 2π , and $P_{1(3)}$ in (12.3) not modulated (an ideal) polarization. On the other hand, $A_{12(32)} P_{1(3)}$ shows an effective polarization. The point that should be noted is that an effective polarization vanishes according to the level of the value of κ (barrier height) as understood from (12.4). Thus, the magnetoresistance becomes 0 under the condition mentioned above.

The change by the magnetic field of the resistance of Fe/Al₂O₃/Fe junction [3] is shown in Fig. 12.3 for example (in general, it is called the magnetoresistance curve). The resistance rises at the magnetic field of ± 20 Oe, and decreases rapidly at ± 50 Oe as shown in this figure. As for the change in this resistance, when the magnetization of an upper and lower Fe layer is parallel, it corresponds to the magnetization curve of figure (b) well, and it is understood that the resistance is small in parallel state, while the resistance is large in antiparallel state. In this case, the coercive force is different due to changing the temperature of the substrate when an upper and lower Fe layer is made.

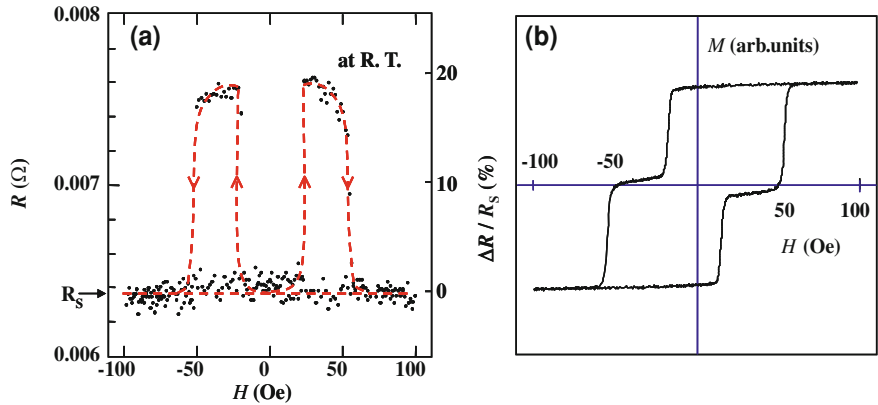
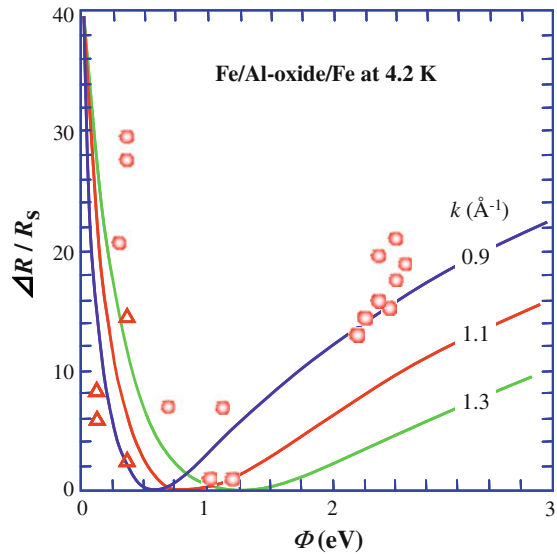


Fig. 12.3 **a** The magnetoresistance curve and **b** the corresponding magnetization curve in Fe/Al₂O₃/Fe junction

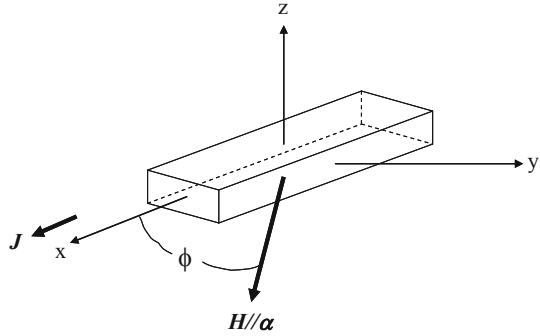
Fig. 12.4 Barrier height dependence of TMR ratio (4.2 K)



12.3 Barrier Height Dependence of TMR Ratio

Fe/Al₂O₃/Fe junctions with different barrier heights can be made. Then, it is possible to discuss the magnetoresistance dependence on the barrier height by the model of Slonczewski described ahead. The result of measurement for the MR ratio at 4.2 K with respect to barrier height is shown in Fig. 12.4 [29]. The sign Δ in the figure is a result reported by other groups about the MR ratio of the junction that uses Fe as an electrode. As a result, the effective polarization of Fe can be evaluated and the MR ratio of Fe/insulating layer/Fe could be estimated.

Fig. 12.5 Relation between electric current ($\mathbf{J}$) and magnetic fields ($\mathbf{H}$) in the galvanomagnetic effect



The solid line in this figure is a result calculated by (12.3), (12.4), and (12.5). In this case, because both magnetic layers are Fe, any of A_{12} , A_{32} , Fermi wave numbers $\kappa_{1\sigma}$, and $\kappa_{3\sigma}$ ($\sigma = \uparrow, \downarrow$) are equal to each other. Therefore, we can calculate the magnetoresistance ratio by using Φ and $P_{1(3)}$ if either $k_{1\uparrow}$ or $k_{1\downarrow}$ is known. Three cases with 0.9, 1.1, and $1.3 \text{ \AA}^{-1}$ are calculated here as $k_{1\uparrow}$. The experiment and the calculation results show that the MR ratio, becomes almost zero at $\Phi = 0.5 - 0.8 \text{ eV}$, and it grows on the both sides. The Φ dependence of both the experiments and calculation is roughly corresponding.

12.4 Comparison Among TMR, AMR, and PHE Effects

It is assumed that the magnetoresistance effect is a kind of the galvanomagnetic effect, which depends not only angles between the electric current and magnetic field, but also on the magnitude of them. It is also the electric field in the plane that each vector of the electric current and the magnetic field makes. When magnetic flux density is vertically applied to the electric current, the electric field is caused vertical to both vectors, which can be discussed along with the Hall effect. In general, the galvanomagnetic effect is given as

$$\mathbf{E} = \rho_{\perp} \mathbf{J} + (\rho_{//} - \rho_{\perp}) (\boldsymbol{\alpha} \cdot \mathbf{J}) \boldsymbol{\alpha} + \rho_H \boldsymbol{\alpha} \times \mathbf{J}, \quad (12.6)$$

where $\rho_{//}$, $\rho_{\perp}$, and ρ_H are specific resistances in the direction of x , y , and z in Fig. 12.5, respectively. $\boldsymbol{\alpha}$ is a unit vector in the direction of the magnetic field.

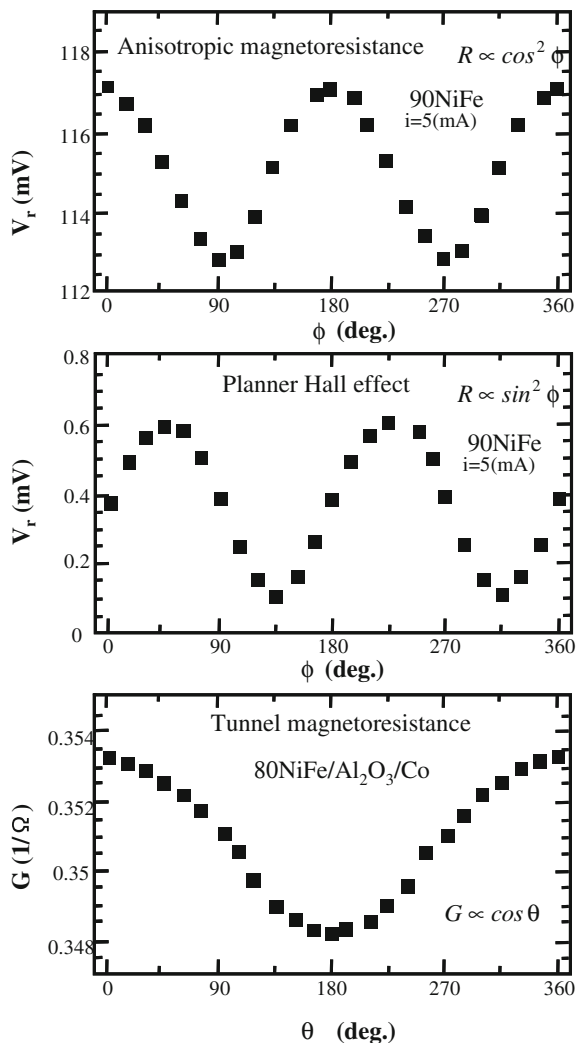
As shown in Fig. 12.5, if $\mathbf{J} = (J_x, 0, 0)$ and $\boldsymbol{\alpha} = (\cos \phi, \sin \phi, 0)$, we have

$$E_x = \rho_{\perp} J_x + (\rho_{//} - \rho_{\perp}) \cos^2 \phi \cdot j_x, \quad (12.7-a)$$

$$E_y = (\rho_{//} - \rho_{\perp}) \sin^2 \phi \cdot j_x / 2, \quad (12.7-b)$$

$$E_z = \rho_H \sin \phi \cdot j_x, \quad (12.7-c)$$

Fig. 12.6 Angular dependence of TMR, AMR, and PHE effects

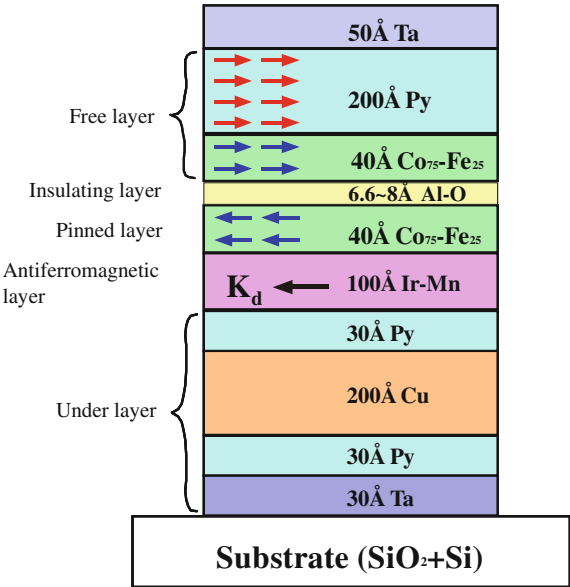


where ϕ is a angle between $\mathbf{J}$ and $\mathbf{H}$. Equation(12.7-a) denotes the so-called anisotropic magneto-resistance (AMR), and (12.7-b) is PHE. Both AMR and PHE are changed by the angle ϕ between the electric current and magnetic fields at cycle π as understood from these equations. On the other hand, the tunneling conductance is expressed as

$$G = G_0(1 + \varepsilon \cos \theta). \quad (12.8)$$

G_0 and ε are constants here, and θ denotes the angle between magnetization of both magnetic layers of the tunnel junction. The experimental result of the angular

Fig. 12.7 Cross-section scheme of spin valve-type junction

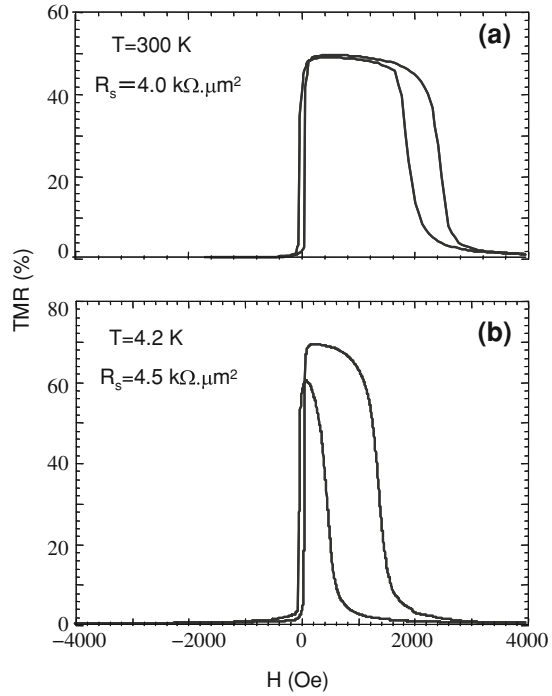


dependence of AMR [30], PHE [30] and TMR [31] is shown in Fig. 12.6a–c. It is understood to satisfy the relations above-mentioned in any case.

12.5 Spin Valve-Type Junction with Exchange Bias Layer

A standard junction was that of three layer types, one of which was made for the first stage of research in the TMR effect. The alloys of Fe, Co, Ni, Fe–Ni, and Fe–Co were used as a material of both magnetic layers and electrodes. The most general combination is $\text{Ni}_{80}\text{Fe}_{20}$ (Permalloy) and Co. Because Permalloy is soft in magnetic characteristics, (coercive force is small) but Co is semi-hard (coercive force is rather large), the antiparallel state of the magnetization can be easily achieved using the difference of coercive forces. Al_2O_3 insulating layer was the best at first stage among NiO, Al_2O_3 , AlN, MgO, HfO_2 , etc. When the tunnel junction is applied to the magnetic head for HDD and MRAM, the strength of the switching magnetic field and the shape of magnetoresistance curve are important, in addition to the change of magnetoresistance ratio and the tunnel resistance. One of magnetic layers is pinned by using a unidirectional anisotropy in the interface between an antiferromagnetic layer and a ferromagnetic layer. The research has progressed to the tunnel junction of a so-called spin valve type in the research of TMR as well as that of GMR. The reports of research on the junction of these types by Sato and Kobayashi [32, 33], Lu et al. [34], and Gallagher et al. [35] are the beginning. The combination of Py and Co has been used as a magnetic layer. Features are to be controlled the switching magnetic field well by the characteristic of this junction of which TMR ratio is larger

Fig. 12.8 Magnetoresistance curve at **a** 300 K and **b** 4.2 K of spin valve-type junction

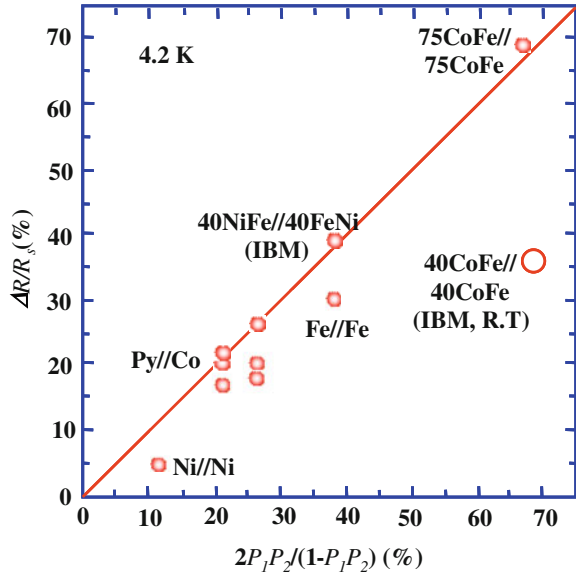


than that of simple three layer ones. Judging from the thermal resistance, IrMn seems to be the best though FeMn, MnRh, and IrMn are used as antiferromagnetic layer. We show the scheme in the cross-section of the junction that we studied at that time in Fig. 12.7 [36].

This junction has a lot of layered structures. Each layer is important to achieve a large TMR ratio and to control the resistance of junction. As for the thickness of film of each layer, it is not necessarily an optimized value. In Fig. 12.8, the MR curve is shown at 300 and 4.2 K of this junction [37]. The hysteresis of MR curve is small at the same time showing big TMR ratio of 50% at the room temperature. Therefore, a large change of resistivity is shown by a small applied magnetic field. These points work advantageously for the application as the read head of HDD.

In addition, the point that should make a special mention is to reach 69% in TMR ratio at 4.2 K. This value shows most agreements with 67% TMR ratio calculated as $P_1 = P_3 = 50\%$ in the (12.1), and ideal junctions in the experiment. Figure 12.9 [36] shows the relation between the theoretical value (horizontal axis) and experimental one (vertical line). We can see that the relationship shown by (12.1) in Sect. 12.2 is well satisfied.

Fig. 12.9 Relation between polarization and TMR ratio (the solid line is a value expected from the model of Julliere)



12.6 Single Crystalline High-Quality Tunnel Junction

It is considered that an interfacial state (electronic state) between the insulating layer and the magnetic layer accomplishes the key role to the TMR effect in the tunnel junction. It is expected to contribute to science and technology by making it an ideal junction as much as possible. It only has to make both electrodes ideally single crystalline. The upper electrode through the Al–O insulating layer (amorphous) in the middle cannot be made monocrystalline. The electrode in one side is therefore epitaxially developed using the single crystalline substrate. The group of AIST promptly paid attention to this respect, and has achieved a splendid result. The author introduces the two examples as follows:

Figure 12.10 shows the transmission electron microscope photograph in the section of the junction epitaxially developed on the Fe(001) by about 150 Å. When the photograph is seen well, the MgO layer is separated to the two layers. A lower layer that grew up to the first stage is amorphous but higher MgO(001) layer with crystallized and high orientation was obtained. In addition, it is understood that the surface of the Fe bottom electrode is more remarkably smoother than the surface of the MgO buffer layer when seen in more detail. This shows that the surface becomes very smooth for single crystal by arranging the azimuth.

Figure 12.11 indicates the value MR ratio when the surface of the Fe electrode is (100), (110), and (211) [38]. For the Fe electrode, the TMR is large in (211) plane, and is the smallest in (100) plane. Whether this orientation dependency reflected the difference of the electronic state by the crystal orientation of the electrode is a difficult point. However, it is interpreted that a relative relation compared with

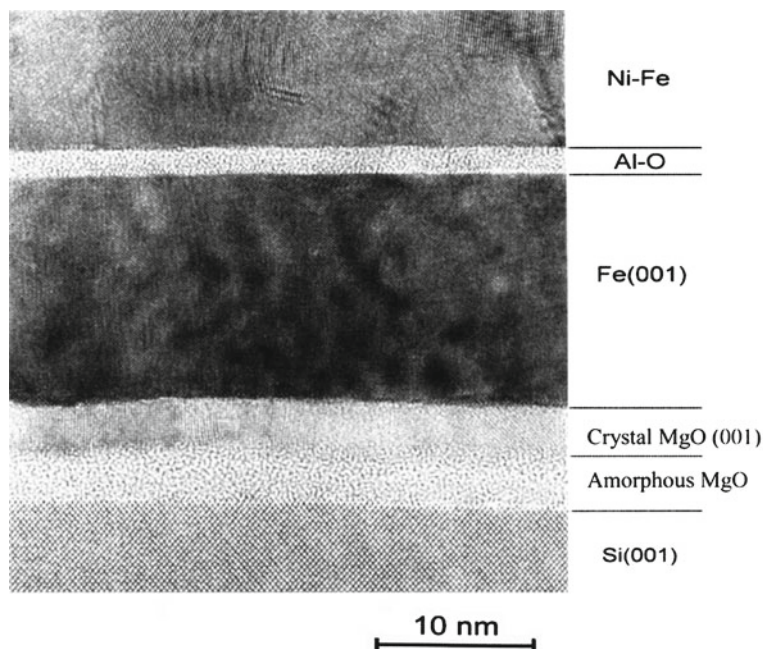


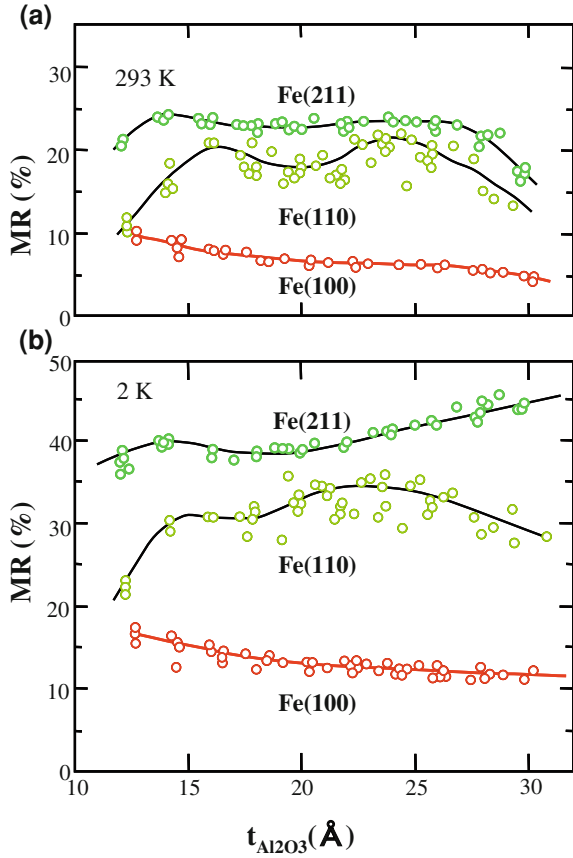
Fig. 12.10 Cross-sectional transmission electron microscope image of high orientation TMR uniting made by using the MgO groundwork layer on silicon substrate

this TMR reflected the electronic state from no change though it anneals. When high quality non-magnetic single crystal is inserted between the electrode, that is, a magnetic layer and Al–O that is the barrier, it is reported for TMR ratio to oscillate with respect to the thickness of the non-magnetic layer (Fig. 12.12) [39]. The cross-section scheme of the layer is shown in Fig. 12.13. The Cu layer is grown epitaxially on the Co(100) plane. The magnetoresistance oscillates because the interference effect depends on the spin by the direction of the movement of the electron. And, this interference effect is caused because the reflectivity of the electron on the Co/Cu field side is different. The research that uses single crystals for electrode is interesting because it is not only a basic research but also the viewpoint of application of the junction to MRAM. The bias dependence of TMR ratio was improved by using the high orientation electrode.

