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General Theory of High- T_c Superconductors*Kaname Matsumoto*

Twenty years after the discovery of high-temperature superconductors, practical superconducting wires made of these materials are now being manufactured, and trials of electrical and industrial applications including a train supported by magnetic levitation, a transmission line, a ship's engine, and many others are being implemented. High-temperature superconductors have again taken central stage as a dream material after long research and development. To give a better understanding of the latest results, the general theory of superconductors is explained in this chapter.

1.1**Fundamental Properties of Superconductors****1.1.1****The Superconducting Phenomenon**

What is the superconducting phenomenon? Figure 1.1 shows the temperature dependence of the electrical resistance of a superconductor. This falls gradually as the superconductor is cooled, before it vanishes suddenly. The temperature at which this occurs is called the *critical temperature* T_c .

When we consider the process whereby water is changed into ice at its freezing point, the state of water and the state of ice are recognized as different phases. The change between two phases is called a *phase transition*, and, in a similar way, the superconducting phenomenon is also a kind of phase transition. The superconductor at temperatures above T_c is in its normal conducting state and has electrical resistance. Here, the electron system does not have order; that is to say, if the order is denoted by ψ , $\psi = 0$. In contrast, by cooling the superconductor to temperatures below T_c , it enters into the superconducting state, and a certain order in the electron system arises. Then, $\psi \neq 0$. When two electrons are united, a *Cooper pair* is generated, and many such pairs are formed in the cooled superconductor. These pairs are expressed by wave functions with exactly the same amplitude and phase, and these overlap each other, resulting in a *macroscopic wave function*. The

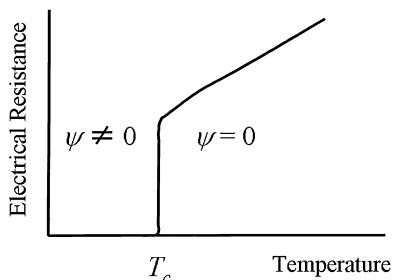


Figure 1.1 A typical temperature dependence of an electrical resistance of a superconductor. T_c is the critical temperature. When $\psi \neq 0$ ($T < T_c$) the material is in the superconducting state, whereas $\psi = 0$ ($T > T_c$) corresponds to the normal conducting state.

macroscopic wave function is given by the above-mentioned order ψ . The electrical resistance vanishes in the case of $\psi \neq 0$; moreover, a variety of other aspects of superconducting phenomena like the *persistent current*, the *Meissner effect*, the *Josephson effect*, and so on, appear. Many textbooks on superconductivity have already been published, and some of these are listed in Refs. [1–6].

A heat loss due to electrical resistance occurs when a current flows in a metal like copper or aluminum. Such a disadvantageous energy loss in an electric power cable cannot be disregarded. The copper wire could melt by the heating which occurs when a large current is applied to a copper coil to generate a strong magnetic field, whereas no energy loss occurs at all even if a large current is applied to a superconductor below T_c , since the superconductor has *zero electrical resistance*. Thus, a strong magnetic field can be generated by a superconducting coil and power can be transmitted by a cable without energy loss.

Figure 1.2 shows the evolution of the critical temperature T_c of superconductors. The superconductivity of mercury was discovered first by Kamerlingh-Onnes in 1911 [7]. Further discoveries of superconducting materials followed, and T_c rose slowly. Cuprate superconductor was discovered in 1986 [8, 9], and, after this, T_c increased rapidly [10], reaching 164 K at the high pressure of 30 GPa [11]. This means that the maximum T_c had already reached halfway toward room temperature (~ 300 K). These materials are called *high- T_c superconductors*. The metallic superconductor MgB_2 , with $T_c = 39$ K, was discovered in 2001 [12], becoming a favorite topic in recent years. Even more surprising, a new material group with $T_c \approx 56$ K was discovered in 2008, this being an iron pnictide, containing iron and arsenide instead of copper and oxygen [13, 14], and this advance led to renewed interest in high- T_c superconductors.

Conventional Nb–Ti and Nb_3Sn superconducting wires are already being put to practical use [15], and the effectiveness of these superconductors has been confirmed by the development of a magnetic levitation train, magnetic resonance imaging (MRI), nuclear magnetic resonance (NMR), particle accelerators, and so forth. These metallic wires are also essential for the construction of the large-scale superconducting coil of a nuclear fusion device, but they need to be cooled to 4.2 K with the aid of expensive liquid helium.

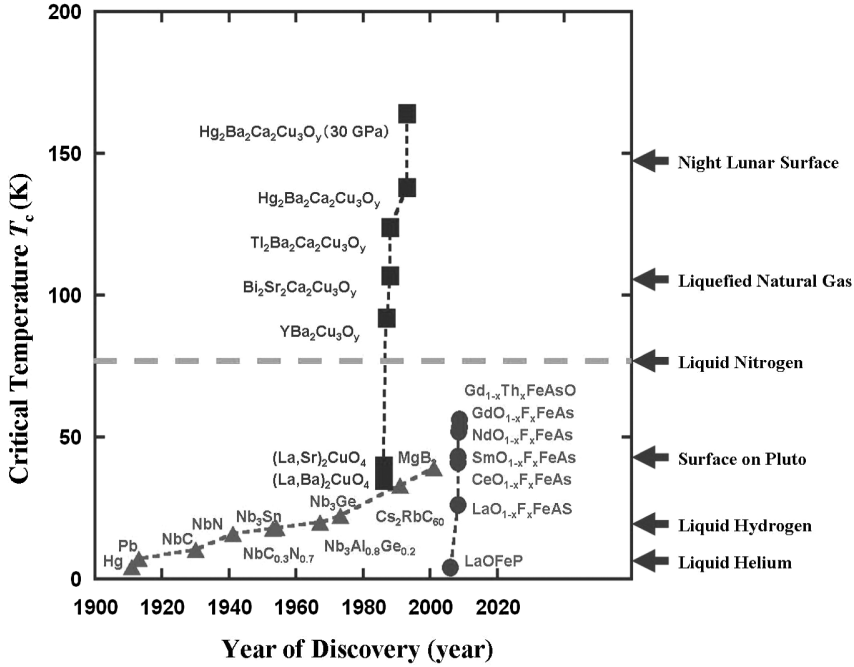


Figure 1.2 The evolution of the critical temperature T_c of superconductors. The series of high- T_c cuprate superconductors were first discovered in 1986. Iron arsenide superconductors, which are other candidates for high- T_c superconductors, were discovered in 2008.

The critical temperature of high- T_c superconductors has now exceeded 77 K for the first time, so that their electrical resistance becomes zero in liquid nitrogen. Unlimited quantities of nitrogen are available in the atmosphere, so that the cost of cooling is greatly reduced, since liquid nitrogen is overwhelmingly cheaper than liquid helium. The application of the high- T_c superconductors to electric power and other industrial technologies, maximizing the effectiveness of using electrical energy, is confidently expected. If a material that exists in the superconducting state at room temperature, namely a *room temperature superconductor*, is discovered, even liquid nitrogen becomes unnecessary to achieve zero resistance, and a huge number of superconductivity applications therefore become possible. The search for materials with higher T_c still continues with great intensity.

1.1.2

Superconductivity and Quantum Mechanics

A knowledge of *quantum mechanics* is necessary to understand the order ψ in the superconducting state. The relationship between superconductivity and quantum mechanics is briefly explained here.

1.1.2.1 Wave-Particle Duality

A subatomic particle such as an electron has particle-like and wave-like properties. For instance, when a particle of mass m moves at speed v , it has energy $E = (1/2)mv^2$ and momentum $p = mv$. Such a particle also has wave-like properties, the wavelength λ being related to the momentum p of the particle by the *de Broglie equation*

$$\lambda = h/p \quad (1.1)$$

where h is Planck's constant. From this *wave-particle duality*, the following *uncertainty principle*, with position x and time t , is given as

$$\Delta x \Delta p \approx h, \quad \Delta E \Delta t \approx h. \quad (1.2)$$

Let us consider the particle to be in a small box of length L . The particle confined in the box shows wave-like properties, there being a standing wave of wavelength such as $\lambda = 2L$, L , and $(2/3)L$, as shown in Figure 1.3. The stationary state of this wave is written as

$$\psi(x) = A \sin(2\pi x/\lambda) \exp(i\theta) \quad (1.3)$$

where A and θ are the amplitude and phase of the wave, respectively. By differentiating the above equation twice, the next equation using $\lambda = 2L/n$ ($n = 1, 2, \dots$) is given by

$$d^2\psi(x)/dx^2 = -(2\pi/\lambda)^2 \psi(x). \quad (1.4)$$

The following *Schrödinger equation* is obtained when rewriting Equation 1.4 by using $E = (1/2)mv^2$ and the de Broglie equation. With $\hbar = h/2\pi$, we find

$$-(\hbar^2/2m)d^2\psi/dx^2 = E\psi. \quad (1.5)$$

ψ is considered to be a wave function of the particle. $|\psi|^2$ corresponds to strength of the wave from a wave-only viewpoint, whereas it means the probability of the existence of the particle from a particle-only viewpoint. Then, the energy of the particle becomes discrete and is given by

$$E = (\hbar^2/2m)(2L/n)^2 \quad (n = 1, 2, \dots). \quad (1.6)$$

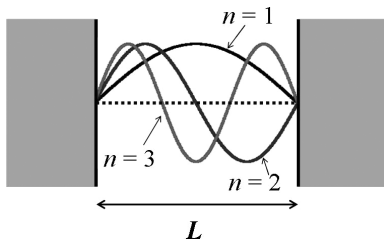


Figure 1.3 The microscopic particle-like electron which is confined in a small box shows wave-like properties. The Schrödinger equation predicts discrete energy levels.

1.1.2.2 Fermion and Boson

It is known that subatomic particles of the natural world are classified into two kinds (*fermions* and *bosons*), this being one of the important conclusions of quantum mechanics. These particles have the intrinsic property of spin. Electrons, protons, and neutrons possess a half-integral spin, so that they are classified as fermions, whereas photons and phonons are classified as bosons since they possess integral spin as opposed to fermions. The composite particle that consists of fermions also becomes a fermion in case of an odd number of particles, depending on the total number of spins, and becomes a boson in case of an even number of particles. For instance, as shown in Figure 1.4, helium-4 (^4He) consists of two neutrons, two protons, and two electrons, resulting in a boson. In contrast, the isotope helium-3 (^3He) is classified as a fermion, since it consists of one neutron, two protons, and two electrons.

There is a big difference between quantum statistics of fermions and that of bosons, as shown in Figure 1.5. Fermions which are confined in the small box repulse each other by virtue of the *Pauli exclusion principle*. Thus, one energy level is occupied by only two fermions (positive and negative spins), while, in contrast,

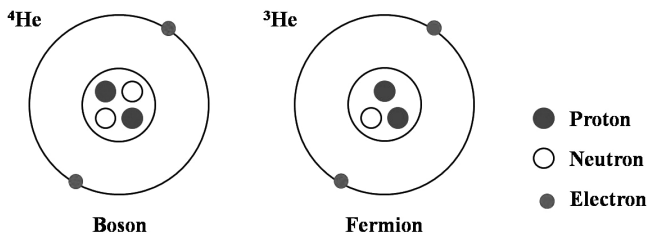


Figure 1.4 Composite particles consisting of fermions becomes bosons or fermions depending on the total number of spins. ^4He with six fermions is a boson whereas ^3He is a fermion.

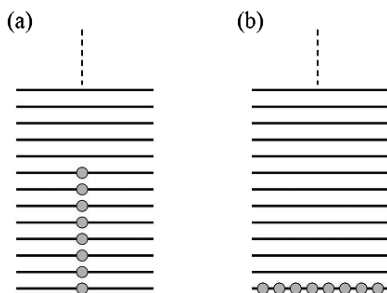


Figure 1.5 Distribution of microscopic particles in discrete energy levels at the temperature of absolute zero. Fermions are shown at (a) and bosons at (b). Fermions are packed one by one from the lowest energy level to the highest; on the other hand, bosons are simultaneously packed into the lowest energy level.

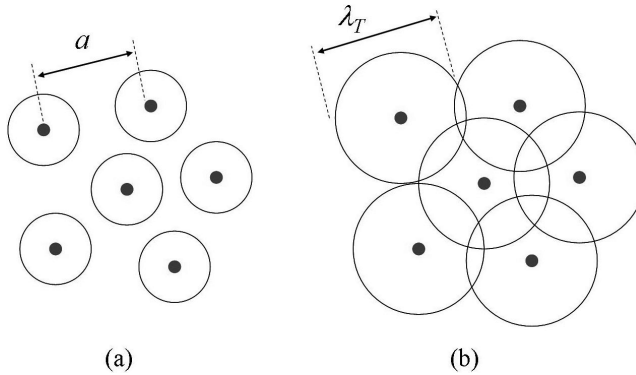


Figure 1.6 Overlapping of gas particles when the temperature is decreased. Gas particles starts to overlap when $\lambda_T \approx a$, where λ_T is the thermal de Broglie wavelength of the particles and a is the average interval between them. High temperature is illustrated at (a) and low temperature at (b).

many bosons can occupy the same energy level. The energy distribution of fermions at the temperature of absolute zero is the state where the particles are sequentially packed from the lowest energy level one by one as shown in Figure 1.5a, but, in the case of bosons, all particles are packed into the lowest energy level as shown in Figure 1.5b.

Suppose that the average distance between gas particles is a and that the *thermal de Broglie wavelength* of the gas particles is

$$\lambda_T \approx h / (2\pi m k_B T)^{1/2}, \quad (1.7)$$

where k_B is Boltzmann's constant, m is the mass of the gas particles and T is the temperature of the gas. As the temperature decreases λ_T becomes long, and the wave functions of the neighboring particles come to overlap when $\lambda_T \approx a$, as indicated in Figure 1.6. In the case of bosons, many particles are condensed to the lower energy level.

This is called a *Bose-Einstein condensation* (BEC) [16]. The particles occupying the same energy level possess the overlapped wave function with the same momentum and energy, and the particle system is represented by the macroscopic wave function ψ . Actually, bosons of ^4He are condensed at $T = 2.2\text{K}$ and show *superfluidity*.

1.1.2.3 Zero Resistance

When electrons are packed into the small box, they are distributed from the lowest energy level to the higher energy levels because electrons are fermions. As a result, the total energy of the electron system is very high. However, if the electrons can be changed into bosons by some means, the total energy of the system can be lowered. The *BCS theory* (Bardeen, Cooper, and Schrieffer, 1957) [17] was based on such an idea, and the essence of the superconducting phenomenon was

brilliantly clarified. The electron pairs, namely the Cooper pairs that united two electrons, are explored in the BCS theory. From the above discussion, Cooper pairs behave as bosons, so that the pairs formed on decreasing the temperature are condensed at the critical temperature T_c to the lower energy level. Since these Cooper pairs have the same wave functions, the electron system is represented by the macroscopic wave function ψ with which many wave functions of the Cooper pairs overlap. ψ is given by

$$\psi = |\psi_0| \exp(i\theta), \quad (1.8)$$

where $|\psi_0|^2$ is the density of Cooper pairs and θ is the phase. The macroscopic wave function ψ is called an *order parameter* which has a certain kind of *rigidity*, and the energy that is called the *energy gap* 2Δ is necessary to break up the Cooper pairs.

The most important feature of a superconductor is its ability to carry current without electrical resistance. The formation of Cooper pairs and the energy gap 2Δ are related to this phenomenon. An individual electron in the normal conducting state is scattered by the phonon and by impurities, and its direction of movement is forced to change; hence, electrical resistance is generated. In the superconducting state, the momentum p of the center of mass of a Cooper pair has the same value for all pairs, and a superconducting current flows in the case of $p \neq 0$, whereas the current is zero in the case of $p = 0$.

When the current is flowing, an individual Cooper pair is not permitted to change its direction of movement because of the strong interaction between the pairs. This is feasible only after a Cooper pair breaks up, but, for this purpose, kinetic energy equivalent to the energy gap must be induced in the Cooper pairs by the flowing current. Actually this current is very large indeed, so that the electrical resistance is not generated by a small current.

1.1.2.4 Origin of Formation of a Cooper Pair

How is a Cooper pair formed? Coulombic repulsive interaction takes place between electrons, and its energy is given by $V(r) = (1/4\pi\epsilon_0)e^2/r$, where e is the electrical charge, r is the distance between the electrons, and ϵ_0 is the permittivity in a vacuum. It is necessary to overcome the Coulombic interaction to enable the electron pair to be formed. The Coulombic interaction in the medium can be written as

$$\begin{aligned} V(r) &= (1/4\pi\epsilon)e^2/r \\ &= (1/4\pi\epsilon_0)e^2/r - (1/4\pi r)e^2(1/\epsilon_0 - 1/\epsilon), \end{aligned} \quad (1.9)$$

where ϵ is a permittivity in the medium. $V(r)$ can be weakened if $\epsilon_0 < \epsilon$, which means that an attractive force between electrons in opposition to the Coulombic repulsive interaction is generated with the medium. Figure 1.7 shows the origin of the attractive force between electrons through the medium. If one electron in the crystal attracts neighboring positive ions, a nearby second electron will be pulled in by these positive charges. This means that an attractive interaction throughout the medium is generated between electrons and overcomes the

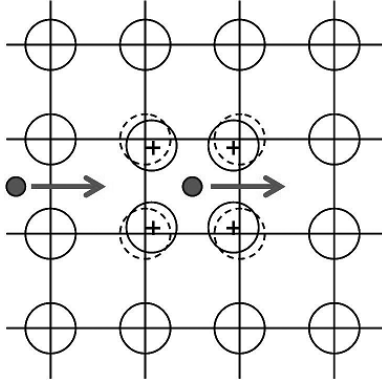


Figure 1.7 The generation of attractive force between electrons in a crystal. The second electron moving in the crystal is attracted by the positive charge of the crystal ions which is produced by Coulomb interaction with the first electron passing there. Thus, two electrons interact with each other through the medium.

Coulombic interaction locally for a short time, becoming an origin of the formation of Cooper pairs. This is the mechanism via *electron-phonon interaction*, and it can explain the origin of conventional low- T_c superconductors [18]. It also confirms that Cooper pairs are formed in high- T_c superconductors. However, the mechanism of the attractive force of a Cooper pair has not yet been established and is still being investigated.

Let us consider the formation of a Cooper pair bearing in mind the uncertainty principle of Equation 1.2. There is a relation $\Delta \approx k_B T_c$ because Cooper pairs break up at T_c . Assuming that the scale of time to establish Cooper pair is t_0 , this leads to $t_0 \approx \hbar/\Delta$ according to Equation 1.2. From this relation, $t_0 \approx 10^{-13}$ and $t_0 \approx 10^{-12}$ seconds are roughly estimated with $T_c = 100$ K and $T_c = 10$ K, respectively. That is, superconductivity cannot be observed if the time is shorter than t_0 . The distance ξ_0 by which the electron moves to form the pair is the *Pippard coherence length* or the *BCS coherence length* [19], given by $\xi_0 = t_0 v_F$ where v_F is the Fermi velocity. For example, $\xi_0 \approx 10^{-9}$ m and $\xi_0 \approx 10^{-6}$ m are roughly obtained assuming the typical Fermi velocities $v_F \approx 10^4$ m s $^{-1}$ and $v_F \approx 10^6$ m s $^{-1}$ when $T_c = 100$ K and $T_c = 10$ K.

1.1.2.5 Josephson Effect

Another result that can be derived because superconductivity is expressed by the macroscopic wave function is shown here. Suppose two superconductors are connected through an extremely thin insulating layer as shown in Figure 1.8. The following Schrödinger equations of superconductors 1 and 2 are given as

$$\begin{aligned} i\hbar(\partial\psi_1/\partial t) &= eV\psi_1 + K\psi_2, \\ i\hbar(\partial\psi_2/\partial t) &= -eV\psi_2 + K\psi_1, \end{aligned} \quad (1.10)$$

where K is the coupling constant for the wave functions across the insulator, e is the electronic charge, and V is a voltage applied between the two superconductors.

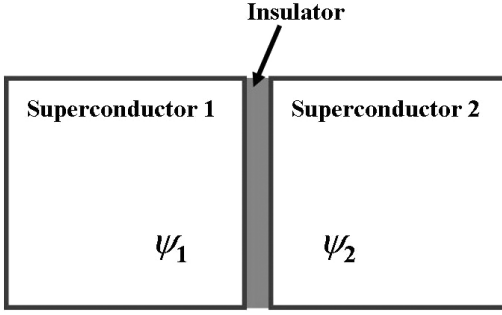


Figure 1.8 The Josephson effect is observed in a system where two superconductors are connected through a thin insulating layer. The superconducting tunneling current J_s depends on the phase difference between the macroscopic wave functions ψ_1 and ψ_2 .