12.7 Tunnel Junction with MgO Barrier

During the first 10 years of the TMR research, the effect of TMR with tunnel barrier layer of an amorphous aluminum oxide (Al-oxide) was the main area of research. After 2004, however, much more attention has been paid to the research on

Fig. 12.11 Crystal orientation dependence of TMR ratio, **a** 293 K, and **b** 2 K



junction whose barrier layer is crystalline MgO. When the electron tunnels through the amorphous Al-oxide barrier layer, scattering is received and information on the wavenumber vector is lost (incoherent tunnel). On the other hand, the electron can tunnel coherently through the tunnel junctions on epitaxially developed layer such as Fe(001)/MgO(001)/Fe(001) junction.

As described in Sect. 12.6, Fe grows epitaxially on MgO single crystal and the interface of Fe and MgO is very smooth. The epitaxial relation is MgO(001)[110]/Fe(001)[010] (see Fig. 12.14). There is only a small lattice mismatch of about 3.5% between Fe–Fe and O–O in-plane distances. Furthermore, the electron population at the MgO interface plane is virtually the same as for the clean MgO surface and the Fe interface plane also behaves like a free Fe surface. Butler et al. [40] and Mathon and Umerski [41] who first showed huge TMR ratio for Fe/MgO/Fe junction emphasize the above points. Most previous theories of tunnel conductance and magnetoresistance have emphasized the density of states of the electrodes. The tunneling matrix elements (tunnel barrier) are almost always neglected or treated as

Fig. 12.12 Polarized resonant tunneling effect in TMR junction with Cu(100) inserted [43]

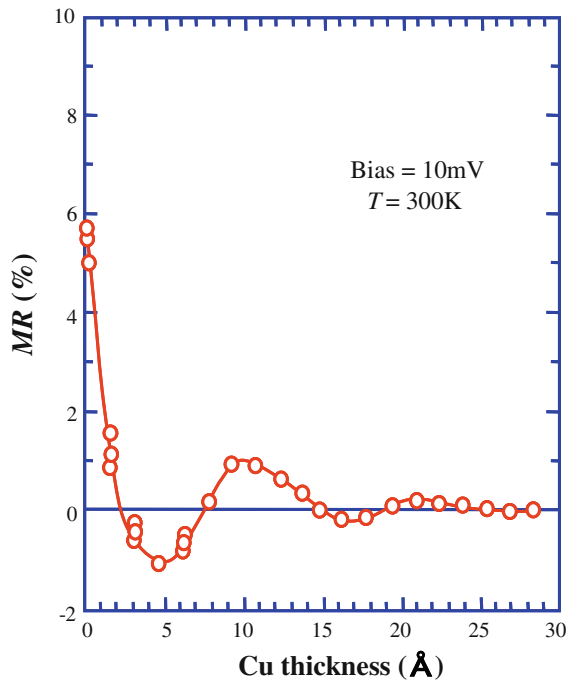
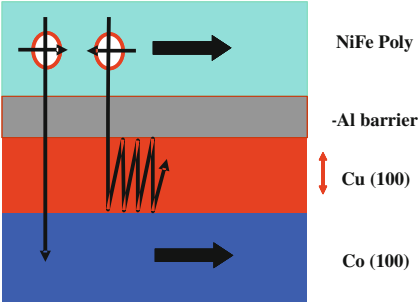
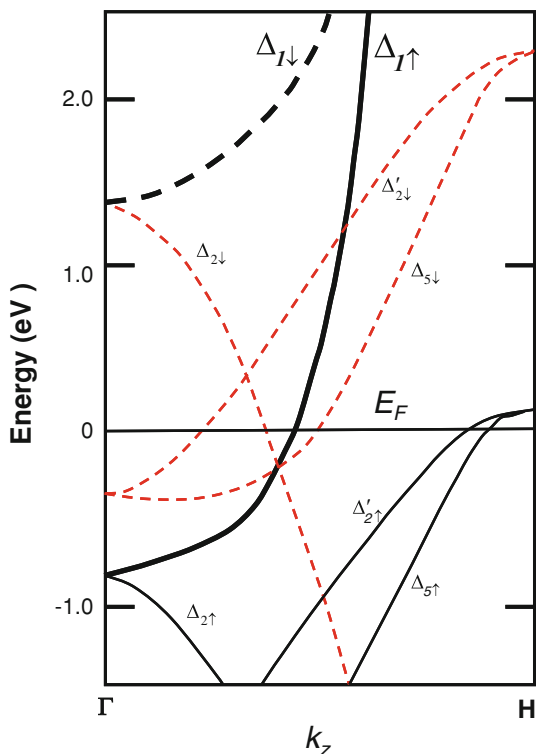


Fig. 12.13 Scheme of interference effect that depends on spin of tunneling electron in Cu(100) layer



inert factors. They pointed out that the nature of the states both in the electrodes and in the barrier layer are extremely important in determining the tunneling conductance. Specifically, they showed that the symmetry of both the propagating states in the electrodes and the evanescent states in the barrier material are crucial to determining the tunnel conductance. Figure 12.15 shows tunneling majority density of states for $k_{\parallel} = 0$ for Fe(100)/8MgO/Fe(100) calculated by Butler et al. As clearly seen in the figure, the decay states inside MgO barrier depend strongly on the band structure (note vertical axis is logarithm). From the figure, main tunneling process is $\text{Fe}(\Delta_1) \rightarrow \text{MgO}(\Delta_1) \rightarrow \text{Fe}(\Delta_1)$. Further, the Δ_1 band is completely

Fig. 12.16 Band structure of Fe. Solid lines show majority spin state and broken lines show minority spin state



ceeded in the observation of as large as 200% TMR ratio at room temperature in 2004 [43, 44].

In addition, the researchers at AIST and Canon-Anelba jointly showed that the huge TMR ratio can be achieved by combining the amorphous ferromagnetic material and the MgO barrier layer named CoFeB by the sputtering method appropriate for the productive process [45]. Afterwards, this technology continued developing [46]. The growth of the TMR ratio at room temperature, using the MgO and Al_2O_3 barrier for years, is plotted in Fig. 12.19.

12.8 Tunnel Junction with Half Metal Electrodes

Half metal material is classified roughly into the oxide system and the metal system. In the metal system, Heusler alloys are very attractive materials since they exhibit a variety of magnetic properties. The authors explain, first, historical details of the Heusler alloy that is a half metallic material: it was discovered by Heusler first in 1903, which had been named commemorating the discoverer [47]. It is notable that the material exhibits strong ferromagnetism though an alloy named Cu_2MnAl is

Fig. 12.17 Magnetoresistance curve of Fe/MgO/Fe junction

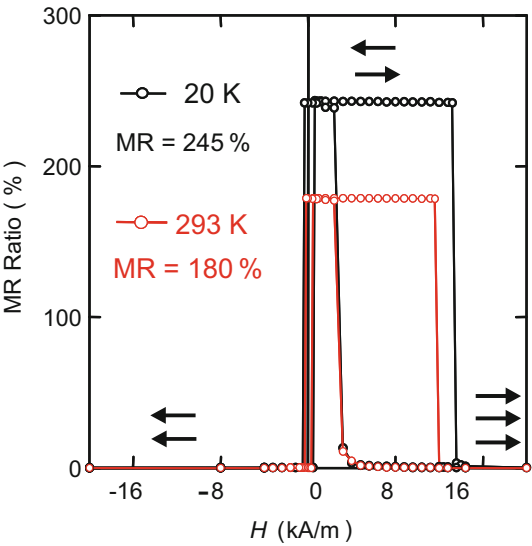
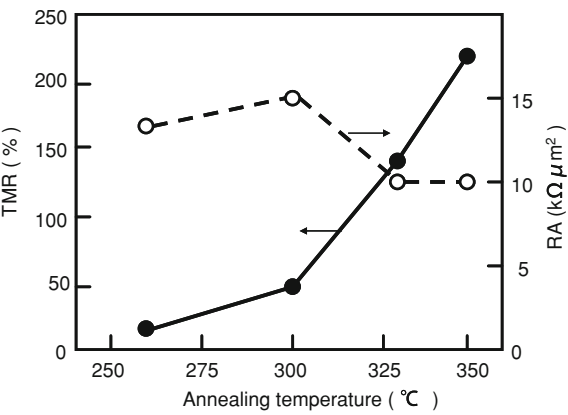


Fig. 12.18 TMR and RA values as a function of annealing temperature for CoFe/MgO/CoFeB tunnel junction



composed only of the non-magnetic metals. After 1983, it attracted attention as a half metal material, though a basic research on the evaluation of physical properties had been studied for about 80 years. Groot et al. [48] in 1983 carried out the band calculation of the Heusler alloy of composition named NiMnSb (called half Heusler alloy) and concluded that this material has the half metal electronic state. From 1995 onwards, the calculated result that compounds such as Co_2MnSi and Co_2MnGe could be the half metal was reported [49]. It again attracted attention in the Spintronics field, since the high Curie temperature of the Heusler alloy is very advantageous for application. Before the explanation of TMR for Heusler electrode, tunnel junction, crystal structure, magnetic moment, Curie temperature, and magnetic anisotropy will be explained.

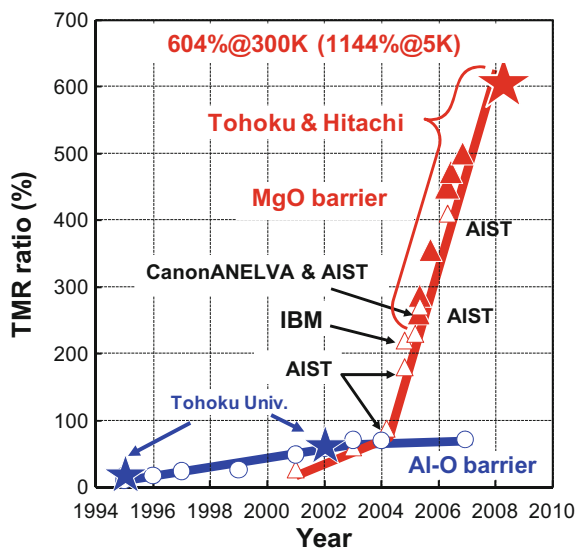


Fig. 12.19 Development of TMR value at room temperature

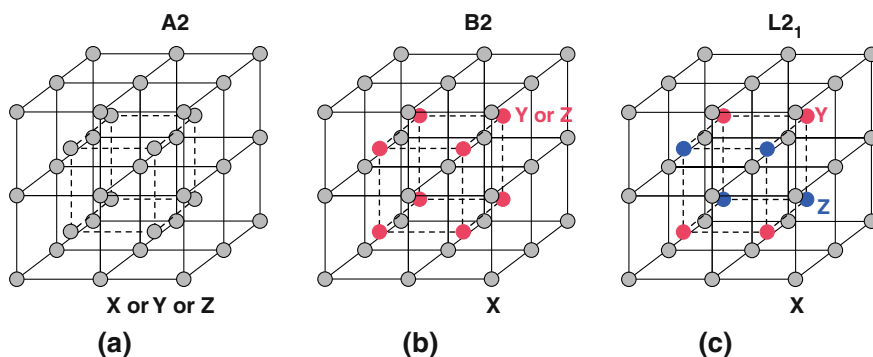


Fig. 12.20 Crystal structure of Heusler alloy

12.8.1 Crystal Structure

Heusler alloy basically has X_2YZ composition, and takes three units lattice structures according to the rule of the atomic ordered arrangement as shown in Fig. 12.20. The elements that enter each of sites are as follows, X: Fe, Co, Ni, Ru, Rh, Pd, Ir, Pt, Cu, Zn, Ag, Cd, and Au/chiefly VIII, IB, IIB family. Y: Ti, V, Cr, Mn, Y, Zr, Nb, Hf, Ta, Gd, Tb, Dy, Ho, Er, Tm, Yb/chiefly III, IV, V, VI, VII family. RE Z: Al, Si, Ga, Ge, As, In, Sn, Sb, Tl, Pb, and Bi/chiefly, III B, IVB family. $L2_1$ structure: the atoms are completely and regularly arranged. $B2$ structure: the Y–Z atoms are irregularly arranged. $A2$ structure: the X–Y–Z atoms are completely irregularly arranged.

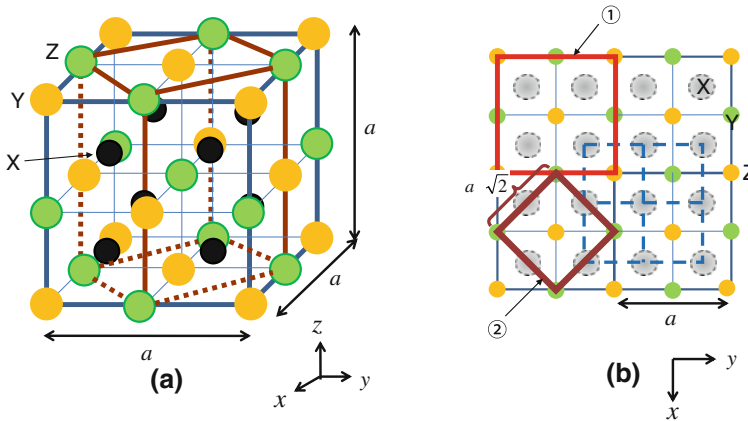


Fig. 12.21 L_{21} structure and its *top view* (4 times)

In X_2YZ , if Y is replaced by X , it becomes X_3Z compound. Mn_3Ga which is described at the end of this section corresponds to this compound. Mn_3Ga is often called Heusler-like compound. We will explain this point briefly. Figure 12.21a is the L_{21} structure and Fig. 12.21b is the top view of Fig. 12.21a, but four times the area. If we cut the crystal as shown in the figure ①, it is the L_{21} structure itself. The crystal cut like ② in Fig. 12.21, the length along c axis being a , is shown Fig. 12.22a. This state corresponds to a part of Heusler compound. But if we expand this figure along c axis as shown in Fig. 12.22b, then the crystal structure changes. This is called DO_{22} structure of Mn_3Ga . In case of bulk Mn_3Ga $a = 3.909$ and $c = 7.098$. The property as half metal, electric conduction characteristic, and magnetic characteristic, etc. of Heusler alloy may be influenced according to the degree of the order. Miura et al. [50] calculated the irregularity dependence of spin polarization and magnetic moment in the Co_2CrAl Heusler alloy. As a result, an ideal state of half metal is achieved in the state of a complete order (L_{21} structure), but the spin polarization decreases rapidly with an irregularity between $Co-Cr$ ($A2$ structure). Therefore, the evaluation of the structure factor is important for developing Heusler alloy. The evaluation of the most popular atomic structure factors can be deduced by the X-ray diffraction experiment. Briefly, it can be estimated by measuring the intensity ratio of the basic lattice line to the superlattice line.

12.8.2 Magnetic Moment, Curie Temperature, and Magnetic Anisotropy

Magnetic moment and Curie temperature have been discussed actively by German researchers for not only 3d transition metal alloys but also for Heusler alloys [51–53].

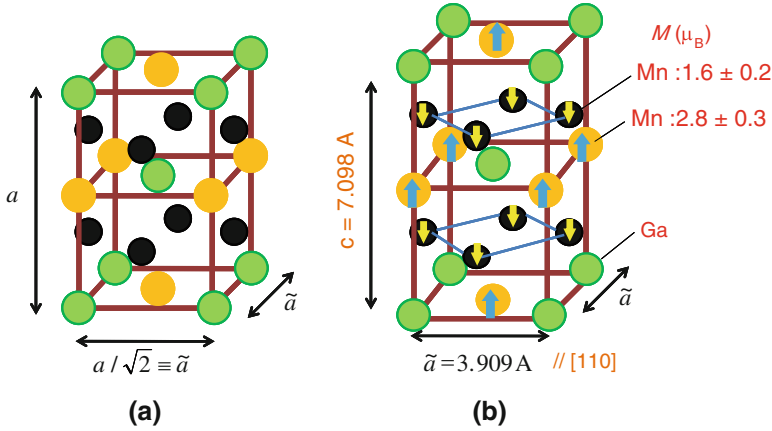


Fig. 12.22 Mn₃Ga D0₂₂ structure

The magnetic moment per atom (in μ_B) is expressed by

$$M = N^\uparrow - N^\downarrow, \quad (12.9)$$

where $N^\uparrow$ ($N^\downarrow$) is the number of majority (minority) spin electrons per atom. Neutrality requires $Z = N^\uparrow + N^\downarrow$, where Z is the number of valence electrons per atom. Eliminating $N^\uparrow$ from (12.9) and above relation one gets the relation between magnetic moment and valence electrons like

$$M = Z - 2N^\downarrow. \quad (12.10)$$

Galanakis et al. show

$$M = Z - 24, \quad (12.11)$$

for most of the full Heusler alloys (Fig. 12.23) [53] and $M_t = Z_t - 18$ for half Heusler alloys [54]. In Fig. 12.23 $\bullet$ shows the alloys satisfying the relation (3) and $\circ$ corresponds to the alloy deviating from this relationship. The values shown in Fig. 12.23 are the calculated ones and experimental results is also well expressed by (12.11). The alloys satisfying (12.11) mean $N^\downarrow = 12$, namely 12 spin electrons are in minority band. For the alloys with relatively large magnetic moment such as Co₂MnSi and Co₂MnAl, TMR effect is studied well. Figure 12.24 shows Curie temperature of Co-based Heusler alloys as a function of the number of valence electrons [55]. Curie temperature is proportional to the number of valence electrons except Co₂CrAl and Co₂VSn alloys.

On the other hand, little has been reported about magnetic anisotropy. Basically Heusler alloys are cubic structure and their magnetic anisotropy should be small. Yilgin et al. investigated magnetic anisotropy for several Heusler alloy epitaxial

Fig. 12.23 Calculated total spin moments for Heusler alloys

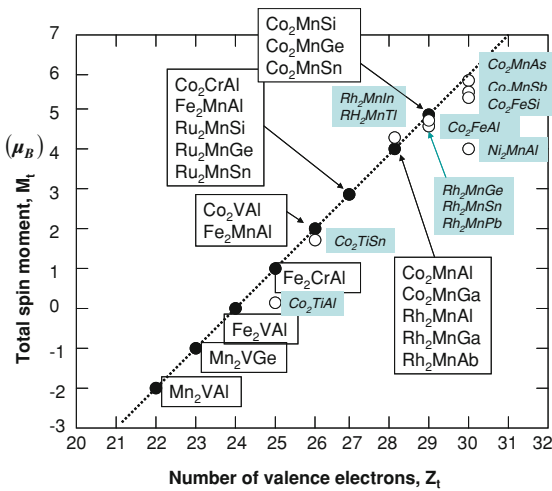
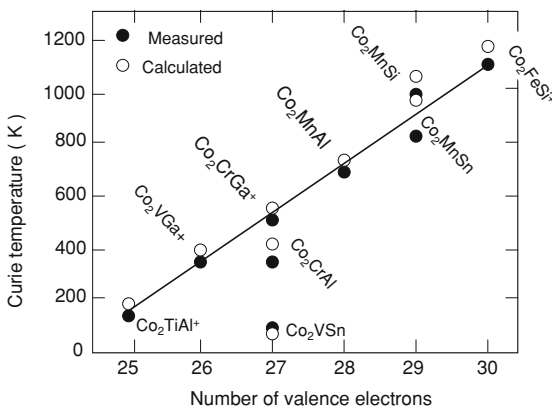


Fig. 12.24 Calculated (○) and measured (●) Curie temperatures versus the number of valence electrons



films. Table 12.3 summarizes crystalline magnetic anisotropy constant and coercive force [56, 57]. As seen in the table crystalline magnetic anisotropy constant K_1 is of the order of 1×10^4 erg/cc or less except B2 structure of Co_2MnSi . In the case of Co_2MnSi K_1 of B2 structure is approximately one order larger than that of L2₁ structure. This origin is unclear at present.

12.8.3 Magnetoresistance

The attempt to improve TMR ratio by using ferromagnetic electrode material with large spin polarization has been made as an approach besides the MgO barrier layer tunnel junction. The so-called half metal is expected for an ideal ferromagnetic material to improve the effect of TMR. It is a material that completely polarizes spin

Table 12.3 Magnetic properties for typical Heusler alloys with different structure

Valence electron no. alloy	Constants	B ₂	L2 ₁
		(400 C Annealed)	
Z = 28	<i>M_s</i> (emu/cc)	720	
Co ₂ MnAl [56]	<i>K₁</i> (erg/cc)	−0.5 × 10 ⁴	
	<i>H_c</i> (Oe)	11	
		(300 C Annealed)	(400 C Annealed)
Z = 29	<i>M_s</i> (emu/cc)	750–800	700–800
Co ₂ MnSi [57]	<i>K₁</i> (erg/cc)	−1.4 × 10 ⁴	−1 × 10 ⁴
	<i>H_c</i> (Oe)	20	18
		(600 C Annealed)	
Z = 29	<i>M_s</i> (emu/cc)	925	
Co ₂ FeAl [58]	<i>K₁</i> (erg/cc)	−1 × 10 ⁴	
	<i>H_c</i> (Oe)	20	
			(300 C Annealed)
Z = 30	<i>M_s</i> (emu/cc)		940
Co ₂ FeSi [59]	<i>K₁</i> (erg/cc)		0

Easy axis is [110]

Table 12.4 TMR ratio for the tunnel junctions with oxide half metal electrodes

Materials	Tc(°C)	Band gap (eV)	Moment (mB/f.u.)	Crystal St.	TMR ratio	Ref.
LaCaMnO ₃ (LCMO)		0.8 1.5	—	Perovskite	LCMO/NdGaO ₃ /LCMO: 86 % (77 K), 40 % (100 K)	[60, 61]
LaSrMnO ₃ (LSMO)	370	1.4		Perovskite	LSMO/STO/LSMO: 1850 % (4.2 K) LSMO/STO/Cα −32 % (40 K)	[62–64]
CrO ₂	398	1.5	2.0	Rutile	CrO ₂ /Natural oxi./Cα −8 % (5 K)	[65, 66]
Fe ₃ O ₄	850	1.3	4.0	Spinel	Fe ₃ O ₄ /Al-oxide/Cα 43 % (4.2 K)	[67, 68]

on Fermi surface (only either one type of electronic spin of the two types of electrons, i.e., electron with spin up, or electron with spin down), of which spin polarization is ideally 100%. The TMR ratio could be expected to become infinity theoretically in the tunnel junction using half metal for the electrodes, based on the Julliere’s model. Half metal material is classified roughly into the oxide system and the metal system. First of all, the related physical quantities such as Curie temperature, energy gap, magnetic moment for each unit molecule (theoretical value), crystal structure, and the TMR ratio of the tunnel junction with these electrodes are collectively shown for typical oxide system half metal reported up to now in Table 12.4. The bandgap of the oxide system half metal is as large as 1 eV, which is advantageous for large

Table 12.5 TMR ratio of typical Heusler alloy electrodes and Al-oxide barrier tunnel junctions

Materials	Crystal structure	TMR ratio	Ref.
NiMnSb	NiMnSb/Al-oxide/NiFe	2.4% (RT), 8.1% (77 K)	[69]
	NiMnSb/Al-oxide/NiFe	9% (RT), 19.5% (4.2 K)	[70]
Co ₂ MnSi	Co ₂ MnSi/Al-oxide/CoFe	33% (RT), 86% (10 K)	[71]
	Co ₂ MnSi/Al-oxide/CoFe	70% (RT), 159% (2 K)	[72]
	Co ₂ MnSi/Al-oxide/Co ₂ MnSi	67% (RT), 570% (2 K)	[74]
Co ₂ CrFeAl	Co ₂ CrFeAl/Al-oxide/Co	6% (RT), 10.8% (10 K)	[75]
	Co ₂ CrFeAl/Al-oxide/CoFe	19% (RT), 26.5% (5 K)	[76]
Co ₂ MnAl	Co ₂ MnAl/Al-oxide/CoFe	40% (RT), 60% (10 K)	[77]

TMR ratio in the high bias voltage. On the other hand, the disadvantage is a point that the Curie temperatures of them are rather low. Each of the Curie temperatures of LSMO, LCMO, and CrO₂ are level with room temperature; therefore, it is difficult to observe a large TMR ratio at room temperature. As understood from Table 12.4, TMR ratios at room temperature of tunnel junction using the oxide system half metal are as small as 10% in the reports of the past, in contrast to the huge TMR ratios observed at low temperatures. Moreover, another feature of oxide system is for the effect of inverse TMR to be observed. In contrast to a usual effect of TMR, inverse TMR effect has a feature that the parallel resistance is large, but the antiparallel resistance is small in respect to orientation of magnetization. It is, physically, a very interesting phenomenon though a huge effect of inverse TMR is not observed at present. Heusler alloys are classified into a half Heusler alloy such as NiMnSb and a full Heusler alloy such as Co₂MnSi. Here, the full Heusler alloy with a large TMR ratio will be simply described as the Heusler alloy, and the authors explain it a little more in detail. The TMR ratios of tunnel junction that combine the Heusler alloy electrode with the amorphous Al-oxide barrier layer are summarized in Table 12.5. In a pioneering research, the composition NiMnSb of the half Heusler alloys was used for an electrode. But the TMR ratio is as small as about 10% even at low temperature [69], which is not enough to prove the characteristics of half metal. Afterwards, in around 2003 the research using a full Heusler with the structures steadier than the half Heusler ones was started and the 10% TMR ratio came to be observed [71]. The breakthrough in the tunnel junction using Heusler alloy began with making the interfaces of the epitaxially developed Heusler alloy between insulators smoothly and cleanly. Sakuraba et al. [72] obtained the ratio of 159% at low temperature for Co₂MnSi/Al-oxide/CoFe tunnel junction with the Co₂MnSi Heusler alloy epitaxially developed on MgO single crystalline substrate. The spin polarization of Co₂MnSi estimated on the basis of Julliere's model from this TMR ratio is as large as 89% (spin polarization of CoFe is assumed to be 50% [73]). It was shown for the first time that the spin polarization of Co₂MnSi is very high. Afterwards, 570% TMR ratio was observed in Co₂MnSi/Al-oxide/Co₂MnSi junction of which composition of both electrodes is Co₂MnSi [74] (Fig. 12.25). However, the TMR ratio was as small as 100% or less at room temperature in the junction using the Al-oxide barrier

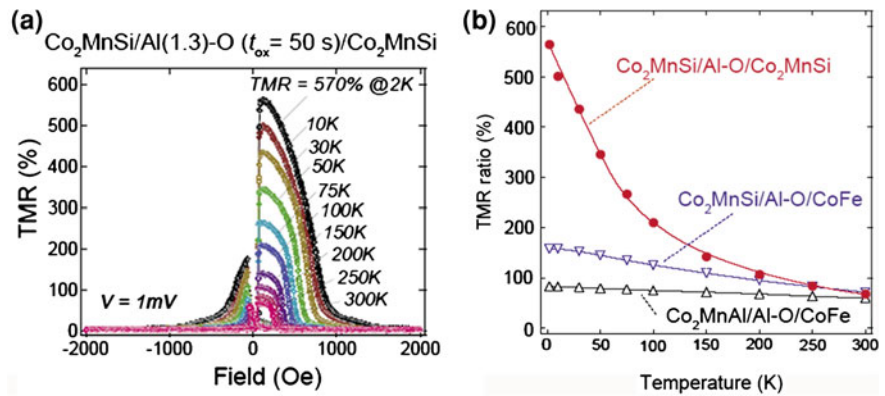


Fig. 12.25 Temperature dependence of TMR ratio of Heusler electrode with Al-oxide barrier tunnel junction

Materials	Crystal structure	TMR ratio	Ref.
Co_2MnSi	$\text{Co}_2\text{MnSi}/\text{MgO}/\text{CoFe}$	217% (RT), 753% (2 K)	[82]
	$\text{Co}_2\text{MnSi}/\text{MgO}/\text{Co}_2\text{MnSi}$	179% (RT), 683% (4.2 K)	[83]
Co_2MnGe	$\text{Co}_2\text{MnGe}/\text{MgO}/\text{CoFe}$	83% (RT), 185% (4.2 K)	[79]
Co_2CrFeAl	$\text{Co}_2\text{CrFeAl}/\text{MgO}/\text{CoFe}$	109% (RT), 317% (4.2 K)	[80]
Co_2FeAlSi	$\text{Co}_2\text{FeAlSi}/\text{MgO}/\text{Co}_2\text{FeAlSi}$	220% (RT), 390% (5 K)	[81]

layer. The analysis of the bias dependence of conductance shows clearly the bandgap of the Co_2MnSi electrodes, but the Fermi level in the gap is very close to the bottom conduction band. This is the reason for the strong temperature dependence of TMR. Recently, the development of the tunnel junction that combines the Heusler alloy with the MgO barrier layer has rapidly advanced. Table 12.6 shows typical results. The lattice adjustment of the Heusler alloy and MgO has an advantage of full possible epitaxial growth up to the above part of ferromagnetic electrode. In addition, the possibility to generate a large TMR ratio was theoretically shown [78] by the synergy effect of the half metal: the coherent tunneling phenomenon and the Heusler alloy separated by the MgO barrier layer. Experimentally, a huge TMR ratio of 200% or more was obtained at room temperature for the tunnel junction that combines the Heusler alloy with MgO [79–83]. There are high expectations for the progress of further research and development in the near future. The growth of TMR ratio of the tunnel junction with Heusler electrode versus year is presented in Fig. 12.26.

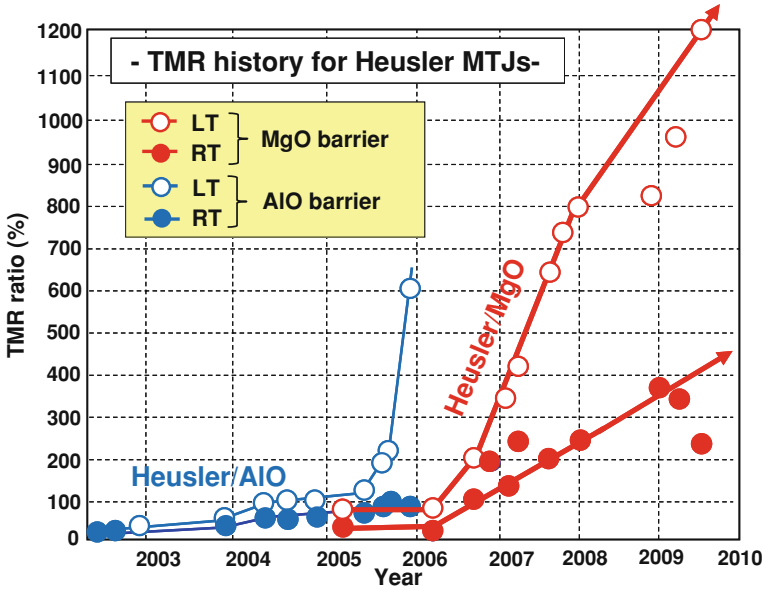


Fig. 12.26 Development of TMR ratio of Heusler electrode tunnel junction

12.9 Other Tunnel Junctions

12.9.1 Giant Magnetoresistance Effect in Granular Structure

We can observe the change of GMR effect of Sect. 11.7 by applying the magnetic field from the outside to that in which both magnetic layers are magnetized in the antiparallel state. That is, we can observe the change of the resistivity accompanied by making the magnetization in parallel. The GMR effect is caused regardless of whether there is an interaction between the magnetizations of both layers. Then, even if it is not always a superlattice or a multilayer film, the GMR effect is expected to be achieved. Paying attention to this respect, Berkowitz et al. [84] and Chien [85] made the system where the nanoscale Co particles were distributed in Cu in 1992. In the system a large GMR effect is comparatively observed. The external magnetic field arranges it in parallel with an increase in the magnetic field though the random direction of the magnetization of the nanoparticle in the demagnetized state. In this case, the magnetization advances by rotation because the particles have single domain-like structures. In general, if the magnetic field higher than 1 Oe–10 kOe is not applied, the change of resistivity is not saturated. Moreover, these relation can be described well by, $\Delta\rho/\rho = 1 - (M/M_s)^2$. The granular film of the Co–Cu system is called a granular metal–metal system, and films such as Co–Ag, Fe–Ag, etc., have been researched. The above-mentioned granular material is a metal, and, anyway, the GMR effect is caused by the spin-dependent scattering of the conduction electrons.

On the other hand, how will it occur when the matrix of the metal is replaced with the insulator?

Fujimori et al. [86] obtained the GMR effect of 8% at the room temperature for Co–Al–O granular films with Co particles distributed in the insulator matrix made of Al-oxide. This system is called a metal–nonmetal granular system. The principle of the GMR effect is quite similar to the above-mentioned tunnel magnetoresistance effect. However, because it is a minute particle that differs from the case of the junction, the charging effect takes part. Moreover, because the magnetization of the particle is arranged by the applied magnetic field, the magnetoresistance curve is the same as that of granular metal–metal system. Therefore, it may not be saturated by the magnetic field easily. Moreover, the electrical resistivity is extremely large, $10^5 \mu\Omega \cdot \text{m}$, compared with that of a granular metal–metal system. The magnetoresistance effect of granular metal–nonmetal systems was observed in Ni–SiO₂ [87] and Co–SiO₂ [88] system in early 1970s. However, the rate of change was only about 1% so no great attention was paid.

12.9.2 Tunnel Magnetoresistance of Magnetic Semiconductors

Along with the long history for the study of anisotropic magnetoresistance effect for 3d transition metal and alloys, magnetoresistance for semiconductor materials have been studied for a long time. The first report of giant magnetoresistance effect was done in the 1960s for single-layered semiconductor film [89]. The term GMR was first used for the effect of semiconductor films but not for artificial metallic thin films. However, the GMR effect was observed only at lower temperatures and the study did not develop further.

On the other hand, the realization of room temperature ferromagnetism for semiconductor materials has attracted much attention and the study of transport including magnetoresistance effect has increased. Pioneering research for tunnel junction with semiconductor electrodes was reported for (GaMn)/AlAs/(GaMn)As [90, 91]. The TMR value was 72% at 8 K. The junction replacing AlAs with GaAs showed about 300% TMR ratio at 7 K [92]. In recent years, huge TMR ratio similar to the value of colossal TMR has been reported for MnAs nanoparticles (electrode)/AlAs (Barrier)/GaMn (spacer)/MnAs (electrode) junction [93]. In addition to the application of huge TMR junctions the relationship between spin polarization and TMR ratio since carriers such as (Ga, Mn)As possess a large spin polarization.

12.9.3 Organic Molecules-Ferromagnet Hybrid Tunnel Junction

Recently, TMR effect of hybrid materials with both organic molecules and ferromagnetic materials has been studied for junctions [94, 95] and granular substances [96]. As the tunnel barrier carbon nanotube, C₆₀, graphene and trigs-

(8-hydroxyquinolino)-Aluminum (Alq_3) were used, there search field forms molecular electronics and will develop further and become an important research field.

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Chapter 13

MRAM

Magnetic memory possesses a great advantage of nonvolatility due to intrinsic magnetic property of memory cell used and has been studied for a long time. The developing order is Ferrite core memory, plane and wire memories using Permalloy thin film, bubble memory by Orthoferrite, and Magnetoresistive Random Access Memory or Magnetic Random Access Memory (MRAM) using Giant Magnetoresistance (GMR) or Tunnel Magnetoresistance (TMR). We will review on the MRAM focusing on the important reports contributed to the development of MRAM. Especially, we will explain in detail the issues of MRAM development using spin transfer torque switching.

13.1 Introduction

When the power supply is turned off, the memory is divided roughly into a nonvolatile memory where the data of the memory are maintained and a volatility memory where the data maintained in the memory are deleted. There are Dynamic Random Access Memory (DRAM) and Static RAM (SRAM) as a volatility memory. On the other hand, the nonvolatile memory that can be acquired in the present market is only Read Only Memory (ROM), for example, the flash memory. In this memory, data cannot be rewritten or even if it can be done, a long time is needed. Therefore, to operate by using both ROM and RAM in the mobile phone, etc., the same data as both parts will be maintained. In such a state, there is a possibility that the majority of the memory of the electronic devices will be replaced with nonvolatile RAM in the future, and the development is hoped for strongly. As nonvolatile RAM, the stage of development or the research includes Ferroelectric random access memory (FeRAM), MRAM, ovonic unified memory (OUM), resistance random access memory (RRAM), and programmable metallization cell memory (PMC), etc. Historically, the word MRAM (magnetic random access memory) was used for planer memory of Permalloy or the memory for the magnetic bubble which were studied

in the early stage of memory research. The author thinks that the memory for the tunnel junction had better been called magnetoresistive random access memory.

13.2 History of Magnetic Memory

It is not certain whether to make any of the first research of magnetic thin film. However, it is from 1950s that comparatively a lot of report of researches came to be published. It can be said that the history of the magnetic thin film research is half a history of the magnetic material research on the bulk mentioned in the foregoing chapter. Especially, a rectangular hysteresis loop of the deposited Permalloy thin film in magnetic field that had been reported [1] in 1955 motivated engineers to be involved in the development of an electronic equipment at that time. Their dreams swelled moreover aiming at the achievement of the thin film element for a super-micro, super-high speed, and cheap computer. However, there were actually a lot of problems. So they did not succeed in practical use as a memory device of the computer. The problems were a control of the scattering and a mass production at that time. Moreover, the flux reversal, or the so-called creeping, progressed naturally, which had a fatal problem that information changes. Part was put to practical use as an electrodeposited magnetic line memory in spite of failure as a memory device of a plate type. The features of the magnetic bubble memory are as follows, nonvolatile information, high speed access, rewritable, radiation resistant, and high reliability. The magnetic bubble of orthoferrites [2] was reported as a magnetic memory by Bobeck of Bell Laboratory in 1967 afterwards. This was called an invention since that of the transistor, and development of the material and a large capacity bubble memory are developed at a marvelous speed [4, 5]. These advantages made the best use of the memory etc., for the electronic automatic exchange, the computer terminal unit, and the space satellite. However, this was replaced with a semiconductor memory that was a rival memory and with the floppy disk and the hard disk which are similar to the magnetic memory. It disappeared from the market very soon. As mentioned above, neither a magnetic memory nor a bubble magnetic memory used with the Permalloy thin film can be developed to a practical use greatly. The thin film making technologies at that time, such as the integration micropattern making technology or the evaluation of characteristics technology, etc., have been made the best use of now, and they have been improved steadily. Now, they have been made the best use of the research of the multilayer film (metallic artificial lattice) that started from the end of 1970 to the beginning of 1980. Meanwhile, giant magnetoresistance effect (GMR effect) of Fe/Cr was reported in 1988 [3, 4]. This discovery has following important meaning.

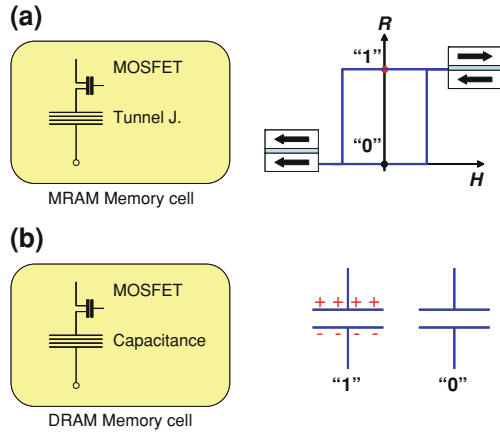
- In the history of magnetic research till then a new material that influenced the society afterwards had been discovered by the means of generation of alloying the compound. But these effects have been found by the new method of piling the different kinds of materials.