Assuming the macroscopic wave functions of $\psi_1 = n_1^{1/2} \exp(i\theta_1)$ and $\psi_2 = n_2^{1/2} \exp(i\theta_2)$ for each area, where n_1 and n_2 are the densities of super electrons and θ_1 and θ_2 are the phases in the two superconductors, we find the following Josephson equations

$$J_s = J_c \sin \phi, \quad \partial \phi / \partial t = 2eV / \hbar, \quad (1.11)$$

where J_c is a critical current, and ϕ corresponds to a phase difference $\theta_2 - \theta_1$ between superconductors 1 and 2. This means that the superconducting tunneling current J_s that corresponds to the phase difference flows through the junction and also that the alternate current proportional to V flows under the condition that the voltage is applied to the junction. This is called the *Josephson effect* [20], showing that the waviness of the electron appears on a macroscopic scale.

1.1.3

Superconductivity and Thermodynamics

Applying the magnetic field to the superconductor, the current induced corresponds to zero resistance, and this response is different from that associated with the normal conducting state. Especially, the behavior of the *quantized vortex* is interesting and the control of the *vortex lines* is very important for practical applications.

1.1.3.1 Superconductor in Magnetic Field

Magnetic flux density $B = 0$ occurs simultaneously with zero resistance in the superconductor. This is called the *Meissner effect* [21]. At this time, $M = -H$ is obtained from

$$B = \mu_0 (H + M) = 0, \quad (1.12)$$

where H is the magnetic field, $M = M(T, H)$ is the magnetization, and μ_0 is the magnetic permeability in a vacuum. The differential Gibbs free energy of the superconductor can be written

$$dG = -SdT - \mu_0 M dH, \quad (1.13)$$

where S is the entropy and T is the temperature. With $T = \text{constant}$, $dG = -\mu_0 M dH = \mu_0 H dH$. By integrating Equation 1.13 from $H = 0$ to $H = H$ in the superconducting state, the energy difference defined by

$$G_s(T, H) - G_s(T, 0) = (1/2)\mu_0 H^2 \quad (1.14)$$

is obtained for a unit volume of superconducting material, where $G_s(T, H)$ is the Gibbs free energy of the superconductor.

Applying the magnetic field to the superconductor, the superconductivity is lost at

$$H = H_c(T). \quad (1.15)$$

$H_c(T)$ is called the *critical field*. When H is applied in the normal conducting state there is no energy change because $M = 0$; hence the Gibbs free energy of the normal conductor is $G_n(T, H) = G_n(T, 0)$. The equation $G_n(T, H_c) = G_s(T, H_c)$ is also obtained, because the superconductor changes to a normal conductor at $H = H_c(T)$. Then, we find the difference in the free energy

$$G_n(T, 0) - G_s(T, 0) = (1/2)\mu_0 H_c^2(T). \quad (1.16)$$

This energy difference is called the *condensation energy*. The relationship described here is shown in Figure 1.9.

1.1.3.2 London Equations

The fundamental equations that explain the Meissner effect are given by the *London theory* [22]. Using the motion equation of a superconducting electron with zero resistance, $m^*(dv_s/dt) = -e^*E$, and superconducting current density, $J_s = -n_s e^* v_s$, we obtain the following equation

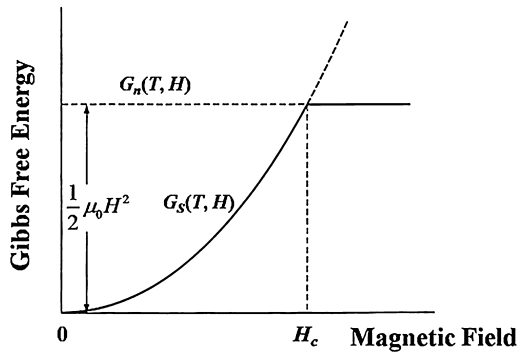


Figure 1.9 Magnetic field dependence of the normal state and the superconducting state Gibbs free energies. The change in Gibbs free energy as a function of magnetic field is expressed by Equation 1.14.

$$\partial \mathbf{J}_s / \partial t = (n_s e^{*2} / m^*) \mathbf{E}, \quad (1.17)$$

where m^* and $-e^*$ ($e^* > 0$) are the mass and the charge of superconducting electron, $\mathbf{E}$ is the electric field, and $\mathbf{v}_s$ and n_s are the speed and the density of the superconducting electron. Combined with the Maxwell equation of

$$\nabla \times \mathbf{E} = -\partial \mathbf{B} / \partial t, \quad (1.18)$$

where $\mathbf{B}$ is the magnetic flux density, we get

$$\frac{\partial}{\partial t} \left(\frac{n_s e^{*2}}{m^*} \mathbf{B} + \nabla \times \mathbf{J}_s \right) = 0. \quad (1.19)$$

Assuming the expression in the parentheses is zero, we obtain the following equation

$$\frac{n_s e^{*2}}{m^*} \mathbf{B} + \nabla \times \mathbf{J}_s = 0, \quad (1.20)$$

which can explain the Meissner effect. Equations 1.17 and 1.20 are called the *first and second London equations*, respectively. Again, combined with

$$\nabla \times \mathbf{B} = \mu_0 \mathbf{J}_s, \quad (1.21)$$

we have

$$\nabla^2 \mathbf{B} = (1/\lambda_L)^2 \mathbf{B}. \quad (1.22)$$

The *London penetration depth* λ_L is given by

$$\lambda_L = (m^* / n_s e^{*2} \mu_0)^{1/2}. \quad (1.23)$$

From Equations 1.22 and 1.23, $\mathbf{B}$ on the surface of the superconductor is obtained. $\mathbf{B}$ as shown in Figure 1.10 is attenuated from the surface within the range of λ_L . The magnetic flux density $\mathbf{B}$ can be expressed as

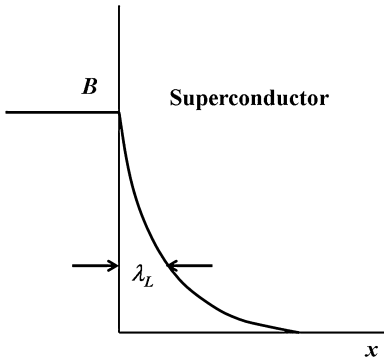


Figure 1.10 Schematic diagram of attenuation of the magnetic flux density $\mathbf{B}$ on the surface of a superconductor. Although the magnetic field penetrates the superconductor within the range of λ_L , the Meissner effect is established in the superconductor which is thicker than λ_L .

$$\mathbf{B} = \nabla \times \mathbf{A}, \quad (1.24)$$

where $\mathbf{A}$ is the magnetic vector potential. We note that we have the following important equation

$$\mathbf{J} = -(n_s e^* / m^*) \mathbf{A} \quad (1.25)$$

by using Equations 1.20 and 1.24 under the appropriate condition. This means that, in the superconductor exposed to the magnetic field, stationary supercurrent is derived by the vector potential in order to establish the Meissner effect. Assuming $e^* = 2e$ (double electronic charge) $= 3.2 \times 10^{-19} \text{C}$, $m^* = 2m$ (double electron mass) $= 1.8 \times 10^{-30} \text{kg}$, and $n_s = 5 \times 10^{27} \text{m}^{-3}$, λ_L can be estimated to be about 53 nm ($\lambda_L \sim 50 \text{nm}$ in Al and $\sim 200 \text{nm}$ in Nb). The superconducting current that flows to the λ_L depth area from the surface excludes the external magnetic field so that the Meissner effect is observed in the superconductor which is thicker than λ_L .

1.1.3.3 Ginzburg-Landau Theory

There is no concept of the coherence length ξ in the London equation. Ginzburg and Landau (1950) [23] proposed the phenomenological theory of the superconductor by using the order parameter $\psi = |\psi_0| \exp(i\theta)$. According to the *Ginzburg-Landau (GL) theory*, when ψ is small, the Helmholtz free energy per unit volume of the superconductor is expanded as a Taylor series of $|\psi|^2$. Thus we have

$$F_s = F_n + \alpha |\psi|^2 + (\beta/2) |\psi|^4 + \dots, \quad (1.26)$$

where F_s and F_n are the Helmholtz free energies for the superconducting state and the normal conducting state, respectively, and α and β are the expansion coefficients. Assuming $\alpha(T) = \alpha_0(T - T_c)$, we have the next relation as shown in Figure 1.11,

$$\begin{aligned} \alpha(T) &> 0, \beta > 0 \quad (T > T_c) \\ \alpha(T) &< 0, \beta > 0 \quad (T < T_c). \end{aligned} \quad (1.27)$$

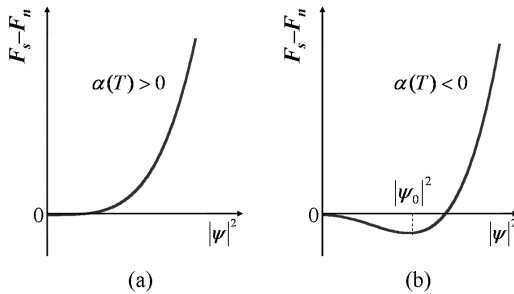


Figure 1.11 Ginzburg-Landau free energy functions $F_s - F_n$ for (a) $T > T_c$ ($\alpha > 0$) and (b) $T < T_c$ ($\alpha < 0$). F_s and F_n are the Helmholtz free energies for the superconducting state and the normal conducting state.

That is, in $T < T_c$, $|\psi| \neq 0$ exists, and

$$|\psi| = |\psi_0| = (\alpha/\beta)^{1/2} = (\alpha_0/\beta)^{1/2} (T_c - T). \quad (1.28)$$

This means the superconducting state is stable at the temperature of T_c or less. Moreover, the relation of $|\psi(r)|^2 = n_s(r)$, which is the density of the superconducting electron, is obtained.

The free energy in the magnetic field is given by the next equation:

$$F_s = F_n + \alpha|\psi|^2 + (\beta/2)|\psi|^4 + (1/2m^*)(-i\hbar\nabla + e^*\mathbf{A})\psi|^2 + (1/2\mu_0)\mathbf{B}^2. \quad (1.29)$$

Taking the variation derivation of the free energy with respect to ψ and $\mathbf{A}$, we obtain the following expressions

$$\alpha\psi + \beta|\psi|^2\psi + (1/2m^*)(-i\hbar\nabla + e^*\mathbf{A})^2\psi = 0, \quad (1.30)$$

$$\mathbf{J}_s = (e^*\hbar/2m^*i)(\psi^*\nabla\psi - \psi\nabla\psi^*) - (e^{*2}/m^*)|\psi|^2\mathbf{A}. \quad (1.31)$$

Because Equation 1.31 with $\nabla\psi = 0$ and $\nabla\psi^* = 0$ corresponds to Equation 1.25, the GL theory contains the result of the London theory. In the one-dimensional system, assuming that ψ is small and $\mathbf{A} = 0$, we get

$$(\hbar^2/2m^*)(\partial^2\psi/\partial x^2) = \alpha\psi. \quad (1.32)$$

ψ in this equation is

$$\psi = |\psi_0|\exp(-x/\xi), \quad (1.33)$$

where ξ is the *GL coherence length*, which is given by

$$\xi(T) = (\hbar^2/2m^*\alpha(T))^{1/2}. \quad (1.34)$$

The GL coherence length is the recovery length to the spatial change in the order parameter. In contrast, the coherence length ξ_0 , the Pippard or BCS coherence length, obtained from the indeterminacy principle described in Section 1.1.2.4 is the characteristic length that shows the extension of the Cooper pair.