- This phenomenon is not magnetically proper in substances where the easiness of magnetization or the energy product is limited. This discovery controls the conduction by changing the direction of the magnetization, or both of conduction and magnetism (magnetoresistive effect).
- It is a phenomenon easily related to a sensor including the magnetic head besides the interest of the physics of phenomenon. Especially, a lot of researchers started the research of the effect of GMR for the reasons mentioned above. The reproduced magnetic head using the GMR element as a result had been put to a practical use for less than ten years. Therefore, the key role for the development of a high density in magnetic recording is being carried out now. In addition, the tunnel magnetoresistance effect (effect of TMR) that shows a large change ratio at the room temperature was reported in 1994 [5, 6], and the research on magnetism and conduction has been activated more and more. Furthermore, realization of large TMR value using MgO tunnel barrier [7, 8] and also the realization of magnetization switching using spin transfer torque [9, 10] accelerated the development of MRAM.

13.3 Principles

In the MRAM being developed now, one of the cells consists of one tunnel junction and one transistor. The comparison with DRAM is shown in Fig. 13.1. Therefore, as long as this method is adopted, it is expected to be difficult that the MRAM could surpass that of DRAM by the capacity. The state of “1” and “0” can be achieved so that the element may operate as a memory (write) and it is necessary to know which the state is (read). The author explains this principle of operation. A full loop of the magnetoresistance curve is shown in Fig. 13.2a and b with a thin line. Writing and reading will be explained by using Fig. 13.2a and b, respectively. First of all, let us think about writing. If the pulsed current is put into the word line, the pulse recording magnetic field is generated. The peak value of this magnetic field is larger than coercive force of a free layer, and the magnetization of a free layer is put into the state that turns to the left (minus). Both of the magnetization are kept parallel even if the magnetic field is made zero (solid arrow in the Fig. 13.2a). As a result, the state of “0” is written. After the magnetic field of $H_c(F_2) < H < H_c(F_1)$ is applied right (direction of the plus) opposite to write the state of “1”, the magnetic field is returned to 0. F_1 and F_2 are free layers and pinned layers here, respectively. The resistivity change at that time changes like the solid line where the magnetoresistance curve in the upper right of Fig. 13.2a is fat, and can achieve the state of “1” that resistance is high. To detect whether state “0” or “1”, the sense electric current shown in Fig. 13.2b, the sense line, is made to flow. Because the resistance is different in the state of “0” and “1”, the output voltage (output of Fig. 13.2b) is different. The state of “0” and “1” can be distinguished according to the value of the sense voltage. In the case of magnetization switching using spin torque which will be explained in the next section, the magnetic field H in Fig. 13.2 will be replaced by injection current J .

Fig. 13.1 **a** MRAM memory and principle of memory, **b** DRAM memory cell and the principle of memory



The writing and reading principle in that case is the same as this explanation. The explanation of the abovementioned is same as that for the principle that reads the one information written in one cell. It becomes MRAM only after the cell is compactly integrated to memorize a lot of information, and to read the information written in each cell at random. To memorize information of one of many cells, one cell at the intersection is specified by following the electric current into the bit line and the word line shown in the inset in Fig. 13.3. Figure 13.3 shows the asteroid curve which will be used for the explanation of magnetization switching. We will apply magnetic fields along both easy and hard axes and the composite field becomes large enough outside the asteroid curve as shown in the following figure.

This means magnetic fields are larger than the anisotropic magnetic fields of the thin film, and the magnetization will reverse. First of all, for reading the electric current must be flowed from the bit line via the cell and the transistor. Depending on whether the magnetization is parallel or antiparallel, the output voltage changes at that time. In a word, "1" and "0" states are identified as mentioned before.

13.4 Spin Transfer Torques and the Change of Cell Structure

13.4.1 Spin Transfer Torque

In the effect of the TMR (same with the effect of GMR), the electric current can be controlled by the direction of magnetization [9, 10]. In contrast, the direction of magnetization may be altered, depending on the current in a spin transfer torque. The current with polarized spin is altered by a relative angle of magnetization for the effect of TMR. Thus the spin-polarized current is needed to cause the spin transfer torque.

Fig. 13.2 Memory of “0” and “1” states of writing (a) and reading (b)

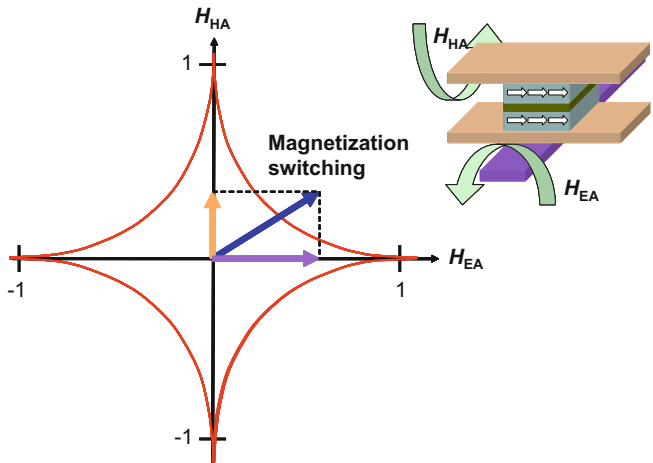
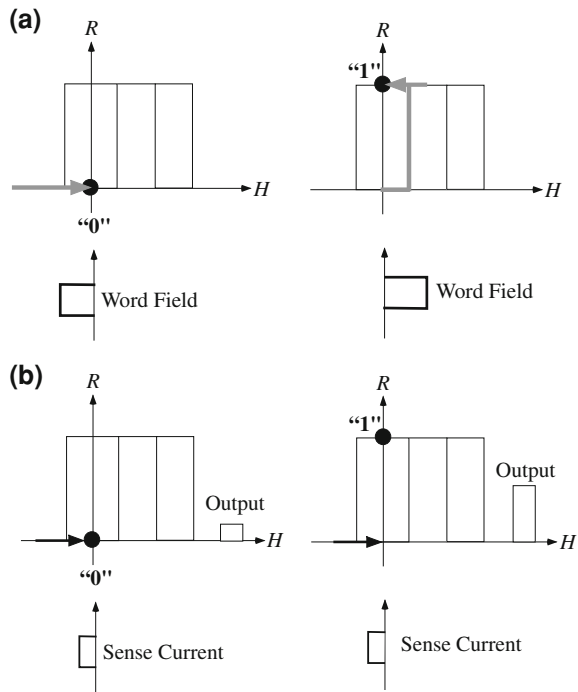
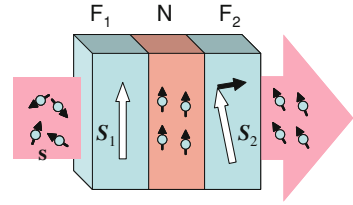


Fig. 13.3 Asteroid curve

For an intuitive image of this physics, it is only thought that the magnetoresistance effect and spin transfer effect (torque) could analogously correspond to “law of action and reaction” of the Newton mechanics (Fig. 13.4). We will explain more

Fig. 13.4 Spin transfer switching (STS)



detail of spin transfer torque: when both ends of ferromagnetic (F_1)/nonmagnetic (N)/ferromagnetic (F_2) junction could be applied by voltage, current flows from right to left, and electron, vice versa, as shown in Fig. 13.4. Each of spin angular momentum of electron in electrodes is denoted as S_1 and S_2 , respectively. The (unpolarized) spin s of the conduction electron which enters in the F_1 layer from a left electrode can be changed to spin-polarized ones parallel to S_1 . When this polarized spin s passes through F_2 layer, the momentum of s can be altered by interaction of s and S_2 and the difference of angular momentum moved to S_2 . As a result, S_2 may receive torque. The direction of the torque received by S_2 is expressed in terms of S_2 and the unit vector of spin s of conduction electron. It is noted that depending on the direction of the current, this torque movement is attenuated and or the direction of spin is reversed. On the basis of calculation by Slonczewski [9], the reversal spin condition is given by

$$\alpha M_s V H_{\text{eff}} < g(\theta) \frac{\hbar}{2} \frac{|I|}{e},$$

where each of the signs α , M_s , V , and H_{eff} is the damping constant, that is, the measure of the gyromagnetic precession, the saturation magnetization, the volume, and the effective magnetic field in F_2 , respectively. The symbol g is a spin transfer efficiency coefficient that is a function of the spin polarization. Each of $\hbar/2$, I and e is the angular momentum, the current, and electron charge. The research to control the magnetization of the magnetic memory has been extensively studied by using this physics. In the memory of high density ($> \text{Gbits}$) of which cell size is 100nm or less, a large current is needed for a conventional magnetic field reversing method. In contrast, even small current makes the reversing possible by the flux reversal technology using this spin transfer torque. This will be described again by the next section. The development of magnetic memory (MRAM) has been increased every year. However, power consumption is as large as about 4 mA per cell in switching of the magnetization due to the magnetic field by the conventional wiring current method. The achievement of the large capacity MRAM was considerably difficult by the cell structure. However, the reversal of magnetization was proven to be possible by spin transfer torque as mentioned above, and the development of magnetic memory (especially, spin-RAM in distinction from the conventional type) has come to be paid to attention. Figure 13.5 shows the writing current at different current density by spin transfer switching (STS) as a function of memory size. The writing current should

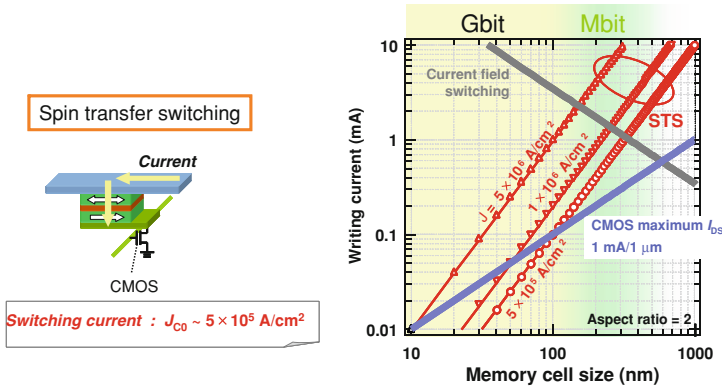


Fig. 13.5 Writing current as a function of memory cell size (calculated)

be smaller than the critical current of CMOS. When the memory size is 100 nm, the current density less than $3 \times 10^5 \text{ A/cm}^2$ is required.

At the beginning of the study of STS, experiment was carried out by using GMR junctions [11–13]. However, due to the small change of MR ratio which corresponds to small output voltage, the study shifts to the experiment using the TMR junctions. The output voltage was not large enough for the TMR junctions with Al_2O_3 barrier [14, 15], but it was large enough for the junction with MgO barrier. Since then, STS research with MTJ and with MgO barrier developed rapidly [16–24]. In 2005, 16 kBit MRAM [25] and then in 2007, 2 Mbit MRAM [26] using STS (Spin-RAM) were realized. However, from the view points of capacity and power consumption they are far from an ideal memory.

13.4.2 From In-Plane Magnetization to Out of Plane Magnetization

The STS technology described in the previous section sheds light on the MRAM developed and researches devoted to this field. However, it was not so easy to reduce the critical current value with keeping the thermal stability of memory cell. Meanwhile, a MTJ with the magnetization direction perpendicular to the cell plane has been proposed. Figure 13.6 shows the change of cell structure schematically.

Then, why is the cell geometry of vertical magnetization advantageous compared with the case in plane? The critical current density J_{c0} necessary to reverse the magnetization according to the spin transfer torque is given by Slonczewski,

$$J_{c0} = \frac{2e\alpha}{\hbar g(\theta)} d M_s H_{\text{eff}}. \quad (13.1)$$

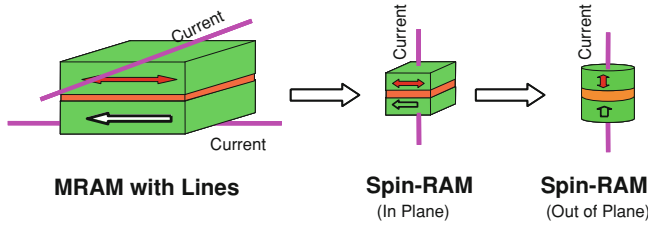


Fig. 13.6 Change of TMR cell in research of magnetic memories

Here, d is the film thickness, on the other hand, the meaning of the other signs has been mentioned in the previous section. The value of 0.5 MA/cm^2 is expected as J_{c0} practically, though details are skipped here. On the other hand, the direction of magnetization in cell tends to turn around easily by thermal energy $k_B T$ by decreasing the size of cell (the signal disappears).

The product of magnetic anisotropy constant and the volume of magnetic substance should be large to prevent this loss of signal. The ratio of both of them Δ is given by

$$\Delta = \frac{K_u V}{k_B T} \quad (13.2)$$

A necessary condition is $\Delta > 60$ for commercial product. After all, the current density and the heat stability shown by 13.1 and 13.2 will mean which to be satisfied easily with a cell of the magnetization in a plane or out of plane. Since the effective magnetic fields H_{eff} in (13.1) are denoted as $H_{k//} + 2\pi M_s$ and $H_{k\perp} - 4\pi M_s$, respectively, depending on the magnetization in the plane or out of plane and K_u in (13.2) is given by $K_u = H_k M_s / 2$, we are able to calculate both J_{c0} and Δ as a function of M_s . The result is shown in Fig. 13.7. Here, it is assumed that in any case of in-plane or out of plane, the magnitudes of the quantities α , g , and d are the same, and 0.01, 0.5, and 2 nm, respectively. The dotted lines in the figure are the case of magnetization in the plane, while the solid line is the one out of plane. Moreover, J_{c0} and Δ are plotted for a few anisotropic magnetic fields. The out of plane magnetization shown by the solid line can be understood by taking the margin overwhelmingly to satisfy the conditions of both $J_{c0} < 0.5 \text{ MA/cm}^2$ and $\Delta > 60$ in the range of M_s between 100 and 400 emu/cm^3 . Therefore, the development of the thin film material with 400 emu/cm^3 or less and the value of perpendicular magnetic anisotropy will be important.

This STS experiment has been carried out for GMR junctions [27] and we wonder at first whether it will contribute to MRAM development due to its small output voltage. However, Toshiba's group reported TbFeCo/CoFeB/MgO/CoFeB/FbFeCo MTJ [28] which has both small critical current and high thermal stability and showed the capability of MRAM with perpendicular magnetization cell. Nowadays the MRAM research with perpendicular magnetization cell increases.

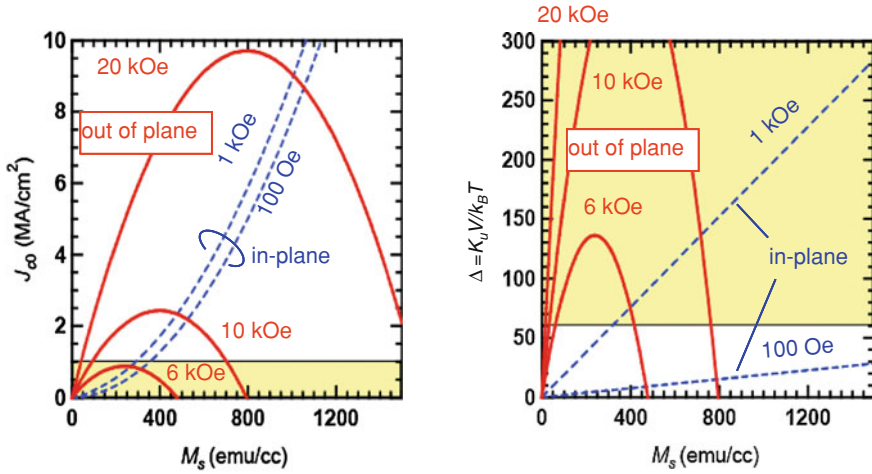


Fig. 13.7 Critical current density (J_{c0}) due to spin injection magnetization reversal and thermal stability ($\Delta = K_u V / k_B T$) as a function of saturation magnetization of junction electrode. Solid curves in figure indicate perpendicular magnetization film, while broken curves indicate magnetization in plane film. Parameters in (13.1) are, $\alpha = 0.01$, $g = 0.5$, $d = 2$ nm, and junction area $\varphi = 100$ nm

13.5 Issues of MRAM Development

MRAM is possessed because it has more of advantages when compared with other memory devices. It has concretely high speed, high density, low voltage drive, high rewriting frequency, and high compatibility of CMOS device. As for the research and development of MRAM, the United States precedes, and the national project started in 1995. In 1999, IBM produced MRAM of 1 kbit and Motorola announced MRAM of 512 bit, and then Motorola increased 256 kbit, 1, 2, 4 Mbit, and capacity steadily afterwards. The trend to the MRAM development rose in 2–3 enterprises also in Japan in 2001 and successive developments have been continued. The technologies required for high capacity MRAM development are basically high output voltage, high speed, low consumption power, large capacity, high reliability independent of the cell structure. Here, we describe various issues for developing MRAM using STS method with perpendicular magnetization cell including some issues pointed out at the beginning of MRAM research.

13.5.1 High Signal Power Output

At the beginning of MRAM research the output voltages from one bit are compared with the reference voltage and “0” or “1” are distinguished with the operation method

of MRAM of the main current now. The reference voltage in bit is just set to the middle of the output voltage (V_H) at the high resistance and output voltage (V_L) at the low resistance. Therefore, the power output in one bit is given by $V = (V_H - V_L)/2$. The output voltage of about $V = 100$ mV is demanded in MRAM of G bit. However, TMR ratio decreases in tunnel junction (MTJ) as the bias voltage increases. Therefore, it is not easy to fill this value. The double-barrier tunnel junction is proposed [29] as an approach that overcomes the voltage dependence. Another approach is to improve the voltage dependence. The high fcc(111) orientation polycrystalline tunnel junction was made [30]. However, such technologies are no more necessary due to an appearance of MgO barrier MTJ with very high MR value. Even for the perpendicular magnetization cell, a high value of MR ratio up to about 100% is required. At first it was small [31], but MR ratio increased gradually and more than 200% MR ratio is reported [32, 33] recently.

13.5.2 High Speed Writing/Reading

It is 1 ns or less though time required to reverse the magnetization is different according to the shape of waves of the applied magnetic field (values and applied time). It is, however, decided to actually limit to the writing, and the reading time depending on the entire circuits, that is, MTJ, transistors for switching on and off, and the cutoff frequency—the cut off frequency is determined by the low pass filter consisting of resistivity, capacity of the wire. It is estimated to be able to write and read both with 10 ns or less now. Factually, the access time of 10 ns or less has been achieved by Motorola in both writing and reading though the degree of integration was low, 512 bit. In the case of spin switching by using spin transfer torque, the switching time itself is 400 ps and very fast. However, there exists a non-reactive time of the order nanoseconds [34]. Although the origin is not completely clear, thermal fluctuation can be considered due to a large injected current. The DRAM access time of both writing and reading is 10–50 ns, while the flash memory needs 10 μ s in writing and 50 ns in reading. It can be said that MRAM has more high speed than those memories. The research target at present is 3 ns.

13.5.3 Low Power Consumption

At the beginning of MRAM study, the reduction of driving current for conductor lines was one of the important issues. To reinforce the magnetic field generated from one conductor line, the method of sticking the ferromagnetic substance outside the conductor line was proposed. Thus, it is a technique for concentrating the magnetic field (cladding method). Magnetic field strength increases so that magnetic flux may concentrate on the ferromagnetic part when the outside in the conductor line was covered with the high permeability ferromagnetic substance such as Permalloy.

As for the result of the experiment and the simulation, magnetic field strength 2–3 times a past result was obtained. Moreover, the result of the simulation showed that the leakage magnetic field to the adjoining bit can be greatly decreased. If the leakage magnetic field to the adjacent bit decreases, it is convenient for the decrease in distance between bits and also raising the integration or more. This method was actually adopted in MRAM of the capacity of 1 Mbit or more.

The magnetization switching method using the magnetic field produced by the current of conduction lines cannot further reduce the consumption power. STS made break through in his problem. By using out of plane STS (magnetization is perpendicular to the cell plane), we were able to reduce the critical current with keeping thermal stability [35–38]. Very small critical current about $10 \mu\text{A}$ ($\approx 10^5 \text{ A/cm}^2$) which corresponds about $1 \mu\text{W}$ consumption power is already reported [39]. In order to make such memory, reasonable saturation magnetization M_s and small damping constant α shown in (13.1) in Sect. 13.4 are required.

13.5.4 High Reliabilities

MTJ uses oxide film that is very thin about 1 nm as a tunnel insulation barrier, and the characteristic is related directly to the size of the power output. Therefore, it is important to make a thin insulating layer on a wide wafer very uniformly from the viewpoint of productivity. The difference as for the junction resistance and TMR ratio on a wafer is at the level that both do not become problems on practical use. To suppress the difference of the characteristic of the MOS structure under MTJ in MRAM, annealing of 350–400°C is carried out. Therefore, thermal stability up to around 400°C is at least required.

The volume of the ferromagnetic substance that bears one bit decreases with decrease of bit size. The magnetization of a very small ferromagnetic substance easily does magnetic reversing by the thermal fluctuation. Therefore, in this case, information cannot be maintained. In the storage medium of HDD, it is assumed that $Kv/k_B T > 60$ is a standard of the thermal stability. The same discussion can be applied also to the bit of MRAM. By using the existing known magnetic materials, we are able to develop a G bit MRAM. But, new materials are necessary for developing MRAM beyond G bit with enough thermal stability.

As mentioned in Sect. 13.3, the magnetization of one cell can be reversed by the synthetic magnetic field that the bit and the word line in each wired cell makes. Naturally, because it is being composed by a lot of cells, the strength of the magnetic field where the magnetization is reversed is to some extent distributed in an actual memory. Assuming that the switching magnetic field shown in Fig. 13.8 is distributed, the asteroid curves corresponding to the minimum and the maximum magnetic field are shown in Fig. 13.9a. The operation margin in this case becomes a slash range in a common part of each margin that has the anisotropic magnetic field of H_{k1} and H_{k2} . In the cell of small H_{k1} , a magnetic reversing occurs by the magnetic field outside from this part, and the magnetic reversal of the cell of large H_{k2} cannot be

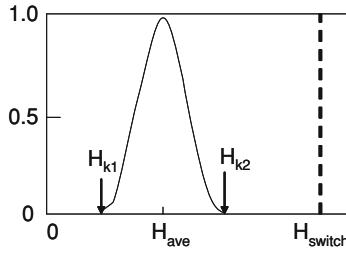


Fig. 13.8 Distribution of anisotropic magnetic field of cell

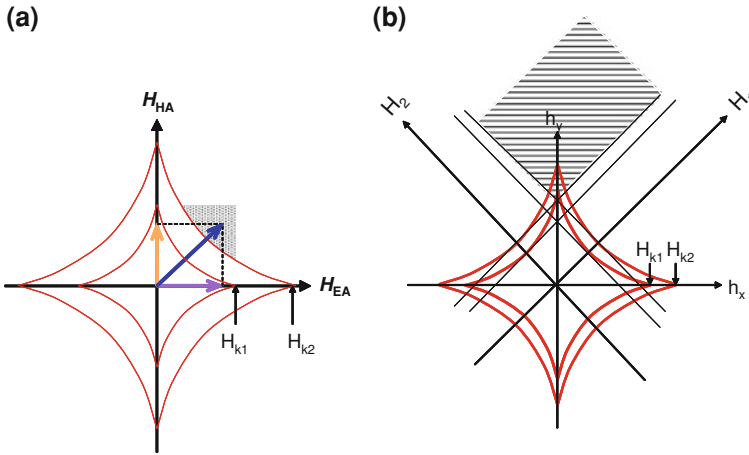


Fig. 13.9 **a** Astroid curves corresponding to two different H_k . The *dashed* region is the operating point window. **b** Toggling operating window

done in an inside magnetic field. Therefore, the difference of the anisotropic magnetic field of each cell will greatly narrow the cell selection. One of the technologies called Toggling method was reported by Motorola as one method of solving this problem [40]. This technology has been taken to 4Mbit MRAM of Motorola. Expecting the verifying energy saving by this technology does not become possible.

13.5.5 Making to Large Capacities

MRAM of M bit is made for trial purposes with k bit already. The size of 1 bit is 1:2 or 1:3 as aspect ratios of both short sides are about $0.5 \mu\text{m}$. It is expected that the bit size becomes about $0.1 \mu\text{m}$ when integrated even in G bit. When the bit size becomes small less than $30 \text{ nm } \phi$ (spin-RAM), the difference of the processing size in addition to the uniformity of the insulating layer also greatly influences the difference of the

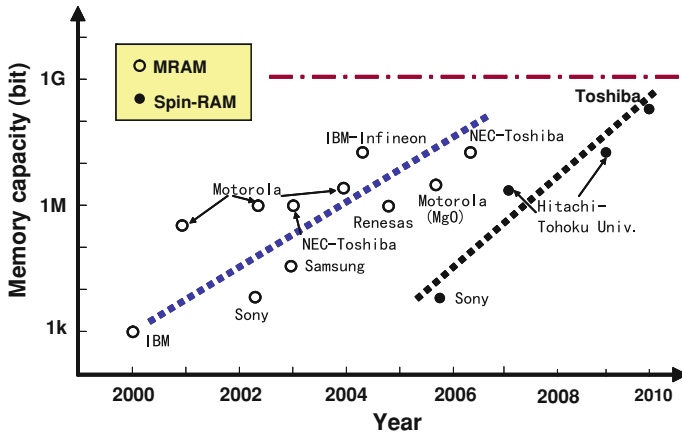


Fig. 13.10 Memory capacity as a function of year

junction resistance. Moreover, it is thought that the difference of shape influences the magnetization process, and it influences the difference of the switching magnetic field. Therefore, the reliability of the microfabrication process becomes very important. Figure 13.10 summarizes memory capacity developed already as a function of year.

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Chapter 14

Technology that Accompanies the Development of Spintronics Devices

I – V measurement of magnetic tunnel junction (MTJ) is very important for the characterization of tunnel junction. Measurement of I – V curve and analysis of the curve will be briefly explained. Also it is described that AFM and STM are useful tool in order to evaluate MTJ. Spin polarization of the electrodes of MTJ is very important value in order to fabricate a high tunnel magnetoresistance (TMR) value junction. The measurement method of spin polarization using tunnel junction will be described. Finally, spin dynamics which is very important in order to apply MTJ for devices is described. Particularly, the experimental method of damping constant measurement, the data reported so far, and the origin of damping constant will be explained.

14.1 Analysis of the I – V Curve

Figure 14.1 gives the cross-sectional view of the barrier height Φ and d in width of the tunnel junction. As the methods of obtaining the barrier height, there are two of the ones; with the analysis of the temperature dependence of the tunneling current according to the theoretical formula of Stratton [1] and with the analysis of the I – V characteristics according to the expression of Simmons [2]. By comparing what we obtained by two methods, the barrier heights of the several junctions are estimated. The results of both were almost the same. Here we introduce the latter method. Figure 14.2 shows typical three I – V curves for Fe/Al₂O₃/Fe junction. The 500 Å thick Fe film was prepared by electron beam evaporation. Moreover, Al₂O₃ was made by naturally oxidizing for 24 h in the temperature controlled bath after Al was made by 50 Å sputtering method. The area of the junction is 1 mm². To change the height of the barrier, the temperature of the oxidation was changed. It is understood that each I – V curve is also nonlinear and the resistance (dV/dI) grows as the oxidation temperature is raised.

When the applied voltage V is smaller enough than Φ in a basis of the model of Simmons, current density J is shown as follows;

Fig. 14.1 Schema of barrier height Φ and width d of tunnel junction

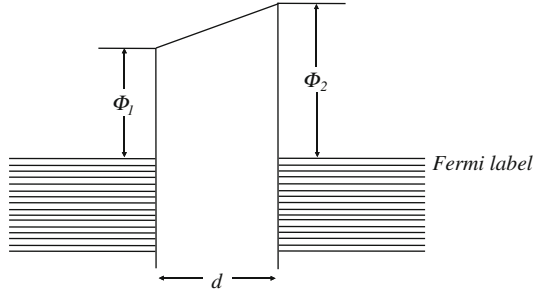
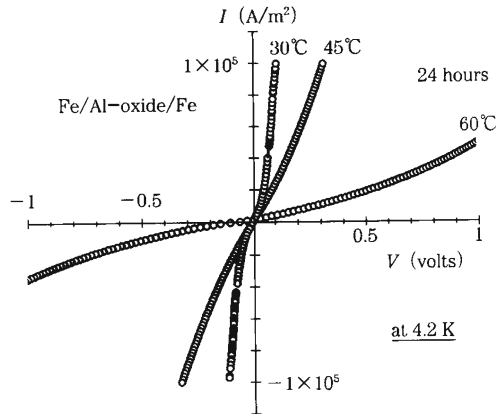


Fig. 14.2 Examples of I – V characteristic of the Fe/Al₂O₃/Fe junction



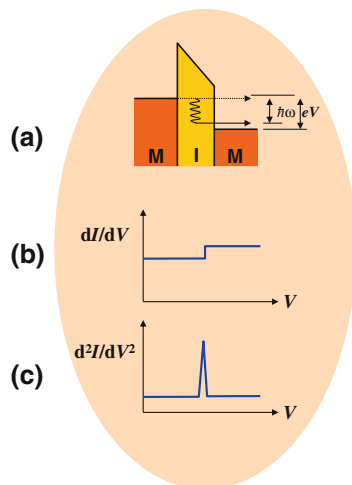
$$J = \theta(V + \gamma V^3) \quad (14.1)$$

$$\theta = \frac{\alpha\beta\Phi^{1/2}}{d} \exp(-\alpha d\Phi^{1/2}) \quad (14.2)$$

$$\gamma = \frac{(\alpha d)^2}{96\Phi} - \frac{\alpha d e^2}{32} \left(\frac{1}{\Phi} \right)^{3/2}. \quad (14.3)$$

Here, $\alpha = 4\pi(2m)^{1/2}/h$ and $\beta = e^2/4\pi h$. Moreover, m , e , and h are the mass of electron, the charge, and Planck's constants, respectively. The I – V curve obtained by the experiment was fitted to the above-mentioned (14.1) so that Φ and d were obtained. Both of the fitting curves were completely corresponding to the experimental results of Fig. 14.2 [3].

Fig. 14.3 Principle chart of IETS



14.2 Inelastic Electron Tunneling Spectroscopy

Inelastic electron tunneling spectroscopy (IETS) is useful enough for the examination of the interface from tunneling current–voltage characteristics. Various excitations that contribute to the inelastic tunneling process of the electron can be seen with the method differing from usual spectroscopy, making the electrode probe, and applying the external electric field. The feature is a high sensitivity. Let us take metal/insulator/metal junction now (Fig. 14.3a, b, and c). The voltage is applied from the outside to this one, and enlarged gradually. The electron tunnels to the level in which only $\hbar\omega$ (corresponding to an inelastic energy) in addition to an elastic tunneling falls if there is an inelastic tunneling process. When this is seen in dI/dV curve, the amount of the step of dI/dV is below 1%. But by seeing in the second derivative d^2I/dV^2 , we can see it as a peak as shown clearly in Fig. 14.3c. The inelastic process can be discussed from the value of energy that corresponds to this peak position (V_0).

We would like to look at the IETS spectrum of the Al/Al-O/Al junction shown in Fig. 14.4 for example. A sharp peak in the neighborhood of zero bias is the one that originates from the magnetic impurity or the charging effect in the junction interface. When the voltage is increased, a broad peak in which it originates in LO phonon of the Al-O and the Al phonon is observed.

From which the peak of the IETS originates should be estimated from excitation energy beforehand. However, a lot of data could be understood from the accumulated data.

Figure 14.5 shows the chart of circuit made in the author's laboratories. To eliminate the influence of the thermal energy, we measured it at 4.2 K. Therefore, the part of the junction as shown in the Fig. 14.5 is stored in the cryostat. Figure 14.6a shows the IETS spectrum measured by using this circuit after annealing at 250 and 400°C for the tunnel junction [4]. Figure 14.6b is a corresponding MR curve. AP and P in

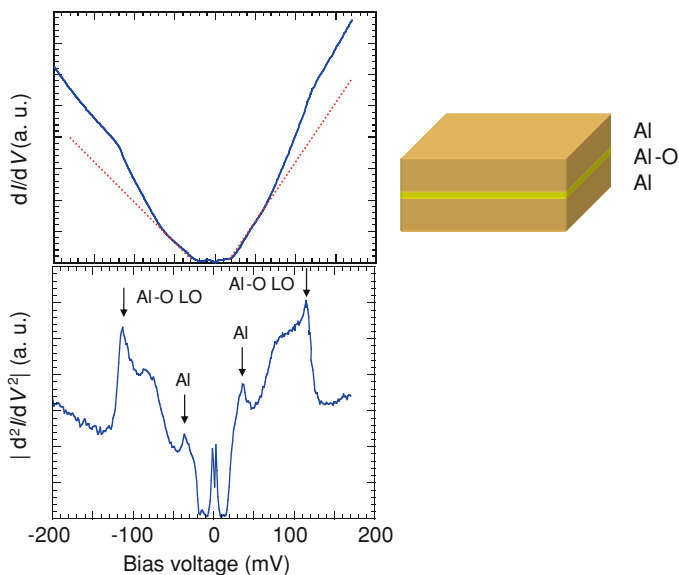


Fig. 14.4 dI/dV curve of the Al/Al-O/Al junction

Sample

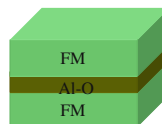
SiO₂/Pt(3 nm)/Ni₈₀Fe₂₀(3 nm)/Cu(20 nm)/Ni₈₀Fe₂₀(3 nm)/IrMn(10 nm)/Co₇₅Fe₂₅(5 nm)/Al(2.0 nm)-oxide/Co₇₅Fe₂₅(4 nm)/Ni₈₀Fe₂₀(20 nm)/Pt(5 nm)

M : Al, Ag, Cu

d_M : 0, 0.2, 0.5, 1.0, 3.0, 5.0, 25.0 nm

Annealing Temperature : 250°C, 400°C

Measurement of IETS : at 4.2 K



Electrical Circuit

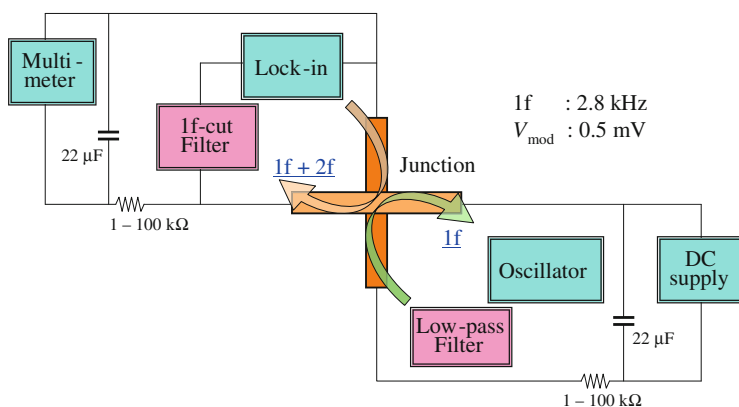


Fig. 14.5 Circuit chart of the IETS instrument

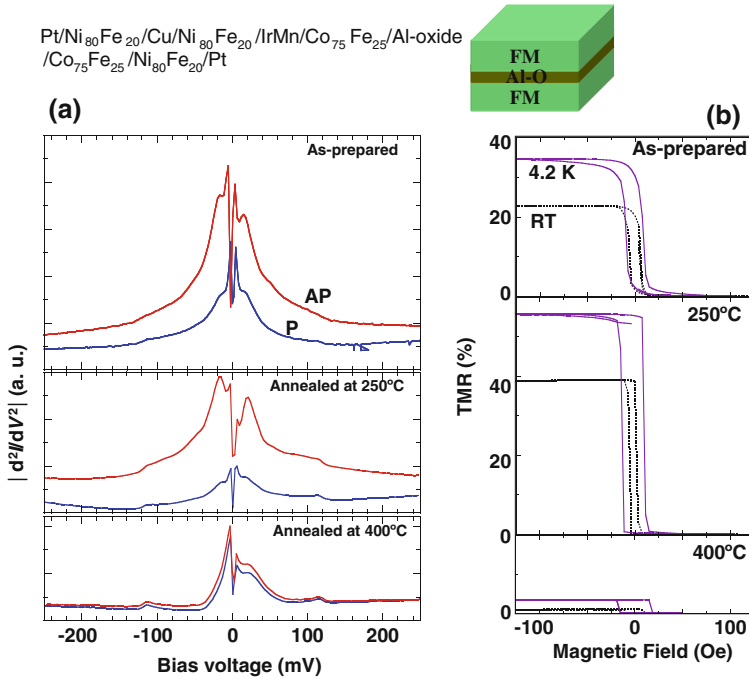


Fig. 14.6 **a** IETS spectrum and **b** MR curve of tunnel junction

Fig. 14.6a correspond to antiparallel state (a large resistance) and the parallel state (a small resistance) of the magnetization in both of magnetic layers, respectively. This means that in the cases to be applied the voltage to + side and to – side, the inelastic excitation has not necessarily occurred similarly. Close up of difference spectrum in Fig. 14.6 and bias dependence of the corresponding standardization MR ratio in Fig. 14.6b. That is, the junction with both sides of the insulating layer is not completely symmetrical.

The advantage of this technique shows that the information of both sides of the insulating layer interfaces is obtained by taking + and – spectrum one, respectively. Moreover, if the difference of spectrum of AP and P is taken, we may consider the spectrum of the difference that originates in magnetism. Figure 14.7 has also shown the bias dependence of the difference spectrum (a) and normalized TMR ratio (b). A clear peak in Fig. 14.7a is observed. A broad peak in zero bias anomaly that originates in the magnetic impurity and the broad peak around 20 mV are observed. By comparing it with Fig. 14.7b, we can see that the junction with higher TMR value exhibits a clear peak around 20 mV. This peak is corresponding to excitation energy of the magnon of the ferromagnetic substance. In addition, the TMR ratio decreases corresponding to the vicinity of the bias of the peak of the magnon when Fig. 14.7a and b is compared (It is clear in the data of 250°C annealing and as-prepared).

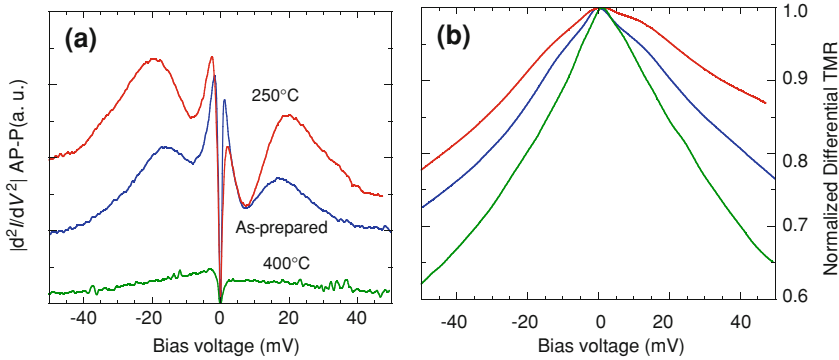


Fig. 14.7 **a** Expanded IETS spectrum for Fig. 14.6a and **b** normalized TMR ratio as a function of the bias voltage

14.3 Conducting Atomic Force Microscope and STM

Both barrier height (Φ) and width (d) can be obtained by analyzing I – V characteristics mentioned in the foregoing section. However, it is an information on average value of the junction obtained from this method. Information on the difference of a local insulating layer due to the interaction of magnetic layer and insulating layer and/or on the nonuniformity in the insulating layer which originates from the distortion of the lattice between the insulating layer and magnetic substance or existence of the oxide other than Al-oxide is not obtained at all. We measured local I – V characteristics by applying the voltage with conducting atomic force microscope (Conducting AFM) between the sample and the explorer. As a result, the obtained Φ and d have been evaluated in the insulating layer by measuring the electric current image [5]. Figure 14.8 shows the experimental setup. The surface of the cantilever chip made of Si_3N_4 is coated with Au in about 400 Å. A topographic image on the surface is obtained by tracing the sampling surface using this.