1.1.3.4 Type I and Type II Superconductors

In the framework of the GL theory, two degrees of freedom of the phase and the amplitude are included in the order parameter. The characteristic lengths that show spatial correlations of the phase and the amplitude are the *GL penetration depth* $\lambda(T)$ and the GL coherence length $\xi(T)$. These lengths are temperature dependent quantities and vary as $(1 - T/T_c)^{-1/2}$ with temperature. The ratio $\kappa = \lambda(T)/\xi(T)$ is called the *GL parameter* and is an important factor in which the magnetic characteristics of a superconductor are decided. Let us consider the influence of the value of κ on the superconducting state.

Assume the case where H is vertically applied to the superconductor as shown in Figure 1.12. When the external magnetic field H_e invades the superconductor locally, the superconductivity is lost in the ξ radius area and the magnetic field energy is decreased in the λ radius area where the magnetization is zero; therefore, the free energy of $G_{core} = (1/2)\mu_0 H_e^2 \pi \xi^2$ per unit length is increased whereas

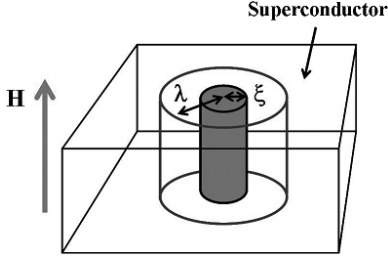


Figure 1.12 Virtually invaded external magnetic field H in the superconductor. The order parameter is lost locally in the ξ radius area and the condensation energy increases there, whereas the magnetic field penetrates in the λ radius area and the magnetic energy is decreased.

$G_{mag} = (1/2)\mu_0 H_c^2 \pi \lambda^2$ per unit length is decreased. We can then get the following total free energy:

$$G = G_{core} + G_{mag} = (1/2)\mu_0 H_c^2 \pi \xi^2 - (1/2)\mu_0 H_c^2 \pi \lambda^2. \quad (1.35)$$

From Equation 1.35, it can be said that destruction of part of the superconducting area is favored when $G < 0$, but the magnetic field is excluded when $G > 0$. Defining the *lower critical field*, $H_{c1} = (\xi/\lambda)H_c$ by assuming $G = 0$ with $H_c = H_{c1}$, we are likely to have $G < 0$ with $H > H_{c1}$ at $\kappa > 1$. According to the more accurate consideration on the basis of the GL theory, the boundary between $G < 0$ and $G > 0$ is given by $\kappa = 1/\sqrt{2}$, and $H_{c1} = (H_c/\sqrt{2}\kappa)\ln \kappa$ is derived. Thus, we can obtain the following criteria:

- a) $\kappa < 1/\sqrt{2}$ $H < H_c$ Meissner state
 $H > H_c$ Normal conducting state
- b) $\kappa > 1/\sqrt{2}$ $H < H_{c1}$ Meissner state
 $H > H_{c1}$ Magnetic field invades partially.

A superconductor in condition (a) is called a *type I superconductor*, and one in condition (b) is a *type II superconductor*. Figure 1.13 shows the magnetic phase diagrams of type I and type II superconductors. The superconductors treated in this book are mostly of type II.

1.1.3.5 Mixed State

Various vortices exist in the natural world. The tornados in Florida in the United States and the Naruto whirlpool in the Naruto strait in Japan are the examples, and are shown in Figure 1.14. When the magnetic field is applied to a type II superconductor, many vortices are formed in the superconductor. This phenomenon is explained as follows.

In a type II superconductor, the magnetic field invades in the form of many vortices where $H > H_{c1}$, and this is called the *mixed state*. The detailed cross-sectional structure of the vortex is shown in Figure 1.15. Since $\lambda > \xi$ in a type II

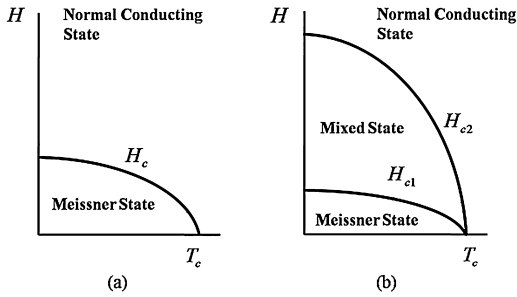


Figure 1.13 Simplified magnetic phase diagrams for (a) a type I superconductor and (b) a type II superconductor. The Meissner state, the mixed state, and the normal conducting state are separated by the H_c , H_{c1} and H_{c2} lines.



(a)



(b)

Figure 1.14 Vortices in the natural world: (a) a tornado in the United States and (b) the Naruto whirlpool in the Naruto strait in Japan.

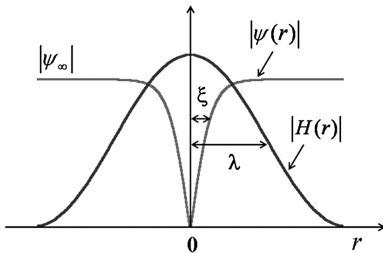


Figure 1.15 Schematic diagram of the vortex structure in a type II superconductor. The vortex has a normal conducting core with radius ξ and is surrounded by a magnetic field with a radius of λ . The confined magnetic flux is quantized, and its value is $\Phi_0 = 2.07 \times 10^{-15} \text{ Wb}$.

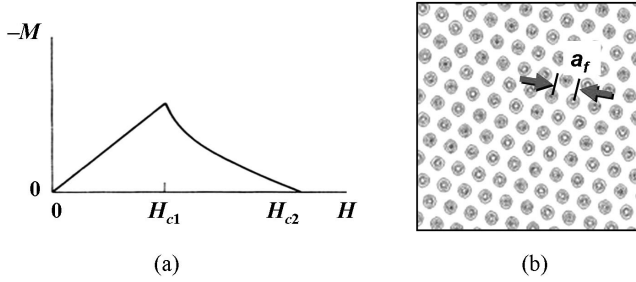


Figure 1.16 (a) Magnetic field dependence of magnetization in a type II superconductor and (b) the typical triangular lattice of vortices in a pure superconductor.

superconductor, the individual vortex line has the normal conducting core with radius ξ and is surrounded by a magnetic field with radius λ . This structure is also called the *flux line*. The shielding current with zero resistance flows in the area λ of the vortex and the magnetic flux is confined within this area. The confined magnetic flux is quantized and is called as the *fluxon*, its value being $\Phi_0 = 2.07 \times 10^{-15} \text{ Wb}$. The shielding current is the macroscopic wave function ψ , and Bohr's quantization condition is fulfilled when the shielding current makes a circuit around the vortex. This is the *quantization of the magnetic flux*. Note that this definition of the term flux line applies to the conventional type II superconductors. However, in the extreme type II superconductors such as high- T_c cuprate, the definition of flux lines becomes difficult as λ becomes larger and larger compared to ξ , so that the concept of vortex line becomes important.

The Meissner state of $M = -H$ is observed in the $M-H$ curve where $0 < H < H_{c1}$, as shown in Figure 1.16a. In the mixed state where $H > H_{c1}$, the superconductivity is maintained up to $H = H_{c2}$ where all the superconductor area is filled with the vortices. H_{c2} is called the *upper critical field*. The values of $\mu_0 H_{c2}$ ($= B_{c2}$) of metallic superconductors are ca. 10–30 T, and those of high-temperature superconductors exceed 100 T. The reason why most practical superconductors are type II is that $\mu_0 H_{c2}$ values of these superconductors are very large. The upper critical field is expressed by

$$\mu_0 H_{c2} = B_{c2} = \Phi_0 / 2\pi\xi^2. \quad (1.36)$$

The vortices form triangular lattices in a pure superconductor with no pinning centers, as shown in Figure 1.16b. The triangular lattice is called the *Abrikosov lattice*, *vortex lattice*, or *flux line lattice* [24]. The lattice interval a_f of the triangular vortex lattice is given by

$$a_f = (2\Phi_0 / \sqrt{3}B)^{1/2}. \quad (1.37)$$

What happens when current $\mathbf{J}$ is applied to the superconductor in the mixed state? At this time, the current exerts the *Lorentz force* of

$$\mathbf{f}_L = \mathbf{J} \times \mathbf{e}_z \Phi_0 \quad (1.38)$$

on the vortices. Here, $\mathbf{e}_z$ is the unit vector in the z direction. Moving the vortices at a speed of $\mathbf{v}_L$ by this force, the electric field

$$\mathbf{E} = \mathbf{B} \times \mathbf{v}_L \quad (1.39)$$

is generated. This motion of vortices is called the *vortex flow* or the *flux flow* [25]. $\mathbf{v}_L$ does not increase infinitely because of the frictional force due to the surrounding environment when the vortices move, and $\mathbf{f}_L$ balances with the viscous force $-\eta\mathbf{v}_L$, where η is the coefficient of viscosity. In the vortex flow state, energy dissipation is generated even while the superconductor is in the superconducting state, and this is a big problem from the viewpoint of practical application. Therefore, *vortex pinning* (or *flux pinning*), which is described in Section 1.3 below, becomes very important.

1.2

Superconducting Materials

The superconducting phenomenon is known to occur in about two thousands kinds of material, including elements, alloys, various metallic compounds, and organic materials. Superconductivity is thus a common phenomenon. The current state of our knowledge of typical superconducting materials is described below.

1.2.1

Superconducting Metals and Alloys

1.2.1.1 Elements

Following the discovery of the superconductivity of mercury (Hg) in 1911, it was confirmed that Pb and Sn can also become superconductors, and afterwards the superconducting elements were identified one by one. Figure 1.17 shows T_c values of the element superconductors in the periodic table [3, 6]. More than 30 elements become superconducting on cooling to an extremely low temperature. In addition, it was confirmed that over 20 other elements become superconducting at high pressure. About half of the elements in the periodic table are currently known to be potential superconductors, but the superconductivity of alkali metal such as Na, magnetic materials such as Co and Ni, and low resistivity materials such as Au, Cu, and Ag has not been confirmed yet.