Moreover, the electric current image is obtained by applying the voltage between the chip and the substrate. The c-AFM has the feature in which both the structure and the conductive characteristics on the surface of the insulating layer are obtained at the same time. Figure 14.9 is topographic image (a) and electric current image (b) on the surface of $\text{Co}(40 \text{ Å})/\text{Al}(13 \text{ Å})/\text{Ni}_{80}\text{Fe}_{20}$ (190 Å)/oxide. First of all, it is understood that both do not necessarily correspond. The electric current flows more in a bright part compared with a dark part in Fig. 14.9b. The chip is set to the bright part (①), the dark part (②), and middle part (③), and the result of measuring the I – V characteristics is shown in Fig. 14.10a, b. It is well understood that the characteristics in the three places is remarkably different. This I – V curve was analyzed by the method of Simmons described in Sect. 14.1. And, the result of the barrier height and width is shown in Fig. 14.10b. As for height, it is understood that there is a difference of about 1 eV in a bright part and a dark part while the width of the barrier is constant,

Fabrication of tunnel junctions

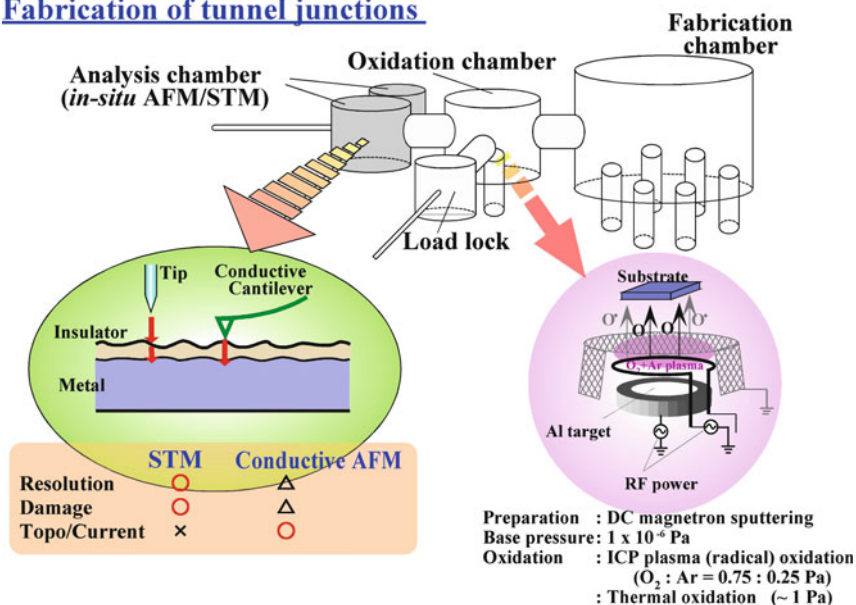


Fig. 14.8 Scheme of conductive AFM experimental device

10 Å. The method of the c-AFM is unsuitable for an initial analysis of the oxidation though it is a very powerful technique for an oxidizing zone of the some thickness. For obtaining the uniform oxide film, it is important to know how the oxidation process is different depending on the difference of the oxidation procedure. Authors examined the reaction process in the first stage of the oxidation on the surface of Al by using in situ STM. We showed that the oxidation progressed selectively from the grain boundary of the Al metal after the surface of the Al was covered with oxygen at in the first stage of the oxidation. That is, the control of the grain shape of the Al metal is important to form the uniform oxidizing zone. In Fig. 14.11, the surface STM imaging of the scanning range of 1.6×1.6 nm of the Al oxide film by radical oxidation (a) and by the plasma oxidation (b) and both section profiles are shown. On the Al oxide film surface a radical oxidation is seen the regularity neither the cycle or height, that is amorphous. On the other hand, clear periodicity is seen as for the Al oxide film surface by the plasma oxidation. This is guessed to be $(\sqrt{31} \times \sqrt{31}) R \pm 9^\circ$ reconstruction surface [6] which to a single crystalline α -Al₂O₃ is theoretically and experimentally reported. The spin polarization rate of the tunnel junction is what reflects the electronic state of the junction interface [7, 8]. In addition, crystalline properties of the upper part of the electrode junction strongly depend on the crystalline structure on the surface of the insulating layer. These results become an important knowledge for designing the tunnel junction with high TMR ratio.

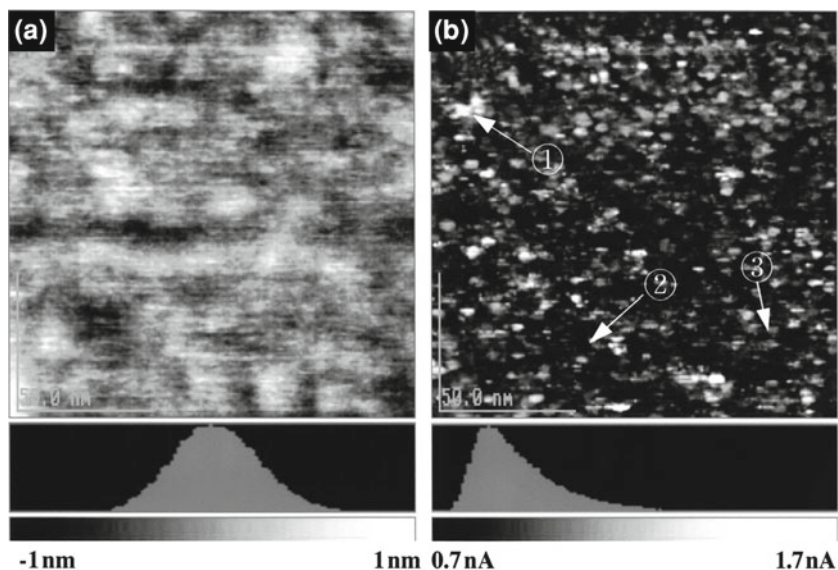


Fig. 14.9 **a** Roughness image and **b** electric current image on the surface of $\text{Ni}_{80}\text{Fe}_{20}/\text{Co}/\text{Al}(13 \text{ \AA})$ -Oxide

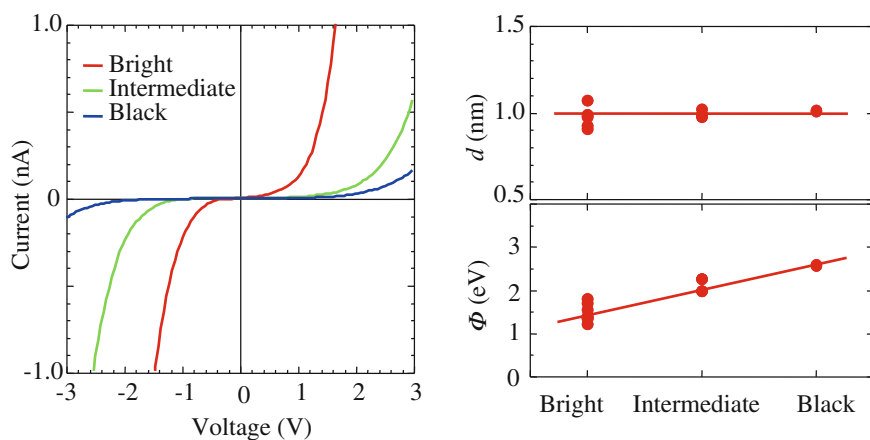


Fig. 14.10 Limited part of the conductive characteristic (I - V characteristics) and corresponding barrier height (Φ) and width (d)

14.4 Measurement of Polarization

It is not too clear when or why the first research using the junction started. However, it seems about the energy gap of the superconductor, using superconductor/insulator/superconductors by Giaever and Megerle [9] in the early 1960. In

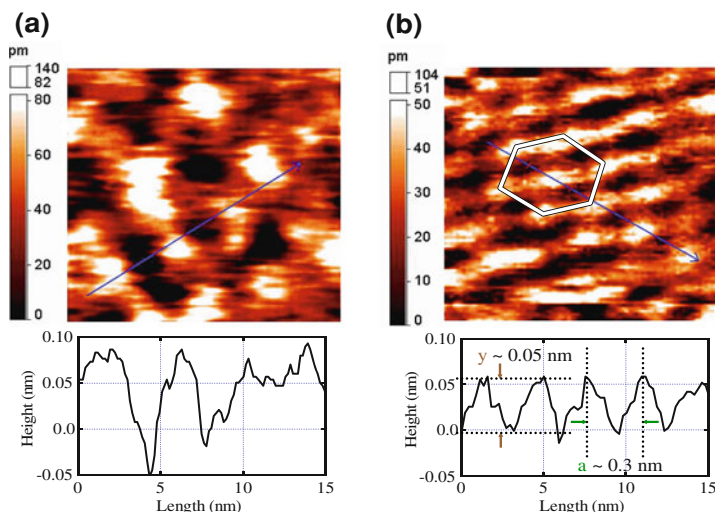


Fig. 14.11 Surface STM imaging and section profile of **a** radical oxidation and **b** plasma oxidation

general, the conduction electron passes the insulating layer according to the quantum effect to some degree and can come off even if the metal or the semiconductor is separated with a thin insulator and the potential barrier is made. Giaever paid attention to this respect, and measured the energy gap of the superconductor from I – V characteristics of various junctions immediately. As a result, even the density of states of the superconductor is clarified. Tedrow and Meservy [10] made the other ferromagnetic substance a superconductor of the junction, and measured I – V characteristics. They obtained the polarization of various metals and alloys by analyzing them. The author explains this method as follows.

In this case, energy gap (2Δ) exists in the Fermi surface of the superconductor. Moreover, the electronic state of (S) has shown the Zeeman splitting because the magnetic field is applied to the bonding surface in parallel. Only the electron of $\uparrow$ spin can tunnel to (S) from (F) when the applied voltage becomes $V = (\Delta - \mu H)/e$, H and μ are the strength and a Bohr magneton, respectively. On the other hand, only the electron of $\downarrow$ spin can tunnel when $V = -(\Delta - \mu H)/e$ (Fig. 14.12). Conductance, $\sigma(V)$, (dI/dV), changes by changing applied voltage. The scheme to explain this in more detail is shown in Fig. 14.13a and b.

In Fig. 14.13a, the voltage (energy) is expressed in the horizontal axis and the density of states of (S) in the vertical axis. Both $\uparrow$ and $\downarrow$ are shown on the same side, different from that of Fig. 14.12. Conductance (standardized by that of the normal conducting state) in such an (S) state is given by (14.4). $N(E)$ is a density of states of (S) and $\beta = 1/kT$.

Fig. 14.12 Shows the scheme of the density of states of ferromagnetic substance (F)/insulator/superconductor (S) junction

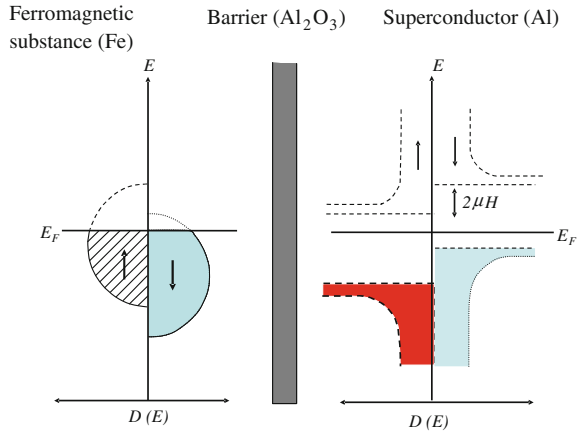
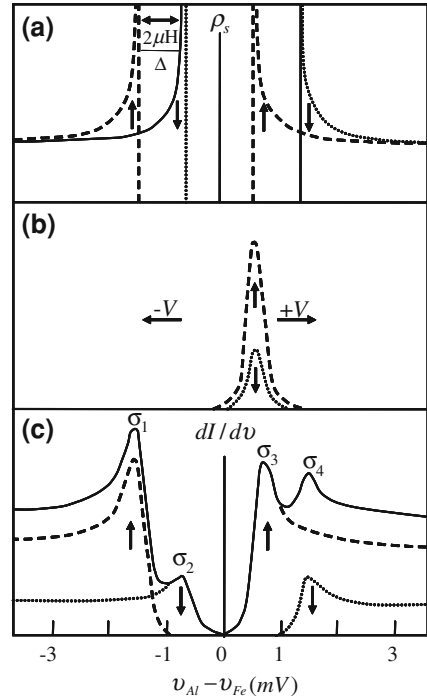


Fig. 14.13 Density of states of ferromagnetic substance/insulator/superconductor



$$\sigma = \int_{-\infty}^{\infty} N_s(E) \frac{\beta e^{\beta(E+eV)}}{\{1 + e^{\beta(E+eV)}\}^2} dE. \quad (14.4)$$

The electron number of $\uparrow$ and $\downarrow$ is assumed to be $n \uparrow$ and $n \downarrow$, respectively. Moreover, the ratio of $\uparrow$ electron is assumed as $\alpha = n \uparrow / (n \uparrow + n \downarrow)$. The conductance at whole by $\uparrow$ and $\downarrow$ electrons is given by

$$\frac{dI}{dV} = \sigma(V) \approx \int_0^{\infty} a N_s(E + \mu H) f(E) dE + \int_0^{\infty} (1 - a) N_s(E - \mu H) f(E) dE. \quad (14.5)$$

Here, $f(E) = \beta \exp\{\beta(E + eV)\} / [1 + \exp\{\beta(E + eV)\}]^{1/2}$.

In Fig. 14.13b $f(E)$ is shown schematically. The height of distribution corresponding to $\uparrow$ and $\downarrow$ spin is proportional to the size of the distribution of the Fermi surface in the (F) layer. On the other hand, spin polarization P using a is given by,

$$P = \frac{n \uparrow - n \downarrow}{n \uparrow + n \downarrow} = 2a - 1. \quad (14.6)$$

In this analysis, (i) both $\uparrow$ and $\downarrow$ shapes of the density of the states of (S) are the same. (The energy axis shifts only to $\pm \mu H$ by the applied magnetic field when the magnetic moment is assumed to be μ). (ii) It is assumed not to cause reversing of the spin by the tunneling.

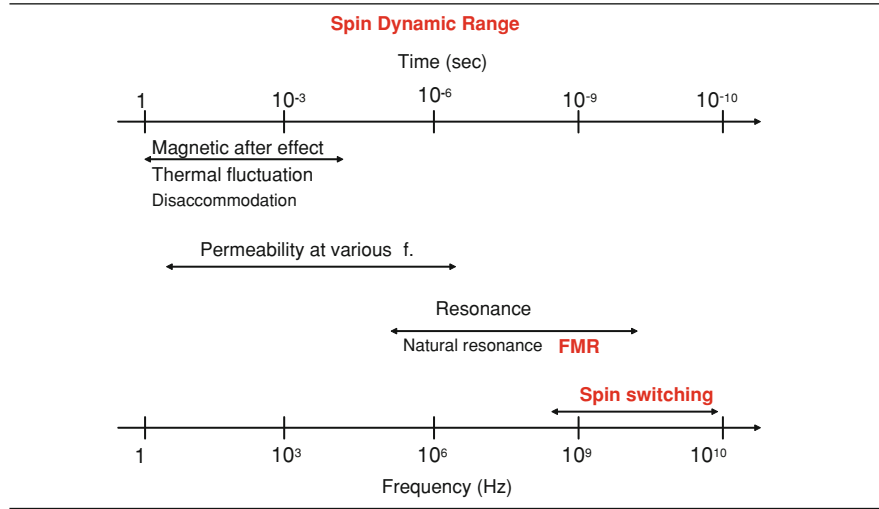
The convolution of (a) and (b) in Fig. 14.13 gives conductance at the voltage V . The entire conductance is given by (14.6) including the sum of that of $\uparrow$ and $\downarrow$. The broken line and the dotted line of Fig. 14.13c show them, and the solid line shows the summation (conductance experimentally obtained). Therefore, the applied voltage dependence of dI/dV is measured, a is given from the peaks ($\sigma_1, \sigma_2, \sigma_3$, and σ_4) of Fig. 14.13c that appear, and the polarization will be obtained by the (14.6). This is called tunneling current spectroscopy. It only has to concretely do as follows. Experimental results of the whole conductance are assumed to be $G(V)$. Moreover, the functional form of conductance in the state that the spin in the superconductive state is not split (applied magnetic field 0) is assumed to be $g(V)$. Then, the relations are given by

$$\begin{aligned} \sigma_1 &= G(-V - h) = ag(-V) + (1 - a)g(-V - 2h) \\ \sigma_2 &= G(-V + h) = ag(-V + 2h) + (1 - a)g(-V) \\ \sigma_3 &= G(V - h) = ag(V) + (1 - a)g(V - 2h) \\ \sigma_4 &= G(V + h) = ag(V + 2h) + (1 - a)g(V). \end{aligned} \quad (14.7)$$

Here $h = \mu H/e$. By considering $g(V) = g(-V)$, a is obtained from (14.7) as $a = (\sigma_4 - \sigma_2) / \{(\sigma_4 - \sigma_2) + (\sigma_1 - \sigma_3)\}$, the polarization P in the (14.6) is given by

$$P = 2a - 1 = \frac{(\sigma_4 - \sigma_2) - (\sigma_1 - \sigma_3)}{(\sigma_4 - \sigma_2) + (\sigma_1 - \sigma_3)}. \quad (14.8)$$

Table 14.1 Timescale of the phenomena related to movements of spin



The values of P measured by the method for Fe, Co, Ni, Co₇₅Fe₂₅, and Ni₈₀Fe₂₀ are 39, 36, 10, 45, and 38%, respectively. Kubota et al. also reported P for (Co₅₀Fe₅₀)_{100-x}B_x ($0 \leq x \leq 30$) alloys [11].

14.5 Spin Dynamics

If the spin dynamics is interpreted as the dynamic magnetization or the magnetization process, it becomes the story of the very wide timescale (Table 14.1). Slow one from 10⁻⁴ to several ten seconds in the wide timescale is called the magnetic after effect in which the slow change of magnetism that occurs from the structural change associated with the ion or vacancy’s migration in the magnetic substance. Especially, the low frequency permeability decreases in a few seconds after demagnetization, which returns to the former value such as the Mn-Zn ferrite and amorphous magnetic substances. Such a phenomenon is especially called disaccommodation (DA).

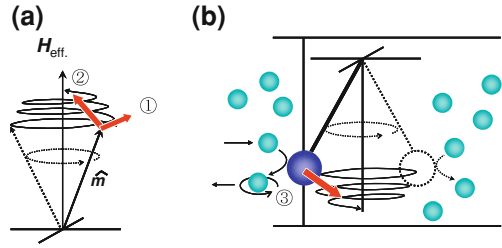
On the other hand, when the volume becomes small in the ferromagnetic substance, the energy of the fine particle vK_u (v : volume, K_u : the uniaxial anisotropy energy of the fine particle) becomes the same level as the thermal energy. Then, the direction of magnetization becomes disturbed, canceling each other, and the magnetization disappears. This is called the magnetic thermal fluctuation after effect, which is one of the important problems that should be solved for the development of a high density magnetic recording media. Signal disappears, therefore, by thermal fluctuation though medium should be made fine particle to increase coercive force of magnetic substance. Moreover, the disappearance of the signal becomes a

problem with a decrease in the size of the cell for the development of magnetic memory (MRAM), where TMR element was used as mentioned in Chap. 13 Sect. 13.5.4 (make to a large capacity). In general, it is called a resonance, that is, the energy of the external force is absorbed when the external force of a vibration frequency just equals the natural frequency of the dynamic system is applied and the vibration increases. The natural frequency for the electron (spin) is ideally the so-called Larmor frequency. However, it does not necessarily resonate at the Larmor frequency because the movement is determined by the place (effective field) that the electron feels. When the high-frequency field is added to the ferromagnetic substance, and the frequency is increased, it reaches the resonance condition. This is called a dimensional resonance or natural resonance, when the permeability shows the peak by a certain frequency (order of MHz). On the other hand, in a paramagnetic resonance (ESR) or a ferromagnetic resonance (FMR), the spin is made to move in a high-frequency field of the small amplitude (of the order of GHz), and the dc magnetic field is increased to reach the resonance condition. Therefore, the dynamics of the spin will be handled from MHz to the GHz order in the resonance phenomena. When the pulse magnetic field is applied from the outside to the ferromagnetic substance and the direction of the magnetization is changed rapidly, the magnetization (spin) changes the direction by the order of ns, which is called the reversing of the spin (spin switching). One of the advantages in which the magnetic substance is used as a memory is the writing and the reading at very short time or high speed. The level of the timescale of this phenomenon is equal to that of above-mentioned FMR. All of the above-mentioned phenomena have been well known since the olden days. For the magnetic after effect, it is undesirable on the application, so that the research how to decrease it has been done. On the other hand, the materials research has been done for the resonance and the spin switching. Especially, the devices including MRAM come to be researched aggressively using the phenomena with both of the magnetic and the conductive properties recently, and many researchers have been interested in the dynamics of the spin at high speed less than 1 ns. Especially, the idea that the electric current with the spin polarization can be injected into the tunnel junction of the ferromagnet/insulator/ferromagnet has been tried for reversal of the magnetization (spin). This is considered to be indispensable for the development of a magnetic memory of large capacity. Therefore, this has attracted the attention of the people concerned with the technology related to this effect. First of all, the Landau-Lifshitz-Gilbert (LLG) equation, Gilbert damping, and spin pumping are mentioned here. Moreover, experimental results of the gyromagnetic movement and reversing the spin are described, and the view to spin switching by the spin injection is described at the end.

14.5.1 LLG Equation and Gilbert Damping

The bar magnet receives the torque (moment of force) and the long axis of the magnet becomes parallel to the magnetic field when putting it in the magnetic field. How does a magnetic moment (spin) that composes the magnet become? A magnetic

Fig. 14.14 Concept chart of (a) Gilbert dumping and (b) swinging of the pendulum



moment has angular momentum in addition to spin. Therefore, the gyromagnetic movement is led around the magnetic field from the relation that the change of the time of angular momentum is equal to the torque as for spin. This gyromagnetic movement attenuates at time, and the direction of spin is corresponding to one of the magnetic field. This behavior can be interpreted because the spin receives the frictional force. The most basic one in the working friction to spin is Gilbert damping. The concept chart of Gilbert damping is shown in Fig. 14.14a and b [12]. Let us compare the gyromagnetic movement of spin to the swinging pendulum to understand this intuitively (Fig. 14.14b). In rubbing against each other of the pendulum to the air molecule of the circumference, the angular momentum and the energy of the swinging of the pendulum are deprived by the air molecule. As a result the swinging of the pendulum attenuates gradually.

The gyromagnetic movement behaves similarly and it is expressed by LLG equation as,

$$\frac{d\hat{m}}{dt} = -\gamma \hat{m} \times \mathbf{H}_{\text{eff}} + \alpha \hat{m} \times \frac{d\hat{m}}{dt}, \quad (14.9)$$

where $\hat{m}$ is spin and $\mathbf{H}_{\text{eff}}$ is a effective field acting to $\hat{m}$. The first term of (14.9) corresponds to torque of gyromagnetic movement (Fig. 14.14a ①) and second term Gilbert damping due to rubbing. Here, γ and α are gyromagnetic constant and Gilbert damping constant (dimensionless), respectively. α is expressed as $\alpha = G/\gamma M_s$, where G is also called Gilbert damping constant having a frequency dimension and M_s is the saturation magnetization. Therefore, Gilbert damping torque is proportional to G .

The damping constant α or G has been discussed for a long time. However, the detail discussion including a quantitative analysis has been made only in recent years. In fact, magnetic relaxation has been focused again after the report of enhancement of G in recent years [13, 14]. Here, first we will describe the origin of damping constant currently carried out by many groups. In spite of the hot discussions no unified interpretation of the Gilbert damping is made now.

Kambersky [15, 16] showed damping constant α for itinerant d electrons as,

$$\alpha = \frac{1}{\gamma M_s} \left[\mu_B^2 D(E_F) / \tau_{\text{sf}} \right], \quad (14.10)$$

similar to the way Heinlich [17] has introduced α by s-d model. Here, μ_B is Bohr magneton, $D(E_F)$ is the total density of state at Fermi level, and τ_{sf} is the spin relaxation time of d electrons. At certain high temperature up (down) electrons in metals mix with down (up) electrons due to the spin-orbit interactions. This degree of hybridization is proportional to the magnitude of spin-orbit interaction coefficient ξ_{so} and to the inverse of the difference of band energy Δ and is in the order ξ_{so}/Δ . The probability of spin flip of electrons through the scattering due to phonon and/or various impurities is in the order $(\xi_{so}/\Delta)^2$. Then,

$$\frac{1}{\tau_{sf}} \approx (\xi_{so}/\Delta)^2 / \tau \approx (g - 2)^2 / \tau, \quad (14.11)$$

where g is g factor of electron spin and $\xi_{so} \approx (g - 2)$ is assumed and τ is the relaxation time of electrons. By using (14.10) and (14.11), we finally obtain,

$$G = \alpha \gamma M_s \approx \mu_B^2 D(E_F) (g - 2)^2 / \tau. \quad (14.12)$$

In Fig. 14.32 in the following section, G values are plotted as a function of $(g - 2)^2$. The experimental data satisfy the relationship of (14.12) in total.

After 2,000 several reports [18–20] for the value of G (in the theoretical paper, λ is used) have been discussed and even the results based on ab initio calculations for the representative ferromagnetic metal have been reported [21–23]. These theoretical calculations treated the relaxation of spins for either intra and/or interband transitions of electron as a function of inverse of electron relaxation time τ at Fermi surface. See the schematic explanation in Fig. 14.15. Since energy $\varepsilon = \hbar/\tau$, it is easy to replace relaxation time by energy. Detail of the calculation is seen in the original paper. The calculated results are also schematically shown in Fig. 14.15. G consists of the conductivity-like and resistivity-like terms. The former decreases with increase of energy and the latter increases. Figure 14.16 shows the numerical calculated results of λ for Fe, Co, and Ni. At about room temperature (≈ 25 mV) λ of Fe, Co, Ni are 5×10^8 , 3.7×10^8 , $2 \times 10^9 \text{ s}^{-1}$, respectively. Experimental results (see Table 14.2 in Sect. 14.5.4) are $\lambda_{Ni} > \lambda_{Co} > \lambda_{Fe}$ and the calculation does not explain the material dependence. However, the absolute value of λ calculated is in agreement with the experimental one.

14.5.2 Experiment

(a) Ferromagnetic resonance (FMR) method

Figure 14.17 shows the principle chart of the FMR. The high-frequency field of 10 GHz is applied as shown in the figure, and the resonance occurs in a certain magnetic field H applied in an orthogonal direction. Then, the resonance condition is expressed by

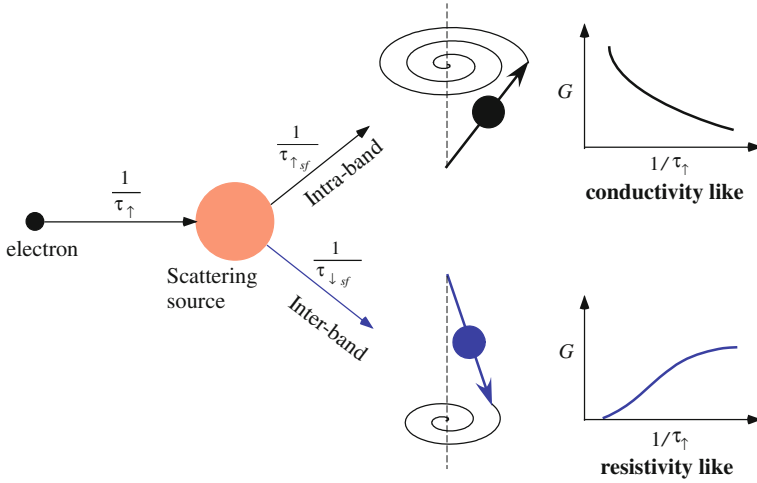
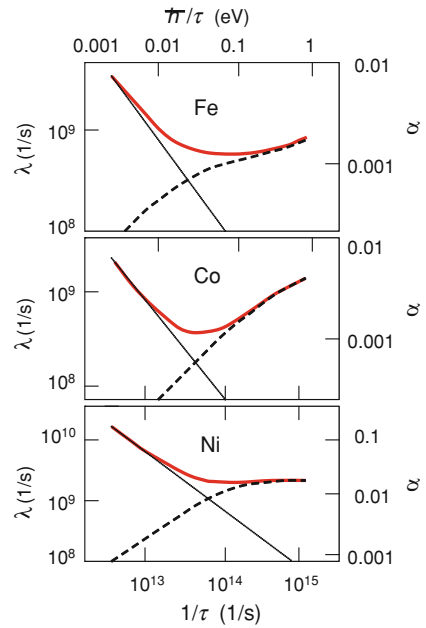


Fig. 14.15 Schematic explanation of Gilbert damping

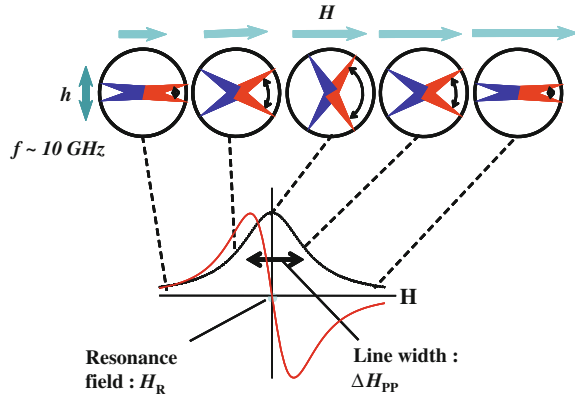
Fig. 14.16 Damping constant λ (or α) as a function of $1/\tau$ calculated for Fe, Co, Ni



$$\frac{\omega}{\gamma} = \sqrt{H_R (H_R + 4\pi M_s)}. \quad (14.13)$$

Hereafter, we describe by cgs unit and here, ω is an angular velocity of the magnetization (Larmor angular velocity), and γ is a gyromagnetic ratio. Moreover, when the

Fig. 14.17 Schematic expression of the oscillation of spin, FMR spectrum and its half-width



defect of the sample can be disregarded, the line width of the FMR spectrum (width of peak of spectrum) is given by,

$$\Delta H_{pp} = \frac{2}{\sqrt{3}} \frac{G}{\gamma M_s} \left(\frac{2\pi f}{\gamma} \right). \quad (14.14)$$

It is proportional to G , though often in the samples, the defect should not be disregarded. Therefore, it is necessary to measure the angular dependence in a right-angle direction of the plane in respect to FMR, to analyze by LLG, and to evaluate G . Mizukami et al. thought that the cause of the increase of the half-width considering the saturation magnetization and structural nonuniformity besides the increase of G and besides the intrinsic G introduced the relations as follows [24, 25],

$$\Delta H_{pp} = \Delta H_{pp}(\alpha) + \Delta H_{pp}(4\pi M_{\text{eff}}) + \Delta H_{pp}(\Delta\theta_H). \quad (14.15)$$

They analyzed their data under the assumption of (14.15) mentioned above. Each of the second and third term of the (14.15) here is caused from the nonuniformity of the saturation magnetization and from that of the angle (Fig. 14.18) between the external magnetic field and the normal to the film side, respectively. θ_H dependence of ΔH_{pp} was measured as actually shown in Fig. 14.18 (● sign in the figure), and the result was obtained from the best fitted (14.15) to determine $\Delta H(\alpha)$. Figure 14.18 shows an example for Permalloy film and the value of G evaluated by (14.14) is $1.1 \times 10^8 \text{ s}^{-1}$ in agreement with that of bulk, $0.8 \times 10^8 \text{ s}^{-1}$.

(b) All-optical time resolved magneto-optical Kerr effect measurement

We are able to obtain G -value by exciting the precession of the magnetization directly in the pulse magnetic field and examine the relaxation process.

Ando et al. [26, 27] constructed the optical system of the measurement by the pump-probe method for this purpose (Fig. 14.19). The pulse width of the Ti : Sapphire

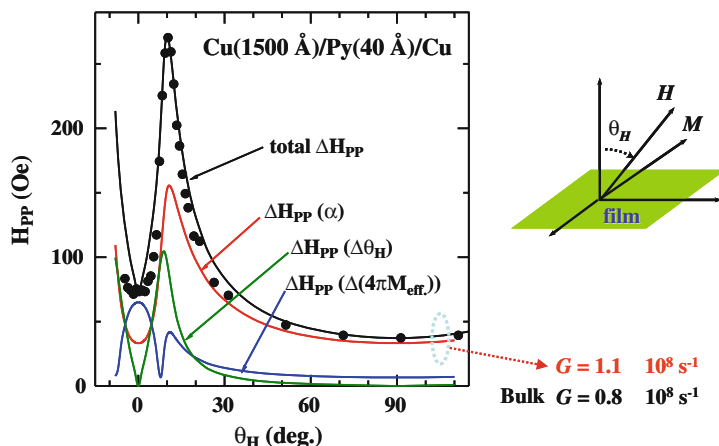


Fig. 14.18 ΔH_{pp} as a function of θ_H , the angle between film normal and applied magnetic field for Cu/Py/Cu trilayer film

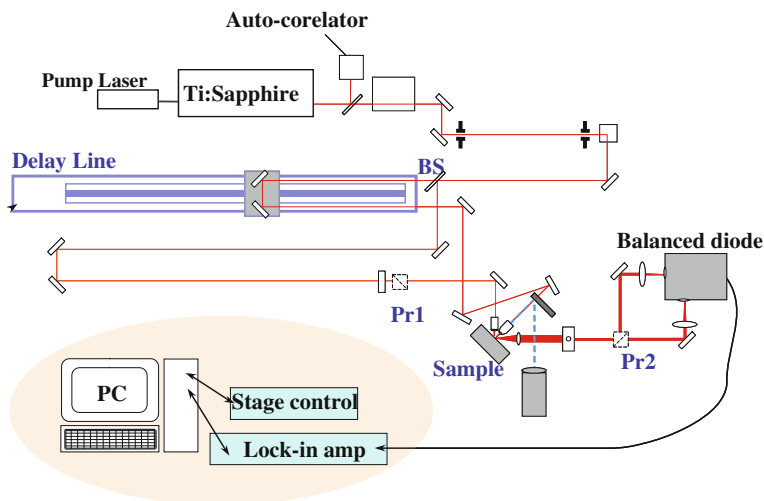


Fig. 14.19 Pump-probe measurement system

laser of about 100 fs was used for the source of light. The pump light and the probe light were divided into 10:1, and the former was condensed in the light switch through delay line. On the other hand, the latter was condensed in the sample through the optical path which made amends for delay line. The difference between the p and s elements of the reflected light were measured with balanced diode (Fig. 14.20).

Figure 14.21 shows the expansion scheme in the part of the sample and the light switch. Moreover, an actual photograph in the part is shown in Fig. 14.22.

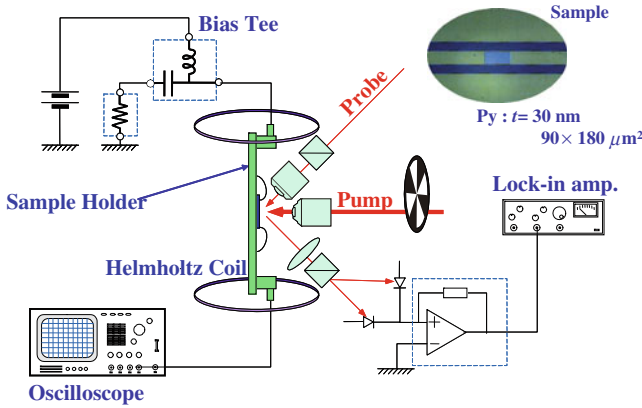
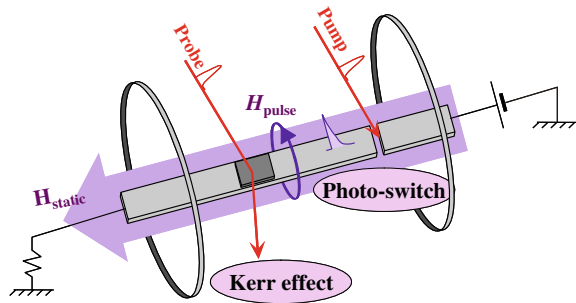


Fig. 14.20 Time resolved Kerr effect measurement system

Fig. 14.21 Expanded figure for sample and photo switch



The pulsed current flows with the photo switch, and the magnetization inclines slightly from the direction of H_{static} that the Helmholtz coil makes by the pulsed magnetic field. This magnetic component is measured by the Kerr effect with probe light. For the convenience of the experiment, the part of the sample and photo switch were made to be separated. The static magnetic field H_{static} (3–36 Oe) in the direction of the easy axis of the sample is applied, and then the light switch was made to work with the pump light. We measured the oscillation of the magnetization when the generated pulse magnetic field of 2 Oe was applied to the orthogonal H_{static} . The result is shown in Fig. 14.23 [26].

The sample is Py thin film with thickness of 30 nm and area of $180 \times 90 \mu\text{m}^2$, formed on the coplanar guide for the light switch and the applying a magnetic field. In the figure shows the experimental result. A clear oscillation of the signal by the precession movement of the magnetization is seen. The cycle of the precession movement is 1 ns or less and the amplitude is attenuated as oscillating gradually by several ns. Moreover, the period of oscillation is shortened as the static magnetic field increases. The effective field in the LLG equation is assumed as $H_{\text{eff}} = H_{\text{static}} + H_{\text{pulse}} + H_k$, and the result of calculating the pulse response signal in respect to the

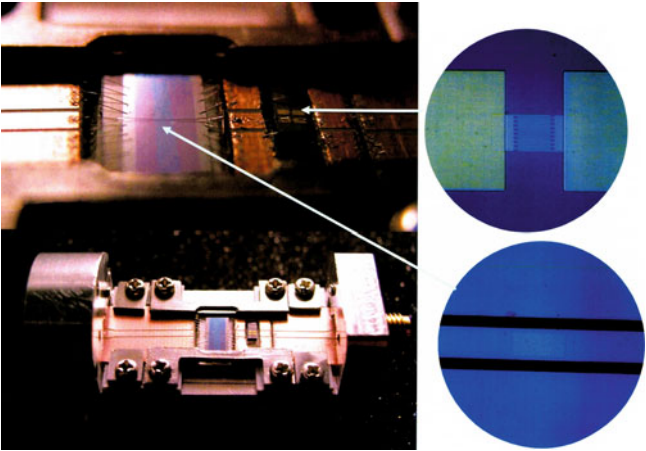
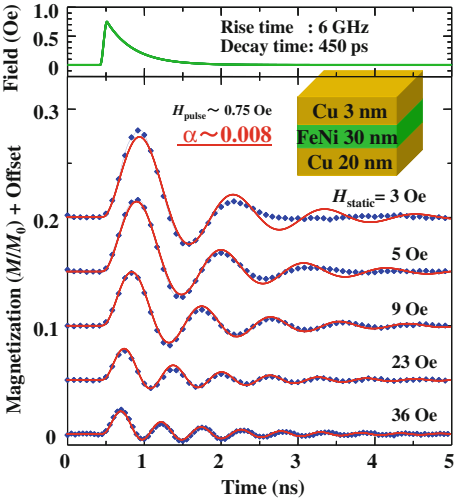


Fig. 14.22 Picture for sample photo switch

Fig. 14.23 Oscillation of magnetization at various static fields for Cu/Py/Cu sample



relaxation constant is shown by the dotted line in Fig. 14.24. As a result of the fitting, $\alpha = 0.008$ was obtained [27]. This value is in good agreement with that of bulk value obtained by FMR experiment. Furthermore, the period of oscillation experimentally obtained as a function of external field agrees well with that of theory.

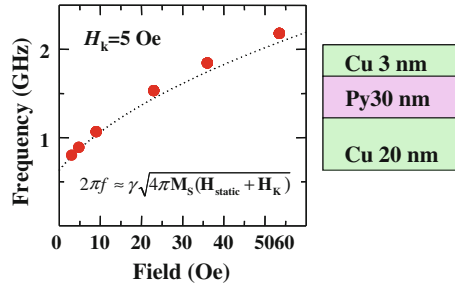


Fig. 14.24 Period of the oscillation of the magnetization as a function of the external magnetic field

14.5.3 Spin Pumping

In the study of artificial super lattice and/or tunnel junction, we investigate magnetic properties of layered structure, where the magnetic layers are joining to various materials. In such cases the Gilbert damping constant G or α enhances when compared with that of single layer magnetic film. This phenomenon is called spin pumping and important research subject in recent years.

To understand this phenomenon, the cross-sectional view of the junction is shown in Fig. 14.25a, b, and c [12]. The spin pumping can be understood intuitively as follows. The air molecule (conduction electron) in N is rubbed against each other to the pendulum that swings on F/N junction field side, deprives of the rotation (spin), and returns in N (left side of Fig. 14.25b). At this time, because the number of air molecules is not changed in N, it can be considered that only the rotation flows from the F layer to the N layer on F/N junction field side and it goes out (spin current). The flow easiness of this spin current to go out strongly depends on the character of the N layer. That is, when the spin relaxation time in the N layer is short like (b), G is not increased (outflow of the spin). On the other hand, G increases when the spin relaxation in the N layer is as large as (c) (spin pumping).

Spin pumping was reported for the first time by the experiment for which Silsbee [28] had used the conduction-electron spin resonance in 1979. They proposed a phenomenological s-d model at the same time. However, the subsequent researches are few, so the phenomenon is not understood enough. If an intuitive picture is promoted further, a new phenomenon according to spin pumping describing the following is forecast. Rubbing against each other the air molecule and the pendulum in the F/N junction interface can be rubbed if it could be seen from the F layer. That is, G increases from the reaction on the F layer field side at the same time as the gyromagnetic movement of the spin generates the spin current. This spin pumping strongly increases G according to the spin relaxation in the N layer. In 1996 Berger showed that G of FM2 increased in FM1/NM/FM2/NM junction theoretically.