The only practicable element superconductors are Nb and Pb, whose T_c values are higher than the temperature of liquid helium (4.2 K). The crystal structure of Nb is body-centered cubic (*bcc*) and its T_c is 9.25 K. Nb is a type II superconductor and its $\mu_0 H_{c2}$ is about 0.3 T. $\mu_0 H_{c2}$ is related to resistivity ρ , and we obtain [26]

$$\mu_0 H_{c2} = B_{c2} = 3.1 \times 10^3 \mu_0 \rho \gamma T_c, \quad (1.40)$$

where γ is an electronic specific heat coefficient. A small amount of oxygen or nitrogen as an impurity in Nb increases $\mu_0 H_{c2}$ because ρ increases. T_c similarly changes because of impurities. The introduction of oxygen or nitrogen atoms into

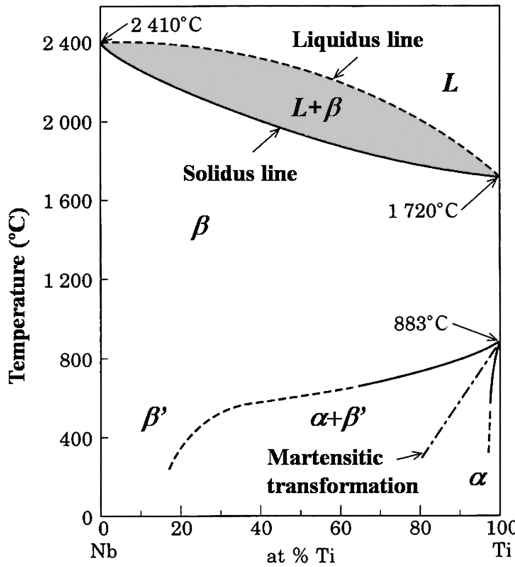


Figure 1.18 Equilibrium phase diagram of Nb–Ti superconducting alloy, which is widely used for applications involving a magnet.

$$T_c = 1.13\theta_D \exp(-1/N(E_F)V), \quad (1.41)$$

where θ_D is the Debye temperature, $N(E_F)$ is the density state of the electron on the Fermi surface, and V is an interaction between electrons. Because $N(E_F)V$ and γ of the β -phase have maximum values in the vicinity of 40 at %Ti and θ_D comes close to the minimum at the same time, the maximum value of T_c is obtained near here. In contrast, since $\mu_0 H_{c2}$ relates to T_c , γ , and ρ as already described, it reaches a maximum in the vicinity of 50 at %Ti. The changes in T_c and $\mu_0 H_{c2}$ as a function of Ti concentration are shown in Figure 1.19 [27]. Although the Nb–Zr alloy was developed earlier than the Nb–Ti alloy it is not used now since its $\mu_0 H_{c2}$ value is inferior to that of Nb–Ti and there are processing difficulties.

1.2.2

Superconducting Compounds

1.2.2.1 A15 Type Compound

The A15 type compound superconductors are important materials for practical use [15]. They include Nb₃Ge, which has the highest T_c in the A15 series, Nb₃Sn, which is widely used, and Nb₃Al, the most recently developed A15 compound.

The A15 type compounds crystallize in the cubic system, as shown in Figure 1.20, and the crystal structure which is described by chemical formulae of A₃B like Nb₃Sn consists of the arrays of two kinds of atoms A and B. The basic superconducting properties of various A15 type superconductors are shown in Table 1.1

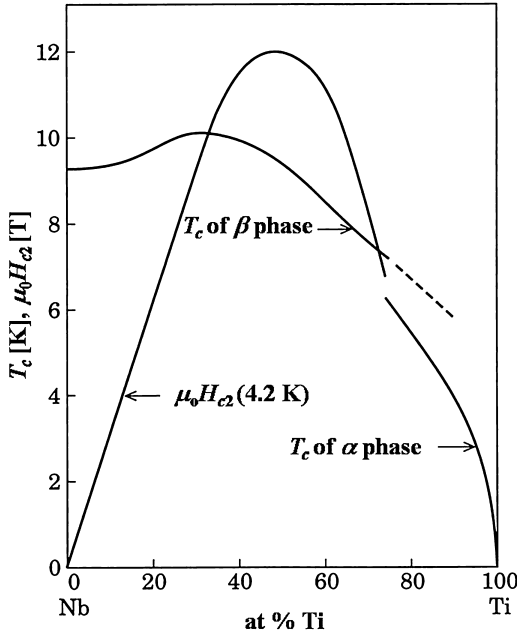


Figure 1.19 Changes in T_c and $\mu_0 H_{c2}$ as a function of Ti concentration in Nb–Ti alloy. The optimized Ti concentration is about 47 wt% Ti.

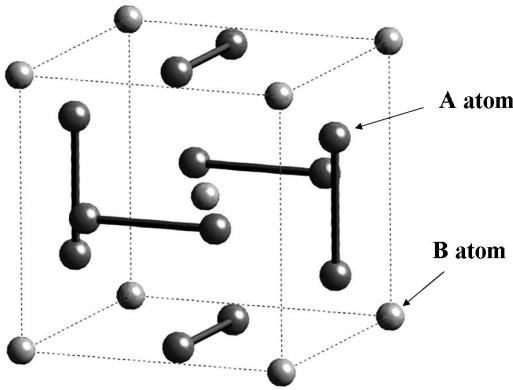


Figure 1.20 The crystal structure of A15 type superconductors with AB_3 intermetallic compounds. A atoms mutually adjoining form a pseudo conducting pathway like a chain.

[28]. T_c and $\mu_0 H_{c2}$ of the A15 materials are higher than those of Nb alloys. Unlike the alloy system, this material exhibits the highest T_c when the atomic ratio of A to B is stoichiometric. The B atoms form a *bcc* structure and the A atoms are mutually orthogonal on the orthogonalization side of the *bcc* lattice-like chain. The nearest neighbor of each A atom is the adjacent A atom on the chain. In the A15

Table 1.1 Lattice parameters, T_c , and $\mu_0 H_{c2}$ of typical A15 superconductors.

Compound	Lattice parameter	T_c (K)	$\mu_0 H_{c2}$ (T)
V ₃ Ga	0.4817	16.5	34.9
V ₃ Si	0.4722	17.1	34.0
V ₃ Ge	0.4769	6.0	—
Nb ₃ Al	0.5187	19.1	32.4
Nb ₃ Ga	0.5165	20.7	34.1
Nb ₃ Si	0.5091	18.2	15.3
Nb ₃ Ge	0.5133	23.2	37.1
Nb ₃ Sn	0.5290	18.0	29

type crystal, the A atoms mutually adjoined form a pseudo conducting pathway which is a strong metallic bond only in one direction. The continuity of the A–A atomic chain contributes to the superior superconducting properties of the A15 materials.

However, the A15 type compound is not necessarily in the stoichiometric ratio of 3:1. For instance, at low processing temperatures the compositions of Nb₃Al and Nb₃Ga tend to be richer in Nb than the formula indicates, though they have 3:1 compositions at a high processing temperature. Nb₃Ge does not have a 3:1 composition at either high or low processing temperatures. In addition, the A15 crystal structure does not exist in the Nb₃Si compound under conditions of normal temperature and pressure, and this can therefore only be formed using high-pressure synthesis or by thin-film deposition from the vapor phase.

The T_c values of fifty or more A15 type superconductors have been confirmed so far. The necessary conditions for higher T_c values are a stoichiometric composition and a highly regular crystal lattice. The T_c increases the more closely these ideal requirements are approached. A good quality crystal can be obtained comparatively easily in the case of Nb₃Sn, V₃Si, and V₃Ga whose stoichiometric compositions are an equilibrium state, so that the application of these compounds to the manufacture of superconducting wires is already advanced. However, in the case of Nb₃Al, Nb₃Ge, and Nb₃Si, whose compositions in the equilibrium state are shifted greatly from the stoichiometric composition, the crystal of high- T_c is not obtained unless it is fabricated in a nonequilibrium condition, so that producing the superconducting wires is problematical. Moreover, the irregularity of atomic order also has a big influence on T_c . The substitution of A atoms with B atoms causes a scission of conducting pathway because A atoms form pseudo conducting chains. Therefore, T_c is not improved by merely achieving an exact 3:1 composition of the A15 phase.

1.2.2.2 Nitride and Chevrel Compound

NbN, whose T_c exceeds 17 K, is a superconductor with the NaCl crystal structure (Figure 1.21) [29]. TaN, NbC, MoC, and other similar compounds also have T_c

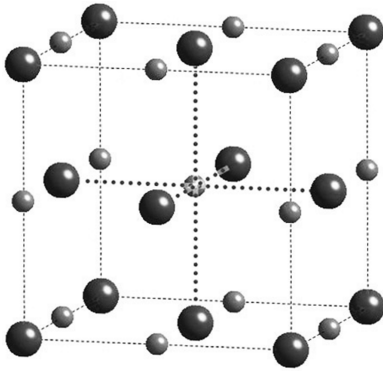


Figure 1.21 The B1 class of AB superconductors have the metallic atom A and the nonmetallic atom B arranged in an NaCl crystal structure.

values exceeding 10 K. NbN is of particular interest from the point of view of its practical use because of its high T_c . The $N(E_F)$ value of this material is not very high, and the strong electron-phonon interaction is thought to be the reason for its high T_c . Usually, NbN is fabricated by the vapor deposition method, and the microcrystalline films exhibit a $\mu_0 H_{c2}$ value of 44 T, though the value for the bulk material is only 8 T.

The Chevrel compound is represented by chemical formulae of $M_x\text{Mo}_6\text{S}_8$, in which M can be Pb, Sn, Cu, a rare-earth metal, or some other metals [30]. The $\mu_0 H_{c2}$ value of a Chevrel compound exceeds 60 T, although its T_c is lower than that of an A15 type compound. Mo_6S_8 forms one cluster, and eight clusters unite loosely via a Pb atom. The distance between the Mo atoms inside the cluster (0.26–0.28 nm) is shorter than the distance between Mo atoms outside the cluster (0.387 nm). Therefore, the conduction electrons are localized within the cluster and have a peculiar electronic structure. The mean free path of the electron of PbMo_6S_8 compound is a lattice constant level and becomes approximately 1/7 compared with that of Nb_3Sn , resulting in the large resistivity, so that the $\mu_0 H_{c2}$ value is thought to be large according to Equation 1.40. It is thought that the electronic coupling between clusters is weaker than that within a cluster; therefore, PbMo_6S_8 can be considered to be a pseudo zero dimensional material.