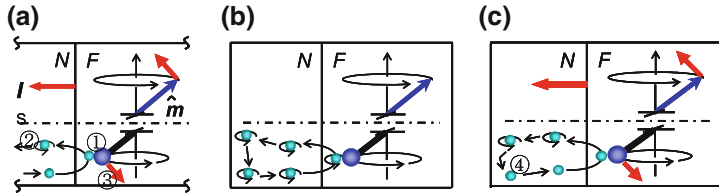


Fig. 14.25 Schematic illustrations of the spin pumping at the F/N interface (a), and spin pumping in cases where the spin relaxation for the N layer is negligible (b) and strong (c) in F/N double layers. The upper parts in (a–c) represent the generation of the spin current (I_s) and Gilbert damping by magnetization precession. The lower parts are diagrams analogous with the rotating pendulum and molecules, to which magnetization precession and conduction electrons are compared, respectively

Let us discuss more quantitatively the spin pumping phenomena by using the model calculation reported by Tserkovnyak et al. [29–31]. A spin current J_s^{pump} is pumped out from ferromagnetic surface to metallic layer (see Fig. 14.26). This leads to a build up of the normal-metal spin accumulation which either relaxes by spin-flip scattering or flows back into ferromagnet as J_s^{back} . The difference between pumped current and back current J_s is approximately expressed as

$$J_s = J_s^{\text{pump}} - J_s^{\text{back}} = \frac{\hbar}{4\pi} g^{\uparrow\downarrow} \left(1 + \frac{g^{\uparrow\downarrow}}{g_N \tanh(L/\lambda_{\text{sd}})} \right)^{-1} \mathbf{m} \times \frac{d\mathbf{m}}{dt}. \quad (14.16)$$

Here, $g^{\uparrow\downarrow}$ is a mixing conductance, g_N is a conductance of normal metal, L is the length of NM (see Fig. 14.26), and λ_{sd} is spin diffusion length. From the equation adding $\gamma J_s / M_s V$ on the right-hand side of (14.9) and (14.16), we found $\alpha = \alpha_0 + \alpha'$, α_0 is the damping constant when $J_s = 0$ and

$$\alpha' = \frac{G'}{\gamma M_s} = \frac{gL\mu_B}{4\pi M_s V} g^{\uparrow\downarrow} \left(1 + \frac{g^{\uparrow\downarrow}}{g_N \tanh(L/\lambda_{\text{sd}})} \right)^{-1} \quad (14.17)$$

is the additional damping constant due to the interfacial F-N coupling. For example, NM is Cu, $\lambda_{\text{sd}} \approx 350$ nm which is much larger than L , α' , or G' becomes zero. On the other hand, NM = Pt case, $\lambda_{\text{sd}} = 3$ nm which is much smaller than L , () in (14.17) is equal to $1 + g^{\uparrow\downarrow}/g_N$. Here, we put

$$\frac{1}{g^{\uparrow\downarrow}} + \frac{1}{g_N} = \frac{1}{g_{\text{eff}}}, \quad (14.18)$$

then,

$$\alpha' = \frac{gL\mu_B}{4\pi M_s S d} g_{\text{eff}}^{\uparrow\downarrow} \left(G' = \frac{(gL\mu_B)^2}{2h S d} g_{\text{eff}}^{\uparrow\downarrow} \right). \quad (14.19)$$

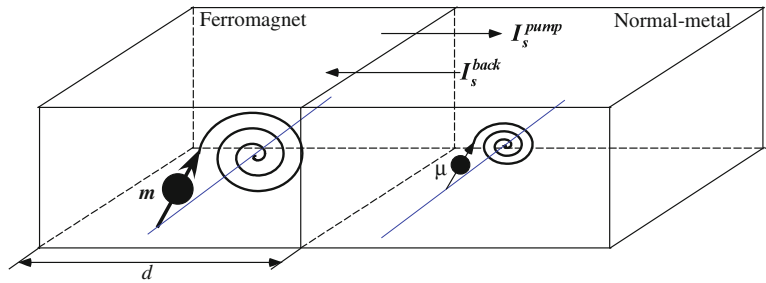


Fig. 14.26 Schematic view of the F-N bilayer. Precession of the magnetization direction m of the Ferromagnet F pumps into the adjacent normal-metal layer N by a spin current J_s^{pump} . This leads to a build up of the normal-metal spin accumulation which either relaxes by spin-flip scattering or flows back into the ferromagnet as J_s^{back}

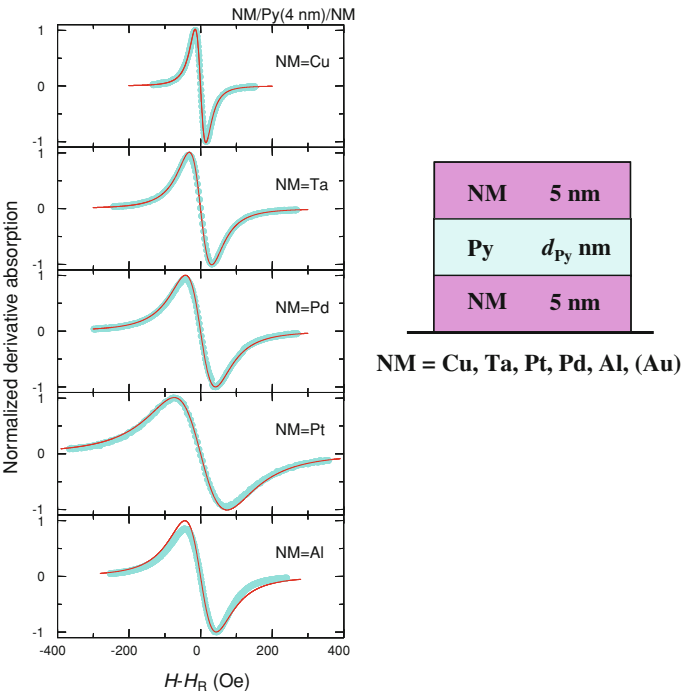


Fig. 14.27 Resonance spectrum of the non-magnetic NM/Py/NM trilayer film

Here, $g_{\text{eff}}^{\uparrow\downarrow}$ is called effective conductance and (14.18) means that the effective resistance is the resistance of magnetic layer ($1/g^{\uparrow\downarrow}$) plus that of normal-metal layer ($1/g_N$).

Fig. 14.28 Py thickness dependence of the G -value in the N/Py/N junction

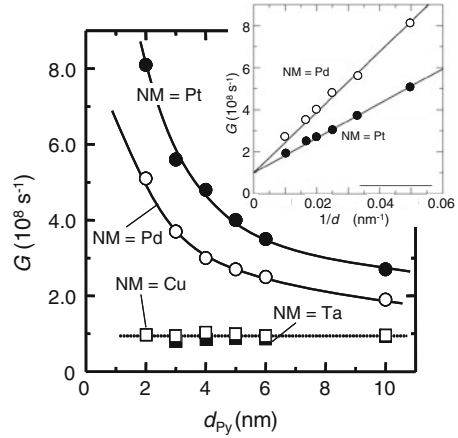


Fig. 14.29 Comparison of the vibrations of the magnetization of the Cu/Py/Cu and Pt/Py/Pt trilayer junction

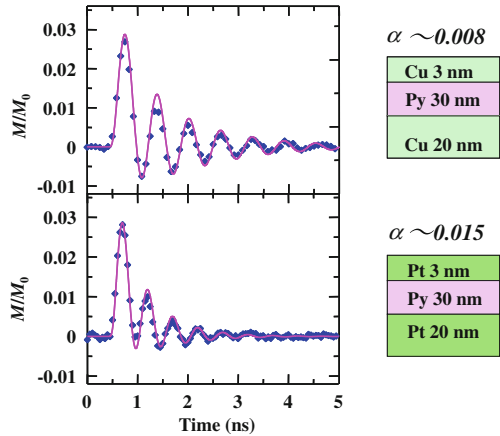


Figure 14.27 shows the spectrum of FMR of the junction where Py is placed with NM (Cu, Ta, Pd, Pt, Al). A spectrum half-power band width especially increases for NM = Pd and Pt as seen in the figure. These data were analyzed by the assumption of (14.17) in Sect. 14.5.2. Figure 14.28 shows the d_{Py} dependence of G in N/Py(d_{Py})/N ($N = \text{Cu, Ta, Pd, Pt}$) [13, 25]. G agrees with the value of bulk Py and is constant for d_{Py} in $N = \text{Cu and Ta}$. On the other hand, G in the samples of $N = \text{Pd and Pt}$ suggests that it is increased in proportion to $1/d_{\text{Py}}$, and supports the model described above. The same matter was also confirmed by other research group. Figure 14.29 shows oscillation of magnetization of Pt/Py/Pt junction with that of Cu/Py/Cu junction. The oscillation for Pt/Py/Pt decreases much faster than that of Cu/Py/Cu. The α value of Pt/Py/Pt estimated from the decay is enhanced and two times larger compared with that of Cu/Pt/Cu. This result is consistent with the data shown in Fig. 14.28.

Fig. 14.30 $\text{Cu}(d_{\text{Cu}})$ thickness dependence of the G -value in $\text{Py}/\text{Cu}(d_{\text{Cu}})/\text{Py}$ junction

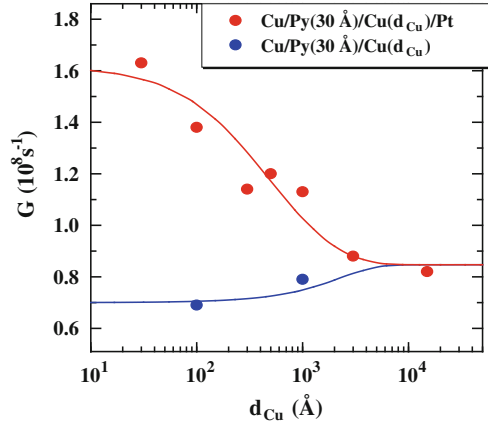
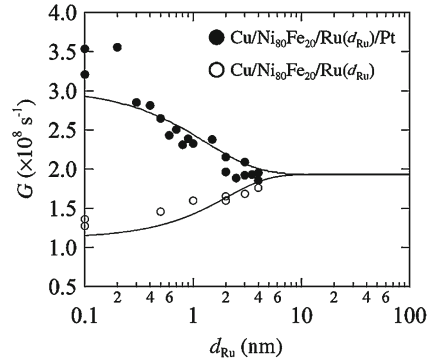


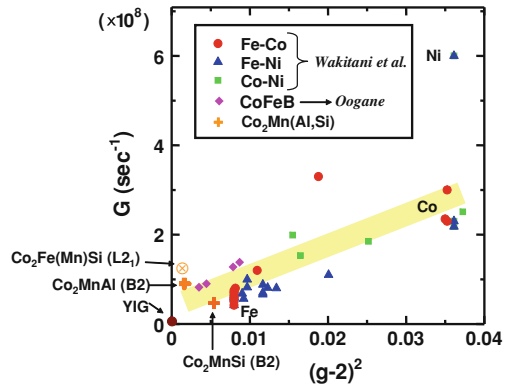
Fig. 14.31 $\text{Ru}(d_{\text{Ru}})$ thickness dependence of the G -value in $\text{Cu}/\text{Ni}_{80}\text{Fe}_{20}/\text{Ru}(d_{\text{Ru}})/\text{Pt}$ junction



In this way, Gilbert damping constant is no more material constant and depends strongly on the NM material touched with ferromagnet. The spin relaxation in NM is due to spin-flip scattering originated in spin-orbit interaction. In fact the spin relaxation in NM is strong in the order of Cu, Ta, Pd and Pt. and supports this conception.

By measuring damping constant for a special junction, we can evaluate the spin diffusion length where the injected conduction electron spin loses the phase information of the spin. Figure 14.30 shows the dependence of G -value in $\text{Cu}/\text{Py}/\text{Cu}/\text{Pt}$ and $\text{Cu}/\text{Py}/\text{Cu}$ junctions on the middle Cu layer thickness. The phenomenological model proposed by Silsbee et al. was developed to calculate the G -value and the middle Cu layer thickness dependence of G -value was calculated quantitatively. The result is shown in Fig. 14.30 by the solid line. The G -value of $\text{Cu}/\text{Py}/\text{Cu}/\text{Pt}$ junction enhances about 1.5 times with compared with that of $\text{Cu}/\text{Py}/\text{Cu}$ junction when the d_{Cu} is less than 50 Å. It decreases with increasing d_{Cu} and both G values for two junctions become nearly same at around $d_{\text{Cu}} = 300 \text{ nm}$. The spin diffusion length used for calculation is 300 nm and it is equal to the experimental value. In Fig. 14.31

Fig. 14.32 G -value as a function of $(g - 2)^2$



the same experiment for Cu/Py/Ru/Pt is shown [32]. Ru film has been used for a long time as exchange bias layer for GMR and TMR junctions and/or buffer or cup layer. However, the spin diffusion length of Ru has not been obtained experimentally. The spin diffusion length estimated from Fig. 14.31 is 2–4 nm. This means that the spin loses its angular momentum near the interface and it behaves as spin sink similar to Pt.

14.5.4 Damping Constant of Various Kinds of Materials

(a) 3d transition metal and alloys

Table 14.2 summarizes the damping constant G or α for various materials [33–49] (M. Oogane, (unpublished); M. Oogane, (unpublished)). If we compare damping constant using α , $\alpha_{\text{Fe}} < \alpha_{\text{Co}} < \alpha_{\text{Ni}}$, and α , Ni is largest in three transition metals. While, $G_{\text{Fe}} < G_{\text{Co}}$, G_{Ni} and the difference of G between Co and Ni is uncertain experimentally. On the other hand, the theoretically calculated value of G for Ni is largest. Figure 14.32 shows G values as a function of $(g - 2)^2$ which is expressed in (14.12) in Sect. 14.5.1, where g was estimated from γ values obtained from FMR spectrum using the relationship $\gamma = g\mu_B/\hbar$. In the figure, G values for YIG and representative Heusler alloys are also shown. In spite of the scattering of data points, we can see that G is proportional to $(g - 2)^2$. We consider that the reason of the scattering of data points is the separation of intrinsic α and extrinsic α due to magnetic inhomogeneities is not enough or another contribution to α in addition to the contribution of orbital magnetic moment expressed by (14.12) in Sect. 14.5.1.

(b) Heusler alloys

After 2,000, various kinds of research have been carried out for Heusler alloys which possess bandgap at Fermi surface, since a large TMR is expected for MTJs with

Table 14.2 Summarized result G and α for 3d transition metal and alloys

Materials	$G(10^7/s)$	$\alpha(10^{-3})$
Fe [33–36]	4.2, 7, 5.7, 7, 6	1.37, 2.28, 1.86, 1.96
Co [36, 37] (M. Oogane, (unpublished))	23.5, 23, 30	10.65, 8.54, 11.14
Ni [39, 40, 43, 44] (M. Oogane, (unpublished))	23, 21.8, 60	64.22, 24.62, 23.33
8CoFe	7.5	2.32
16CoFe	5.0	1.47
29CoFe	6.0	1.71
35CoFe	7.0	1.96
51CoFe	8.0	2.28
73CoFe	12.0	3.72
85CoFe	33	11.62
50CoFe	13.8	2.00
75CoFe	11.0	4.15
90CoFe		4.3
40NiFe	8.2	3.7
50NiFe	5.7	2.76
80NiFe		7.8
58NiFe	6.8	3.09
75NiFe	6.6	3.73
75NiFe	8.8	4.97
75NiFe	7.0	3.96
77NiFe	8.1	4.61
80NiFe	8.0	4.92
90NiFe	11	8.96
20NiCo	21	11.24
50NiCo	19.93	11.98
60NiCo	15.35	10.21
70NiCo	14.38	11.0
80NiCo	18.49	19.1
90NiFe	25.13	35.3
3SiFe [38, 45]	6.1, 7.2	
Fe ₄₀ Ni ₄₀ B ₂₀ [46]	5	
Fe ₈₀ B ₁₃ Si ₅ C ₂ [47]	7	
Fe ₁₉ Ni ₇₁ P ₁₄ B ₁₆ [48]	2	
Co _{96-x} Cr _x Ta ₄ [49]		9–19
Co-Cr-Pt [49]		10–40

Co-Fe [36], (M. Oogane, (unpublished)) Fe-Ni (M. Oogane, (unpublished)), [38–42] Co-Ni (M. Oogane, (unpublished))

Heusler electrode. Also damping constant of Heusler alloys has been discussed correlating with the density of state of Heusler alloys. Table 14.3 summarizes the damping constant of representative Heusler alloys [50–54]. G or α for Co₂MnSi and Co₂FeAl is much smaller than that of Fe which is the smallest value in the 3d transition metal and alloys. Figure 14.33 shows α of Co₂MnAl_xSi_{1-x} and Co₂Fe_xMi_{1-x}Si alloy systems as a function of total number of valence electron N . α exhibits a broad

Table 14.3 G and α values for typical Heusler alloys

	$G(\text{MHz})$	$\alpha(10^{-3})$
NiMnSb [50]	31	2.9
Co ₂ MnAl [51]	80	6
Co ₂ MnSi [52]	37	3
Co ₂ FeAl [53]	17–41	1–2
Co ₂ FeSi [54]	120	7

Ref. NiFe: 8×10^{-3}

Fig. 14.33 α as a function of valence electron number for Co₂MnAl_xSi_{1-x} and Co₂Fe_xMn_{1-x}Si alloy systems

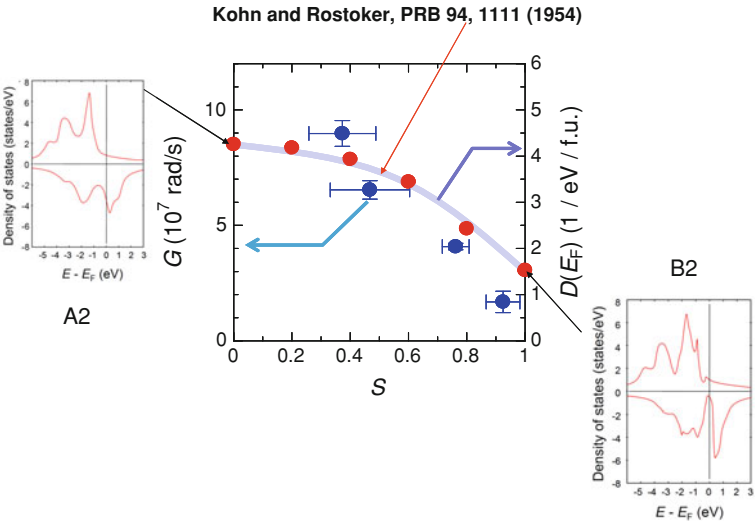
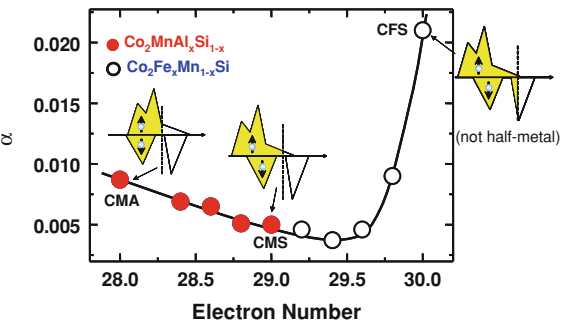


Fig. 14.34 Damping constant G and density of state at Fermi surface as a function of ordering parameter S

minimum around $N = 29\text{--}29.5$. This experimental results supports the theoretical prediction $\alpha \propto \xi^2 (D_{\uparrow} + D_{\downarrow})$, where ξ is the spin-orbit interaction coefficient for d band and $D_{\uparrow}$, $D_{\downarrow}$ are the density of states at Fermi surface for $\uparrow$ and $\downarrow$ spins, respectively. Here, it should be noted that G values shown in Table 14.3 and Fig. 14.32 are not always in agreement. This is due to the disagreement of sample heat treatment

and is different extrinsic terms. Figure 14.34 [53] also shows the discussion of G in comparison with the density of state for Heusler alloy films [53]. Both G and density of state at Fermi surface calculated theoretically decrease similarly with increase of ordering parameter and suggest $G \propto D(E_F)$.

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