1.2.2.3 MgB_2

The highest T_c of the metallic superconductors represented by the A15 type was not improved for a long time. This situation was changed greatly by the discovery of the MgB_2 superconductor in 2001 [12]. T_c of this material is 39 K, and up to now this is the highest value found for a metallic superconductor. What causes this high T_c ? T_c is determined by three parameters, namely θ_D , $N(E_F)$, and V , according to the BCS theory as given by Equation 1.41. In the initial investigation of the isotope effect, a T_c change of 1 K was observed by the substitution of boron ^{10}B

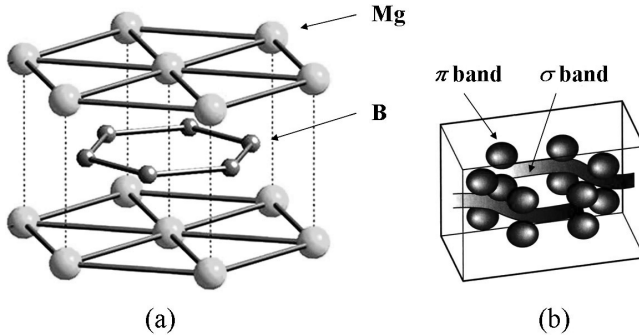


Figure 1.22 (a) Crystal structure of MgB₂, showing the triangular lattice of Mg atoms and the honeycomb structure of B atoms. (b) π band and σ band in MgB₂.

atoms by ¹¹B atoms in MgB₂, and the existence of a strong electron-phonon interaction with B atom was confirmed. Because the $N(E_F)$ in MgB₂ is not especially large (like Nb₃Sn), it is thought that large V causes high T_c .

MgB₂ has the *hcp*-like structure, as shown in Figure 1.22. The honeycomb structure formed with the B atoms is sandwiched by the triangular lattice formed by the Mg atoms, and these are stacked in the direction of the *c*-axis of MgB₂. Mg, which is bivalent, ionizes and supplies one electron per B atom. The honeycomb structure in MgB₂ formed with B atoms resembles that of benzene, the main difference being that the honeycomb lattice with B atoms forms a two-dimensional network and the electrons can move around in the network. The π band in MgB₂ contributes to conduction in the B layer and also contributes to conduction in the *c*-axis direction by uniting the upper and the lower B layers through inert Mg ions. On the other hand, the movement of the electrons in the σ band is restricted in the B layer, and the electrons contribute only to conduction in this layer. Two bands in different dimensions exist in MgB₂.

It is thought that MgB₂ is a multi-gap superconductor with two superconducting energy gaps and that this is because the electron-phonon coupling constants for the σ band and the π band are different [31]. The research into the fabrication of wires and thin films of MgB₂ is advancing. The resistivity of thin films of MgB₂ is so high that $\mu_0 H_{c2}$ increases up to 51 T [32], and this tendency is similar in the case of thin films of NbN.

1.2.3

Organic Superconductors

An organic superconductor consisting of the organic compound TMTSF was first made in 1980 [33], and after this the (BEDT-TTF)_{2X} superconductor, with a T_c of >10 K, was synthesized. The structures of these molecules are shown in Figure 1.23. TMTSF works as a donor which supplies the electrons, and TMTSF

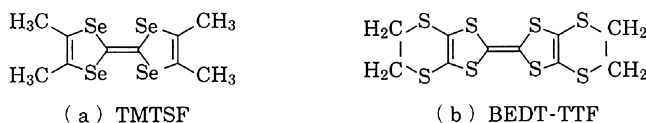


Figure 1.23 Structures of typical molecules that form organic superconductors. (a) TMTSF and (b) BEDT-TTF.

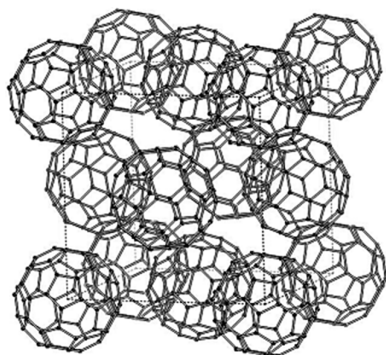


Figure 1.24 The fcc structure consisting of C_{60} molecules. Although C_{60} is not itself a superconductor, it becomes a superconductor when alkali metals are added.

molecules are piled up in a pillar shape when combining with the ClO_4 acceptors that receive electrons. Thus, one-dimensional conduction occurs because the π electrons overlap in this direction. BEDT-TTF also acts as a donor. For instance, the π electrons exist on the network crystal face that consists of sulfur (S) when it combines with iodine (I) acceptors, and two-dimensional conduction appears. It is known that these materials show BCS-like behavior, and a T_c of >10 K has been confirmed in the β (BEDT-TTF)- $2ICl_2$ superconductor under high pressure.

The C_{60} molecule, which is called a fullerene and is shaped like a soccer ball, was discovered in 1985 [34], and the solid composed of these molecules has been found to show superconductivity by carrier doping. The σ electron strongly takes part in uniting the C_{60} molecule, whereas the π electron takes part in intramolecular interactions comparatively freely. Although C_{60} molecules form an fcc structure, as shown in Figure 1.24, there is a large amount of space between them by piling up the huge C_{60} molecules. The metallic atoms which supply the carriers are accommodated in this space. The carriers flow through the C_{60} molecules in contact with each other and bring about superconductivity. The first C_{60} superconductor discovered was K_3C_{60} with a T_c of 18 K [35], and the T_c of Cs_3C_{60} was then found to be as high as 38 K [36]. T_c tends to rise as the lattice constant increases since the π orbital overlap of C_{60} is reduced as the lattice spacing extends and the bandwidth becomes narrow, resulting in the increase of $N(E_F)$.

The $\mu_0 H_{c2}$ of these materials is also very high, reaching 54 T in K_3C_{60} and 78 T in Rb_3C_{60} . It is found from observation of the isotope effect that these materials are typical BCS superconductors with a strong electron-phonon interaction.

1.3

High- T_c Oxide Superconductors

There is an enormous variety of oxide materials in existence, and the superconductor with the highest T_c is now an oxide. Hence, oxide superconductors, including the highest- T_c superconductor, form the main theme of this book and these are briefly described here.

1.3.1

Early Oxide Superconductors

Many oxide superconductors were investigated before the discovery of the high- T_c cuprate superconductors. $LiTi_2O_4$ with a T_c of ~ 14 K [37], $SrTiO_{3-x}$ (~ 0.5 K) [38], and $BaPb_{1-x}Bi_xO_3$ (~ 13 K) [39] have created acute interest from the viewpoint of the peculiar electron-phonon interaction.

$BaPb_{1-x}Bi_xO_3$ and $Ba_{1-x}K_xBiO_3$, which was discovered later, have the $BaBiO_3$ structure as the host crystal. This is called the *perovskite structure* and is represented by the general chemical formula ABO_3 , where A and B are metal atoms. In the perovskite structure, as shown in Figure 1.25, atom A is at the origin and atom B is at the body-centered position, and the oxygen atoms surrounding the B atom form an octahedral structure, and in this way the three-dimensional network of BO_6 octahedra is formed. The formal electric charge of the Bi atom (B site in the ABO_3 structure) is Bi^{4+} ($=6s^1$) for $BaBiO_3$. A Bi atom in isolation is a metal because

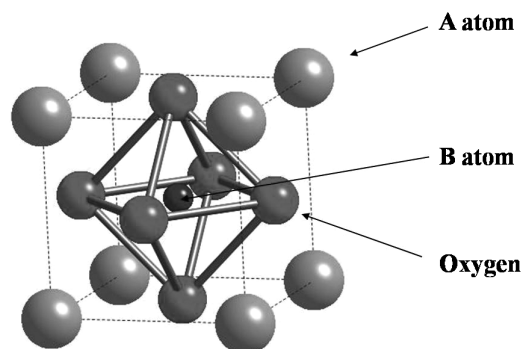


Figure 1.25 The perovskite structure of ABO_3 compounds (e.g., $BaBiO_3$, $SrTiO_3$, etc.). The superconductivity appears in the case of $BaBiO_3$ on substituting Bi sites with Pb ion.

half the 6s band is filled with an electron. However, because of the strong electron-phonon interaction, the electric charge of the Bi atom actually couples strongly with a ‘brezing’ mode, which is the expansion and contraction of the BiO_6 octahedron. Therefore, the electric charge changes from Bi^{3+} to Bi^{5+} at intervals of one site, and the charge-density wave state which is the concentration of a distortion and an electronic density of a periodic lattice is formed, resulting in an insulator.

This strong electron-phonon interaction is weakened by substituting the Bi site with a Pb ion and the metallic state appears in the case of $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$. That is, Bi^{4+} ($=6s^1$) which is the average formal valence is diluted with Pb^{4+} ($=6s^0$), and the filling of the 6s electronic band is thought to be decreased. Superconductivity of $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ appears in the neighborhood of the *metal-insulator transition* boundary. The generation of metals or superconductors by changing the filling factor of the band from the insulating materials caused by a *strong electron correlation* is analogous to the case of the high- T_c cuprate superconductors. However, substituting the Bi site of $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ with Pb will give disorder to the network of conduction. Therefore, the $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ system, in which the Ba^{2+} site that does not take part directly in the conduction is substituted by K^+ ion, was investigated, whereupon it was found that $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ metalizes when $x \approx 0.4$ and simultaneously becomes the superconductor with $T_c \approx 30 \text{ K}$ [40]. This was the oxide with the highest T_c (with the exception of the cuprate superconductors) until 2008.

1.3.2

Cuprate Superconductors

1.3.2.1 Crystal Structure

$\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ superconductor, discovered in 1986, is a copper oxide superconductor [8, 9]. This material became the forerunner of the series of high- T_c superconductor discoveries which followed. The basis of high- T_c superconductors is the CuO_2 layer. This layer becomes the platform for the superconductivity occurrence. The high- T_c superconductors are also called the *cuprate superconductors*, and their basic properties are summarized in Table 1.2 [3, 6].

Table 1.2 Crystal system and lattice parameters of typical high- T_c cuprate superconductors.

Superconductor	Crystal System	a (nm)	b (nm)	c (nm)
$\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$	Tetragonal	0.3790	–	1.323
$\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$	Tetragonal	0.3945	–	1.217
$\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$	Orthorhombic	0.3823	0.3887	1.168
$\text{Bi}_{2.2}\text{Sr}_2\text{Ca}_{0.8}\text{Cu}_2\text{O}_8$	Orthorhombic	0.5414	0.5418	3.089
$(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$	Orthorhombic	0.5404	0.5415	3.708
$\text{HgBa}_2\text{CaCu}_2\text{O}_{6+x}$	Tetragonal	0.3858	–	1.266

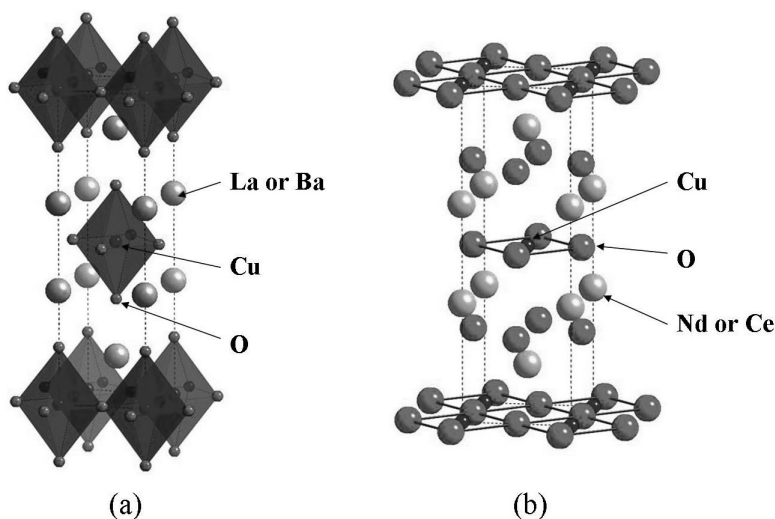


Figure 1.26 Crystal structures of (a) $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ and (b) $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ superconductors.

The crystal structures of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ and $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ [41] superconductors are shown in Figure 1.26. $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$, in which some of the La^{3+} ions are substituted by Ba^{2+} ions, has a structure referred to as the K_2NiF_4 structure. This material has a layer structure in which the (La, Ba) layers and the CuO_6 octahedrons are stacked alternately, and the CuO_2 layers are formed parallel to the bottom face. Although LaCuO_4 itself is in the antiferromagnetic state, as the concentration x of Ba^{2+} ions increases, the holes that become carriers are implanted into the CuO_2 layers, and concurrently T_c starts to increase, achieving a maximum value of 38 K. However, if substitution continues, the carriers start to overdope and T_c decreases. If Sr^{2+} ions are used instead of Ba^{2+} ions to replace the La^{3+} ions, a high- T_c superconductor is also produced. As for $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ in which Nd^{3+} ions are substituted by Ce^{4+} ions, the carriers of this material are electrons instead of holes. Although $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ has a structure similar to that of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$, this structure consists of the planar CuO_2 layers in which the apical oxygen atoms above and below the Cu atoms are eliminated. Superconductivity with $T_c = 25$ K is achieved when the concentration of Ce^{4+} ions is $x = 0.14$, and T_c disappears with additional Ce^{4+} ions. In both $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ and $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$, the superconductivity appears side by side with antiferromagnetism.

Figure 1.27 shows the crystal structure of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ cuprate superconductors. $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO or Y123) is the superconductor whose T_c was above the temperature of liquid nitrogen (77 K) for the first time and reached 93 K [10]. In this material, layers of Y atoms are sandwiched between the two adjoining pyramid-type CuO_2 layers. Moreover, there is a triple periodic structure in which Y and Ba atoms are in line as Ba–Y–Ba, and there are also one-dimensional chains of Cu–O–Cu in the direction of the b -axis of the crystal.

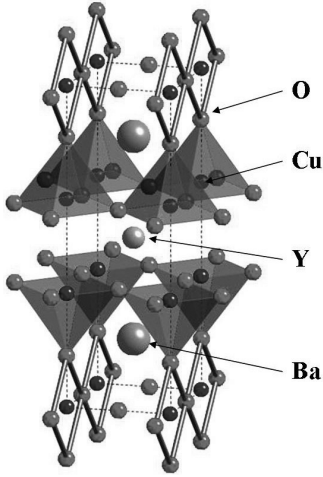


Figure 1.27 Crystal structure of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ superconductor showing two adjoining pyramid-type CuO_2 planes and CuO chains in the unit cell.

The oxygen deficiency, expressed by x in the chemical formulae of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, plays an important role in the hole implantation into CuO_2 layers. The amount of the oxygen deficiency is controlled by incomings and outgoings of the oxygen on the CuO chains. T_c reaches a maximum of 93 K at $x \approx 0$ (orthorhombic system, Ortho I) and becomes 60 K at $x \approx 0.5$ (orthorhombic system, Ortho II), then superconductivity disappears at $x \approx 0.7$ (tetragonal system, Tetra). The lattice constants of Ortho I are $a = 0.382$ nm, $b = 0.388$ nm, and $c = 1.168$ nm, and since a local distortion is caused by the difference between the lattice constants a and b , the twin is introduced to ease this distortion.

On the other hand, there are $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ (2201 phase), $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ (2212 phase), and $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ (2223 phase) in the Bi-based cuprate superconductors, which are used widely for wire applications, and these show $T_c = 30$ K, 95 K and 110 K, respectively. 2212 and 2223 are the materials where Sr and Ca, the alkaline earth metals with bivalent ions, are added to 2201 at the same time, and the latter showed a T_c of over 100 K for the first time [42]. In the phases of the Bi-based superconductors, the perovskite layers are sandwiched between the Bi_2O_2 layers, as shown in Figure 1.28, and the number of CuO_2 layers increases in this order. Tl-based and Hg-based superconductors have similar crystal structures [11, 43].

1.3.2.2 Electronic Structure

To understand the basic electronic structure of the high- T_c cuprate superconductor, it is necessary to think about La_2CuO_4 , which is the host crystal of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ discovered first. Considering the ions La^{3+} and O^{2-} , two electrons move from the layer of La_2O_2 to CuO_2 for electric charge neutralization in this material, and the

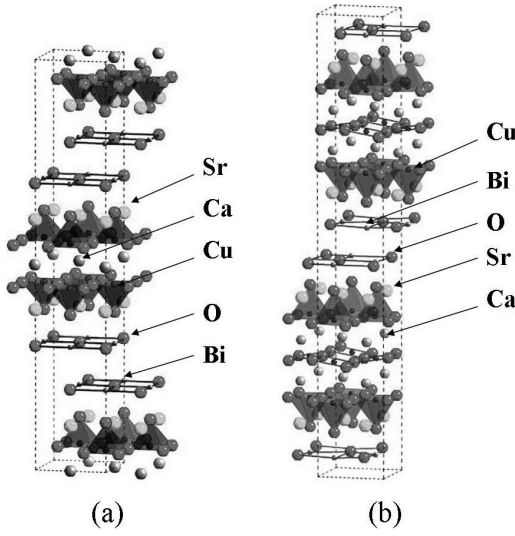


Figure 1.28 Crystal structures of (a) $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ (2212 phase) and (b) $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ (2223 phase) superconductors.

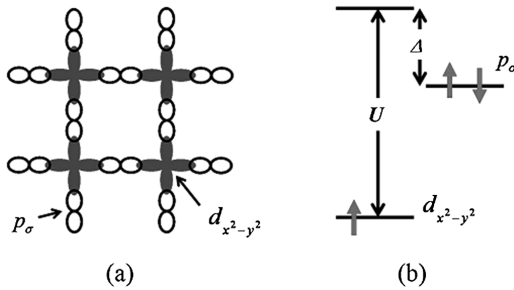


Figure 1.29 (a) A CuO_2 plane viewed from above, showing that each copper contributes a $d_{x^2-y^2}$ orbital and each oxygen either a p_x or a p_y orbital. (b) Simplified corresponding energy levels showing the energies of $d_{x^2-y^2}$ and p_{σ} orbitals.

charge distribution of $(\text{La}_2\text{O}_2)^{2+} (\text{CuO}_2)^{2-}$ is obtained as the average. Here, let us consider the electronic structure of CuO_2 plane. The electronic configurations of $3d^9$ for Cu^{2+} and $2p^6$ for O^{2-} are placed in the CuO_2 layer. The Cu^{2+} ion in the CuO_2 layer has one hole within the orbital of $d_{x^2-y^2}$ that expands the bonds in the direction of four oxygen ions. On the other hand, all p_{σ} orbits of O^{2-} ions that surround the Cu^{2+} ion are occupied by the electrons. The $d_{x^2-y^2}$ orbital of the Cu^{2+} ion and the p_{σ} orbital which expands in the direction of the Cu^{2+} ion are shown in Figure 1.29. The energy of the $d_{x^2-y^2}$ orbital is lower than that of the p_{σ} orbital. However, if the electron is coercively packed into the $d_{x^2-y^2}$ orbital, the energy rises because

of the Coulomb repulsive force between electrons. This energy U is large (8eV). This effect is due to the electron correlation [44]. Therefore, though the energy of the $d_{x^2-y^2}$ orbital appears to be lower than that of the p_σ orbital, this orbital is not fully occupied with the electron, and thus the Cu^{2+} ion becomes a magnetic ion of spin $S = 1/2$.

For instance, let us substitute Ba^{2+} ions partially for La^{3+} ions. At this time, the electrons on the O^{2-} ions are removed, and the holes are injected into the CuO_2 layer. The electric conduction property appears because the injected holes can freely move round in the crystal. Moreover, the hole erases the spin of the Cu^{2+} ion site by the exchange interaction. The adjacent spins on the Cu^{2+} ions mutually cause the antiferromagnetic interaction J in the CuO_2 layer [45]. By injection of two holes into the CuO_2 layer, the four antiferromagnetic couplings surrounding a hole are broken by the disappearance of spin due to the exchange interaction, and as a result the increase in the total energy of $8J$ occurs. On the other hand, the increase in energy becomes $7J$, by the formation of adjacent two holes, as shown in Figure 1.30. Thus, the energy difference $J = 8J - 7J$ can be assumed to be the glue between the two holes. The hole pair is also assumed to be a Cooper pair though its mechanism is different from that of the BCS superconductors. The phase separation to the two areas of hole and spin, however, occurs when the kinetic energy of the hole is small [46]. It is thought that superconductivity appears when the attractive energy and the kinetic energy of the hole balance well and also the antiferromagnetism disappears by thermal fluctuation. This is a qualitative explanation of the appearance of superconductivity in the cuprate superconductors, suggesting that superconductivity occurs near the insulator.

1.3.2.3 Anisotropy and Vortex Lattice Melting

The CuO_2 layer structure is reflected in the cuprate superconductors, and two-dimensional characteristics appear to a remarkable extent in the various physical properties. The ratio of the out-of-plane resistivity ρ_c to the in-plane resistivity ρ_{ab} in the CuO_2 layer becomes $\rho_c/\rho_{ab} \gg 1$. This means that the carriers cannot move easily in the direction of the c -axis and that its effective mass m_c is relatively larger than the in-plane effective mass m_{ab} . Of course, the cuprate superconductors are

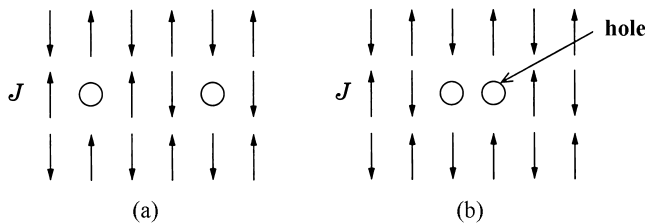


Figure 1.30 Schematic illustration showing a possible mechanism to generate hole pairs in a CuO_2 plane. (a) Increased energy is $8J$, and (b) increased energy is $7J$.

Table 1.3 Superconducting parameters of the cuprate superconductors.

Superconductor	T_c (K)	λ_{ab} (nm)	λ_c (nm)	ξ_{ab} (nm)	ξ_c (nm)	$\mu_0 H_{c2\perp}$ (T)	$\mu_0 H_{c2\parallel}$ (T)
$\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$	38	100	2–5	2–3	0.3	60	—
$\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$	93	150	0.8	1.6	0.3	110	240
$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$	94	200–300	15–150	2	0.1	>60	>250
$\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$	107	150	>1	2.9	0.1	40	>250
$\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$	125	200	>20	3	0.5	28	200
$\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$	135	130–200	0.7	1.5	0.19	108	—

type II superconductors. The effective mass ratio relates to the anisotropic parameter γ_a , the coherence length ξ , the upper critical field H_{c2} , and the penetration depth λ as shown by the following expressions

$$(m_c/m_{ab})^{1/2} = \gamma_a = \xi_{ab}/\xi_c = H_{c2\parallel}/H_{c2\perp} = \lambda_c/\lambda_{ab}, \quad (1.42)$$

where $\parallel$ denotes the case where magnetic field is applied parallel to the layer, and $\perp$ corresponds to the perpendicular case. Using the angle θ between the direction parallel to the CuO_2 layer and the direction of magnetic field, $H_{c2}(\theta)$ is given by

$$H_{c2}(\theta) = H_{c2\parallel} / (\cos^2 \theta + \gamma_a^2 \sin^2 \theta)^{1/2}. \quad (1.43)$$

This anisotropic model is called the *effective mass model* [47]. Superconducting parameters of the high- T_c cuprate superconductors are summarized in Table 1.3. As for $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$, $\gamma_a \approx 5$ and $\gamma_a \approx 24$ are reported, respectively. In $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, ξ_c is shorter than the c -axis lattice constant, but ξ_{ab} is longer than the a/b axes lattice constant. ξ_c is extremely short in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$, for example, so that the wave function of Cooper pairs is confined in the CuO_2 layer and two-dimensional properties become remarkable. In this case, the *Lawrence-Doniach model* [48] is used to explain the anisotropic properties.

By applying the magnetic field to the high- T_c cuprate superconductor, some peculiar features are observed. For instance, (i) because the coherence length is very short, the cores of the quantized vortices are small so that the pinning strength is weak; (ii) when the vortices vertically penetrate the CuO_2 layers, the vortices bend easily because the superconducting coupling between the CuO_2 layers is weak [49]; (iii) the Abrikosov lattice easily melts in the neighborhood of T_c by the effect of thermal energy [50]. As a result, the influence of the thermal fluctuation becomes remarkable in the cuprate superconductors, and the phase transition between the normal conducting state and the superconducting state becomes indistinct.

In the neighborhood of H_{c2} , though the amplitude of the superconducting order parameter is developing, the phase is changing with time, and a liquid state of the

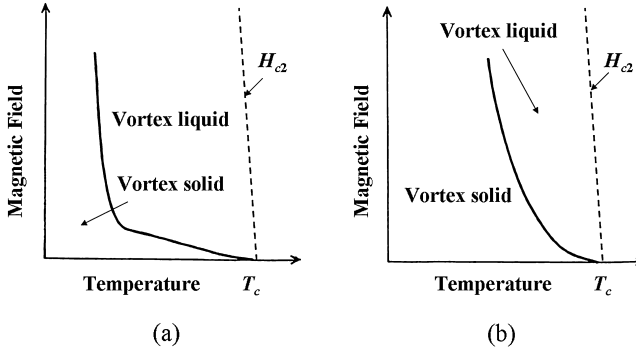


Figure 1.31 Comparison of the melting lines and H_{c2} lines for (a) $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ and (b) $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. The vortex liquid area of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ is wider than that of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$.

vortex lattice, which has no long-range order, is formed (*vortex liquid state*). However, a solid state of the vortex lattice in which the phase freezes exists (*vortex solid state*) in the magnetic field area considerably less than H_{c2} . Therefore, the melting transition of the vortex lattice from the vortex solid to the vortex liquid occurs in the intermediate area. This is a first-order transition. Schematic views of the *melting lines* of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ are shown in Figure 1.31. In the case of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$, the area of the vortex liquid state is very wide because of the strong two-dimensional features; in contrast, the area of the vortex liquid state is comparatively narrow in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$.

1.3.2.4 Vortex Glass and Bose Glass

If every quantized vortex is pinned by the crystalline defects which exist in the superconductors, the vortices will be stabilized to the vortex solid state. When the pinning centers are distributed at random, such as oxygen vacancies, the appearing vortex solid is called a *vortex glass phase* [51]. Though the vortex glass has no periodic long range order similar to the spin glass, the vortices are frozen in a certain kind of orderly state, which depends on the condition of the sample. Under such a condition, we get the resistivity

$$\rho = \lim_{J \rightarrow 0} (E/J) = 0, \quad (1.44)$$

where E is the electric field and J is the current density. Then, the true state of superconductivity with $\rho = 0$ is achieved when $J \rightarrow 0$. The vortex liquid – vortex glass transition is a second order transition. In addition, if the crystal defect has the c -axis correlation, such as columnar defects caused by heavy ion irradiation or twin boundaries, the vortices are pinned and stabilized by these defects when the magnetic field is applied parallel to the c -axis. This vortex solid phase in which the vortices are stabilized by the c -axis-correlated defects is called the *Bose glass phase* [52]. For the practical use of the high- T_c cuprate superconductors, the control of these defects becomes very important.

1.3.3

Other High- T_c Oxide Superconductors

Up to now, virtually the only high- T_c superconducting materials known are the cuprate superconductors described above. It has always been a big mystery why only the cuprate superconductors exhibit high- T_c . To break this situation, the oxide superconductors other than the cuprates have been searched aggressively. The studies on $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ and $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ were the first attempts at this; afterwards, the Sr_2RuO [53], $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ [54] and so on were studied as these were interesting superconducting oxides which do not include the CuO_2 layer. After the discovery of La–O–Fe–P superconductors [55], the ongoing search for new superconductors has yielded a family of $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$ oxypnictides composed of alternating $\text{LaO}_{1-x}\text{F}_x$ and FeAs layers with a T_c of 26 K in 2008 [13], and this T_c value can be raised to 56 K by replacing La with Sr and Sm [14].

The crystal structure of the typical iron-based superconductor $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$ (1111 phase) is shown in Figure 1.32. This compound has a layered structure which consists of FeAs, and electron doping from the LaO layer into the FeAs layer occurs. The ternary iron arsenide BaFe_2As_2 (122 phase) also shows superconductivity at 38 K by hole doping with partial substitution of potassium for barium [56]. These are analogous to the relationship between $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ and $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ superconductors. The crystal structure of BaFe_2As_2 is shown in Figure 1.32 also. There is a single layer of FeAs in the unit cell in the LnOFeAs (Ln: lanthanoid) system, while there are double layers of FeAs in BaFe_2As_2 . The similar structure iron-based superconductor of FeSe (11 phase) with a T_c of 14 K was discovered later [57]. The anisotropic superconducting character of these compounds makes them similar to the well-studied superconducting cuprate oxides. The discovery of further high- T_c materials is expected because there are many combinations of the carrier supply layer and the superconducting layer in

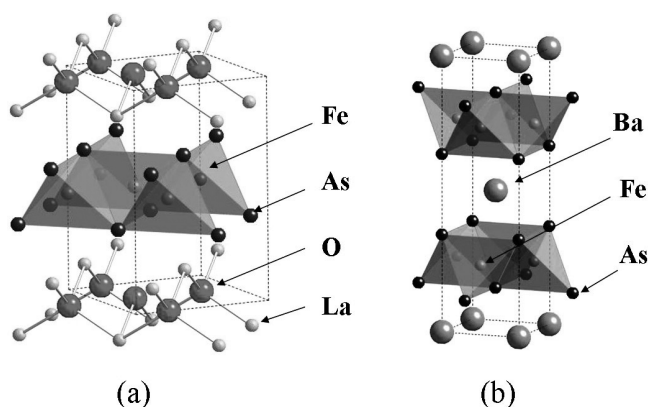


Figure 1.32 Crystal structures of iron-based high- T_c superconductors: (a) $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$ (1111 phase), and (b) BaFe_2As_2 (122 phase).

these materials. Though BaFe_2As_2 and FeSe are not oxides, it is thought that a similar mechanism for the generation of superconductivity exists in these iron-based materials.

Since the $\mu_0 H_{c2}$ of these materials is very high and the coherence length is relatively short, the superconducting current passing through the grain boundary could be small, as in the case of the cuprate superconductors. The knowledge obtained from the research into cuprate superconductors will be useful for the solution of the problem.

1.4

Critical Currents and Vortex Pinning

Because the electrical resistance is zero, superconducting wires can carry a very large current without energy loss. Here, the relationship between critical currents and vortex pinning (or flux pinning) is briefly explained.

1.4.1

Critical Currents and Current–Voltage Characteristics

1.4.1.1 Current–Voltage Characteristic

It is very important to be able to pass large currents without electrical resistance through superconductors for many applications. The maximum current obtainable is called the *critical current* I_c . Moreover, the critical current per unit cross-sectional area of superconductor is called the *critical current density* J_c . The typical change from the zero-resistance state to the finite resistance state by applying the current to the superconductors is shown in Figure 1.33. The current when the voltage is generated corresponds to I_c . The electrical resistivity standard such as

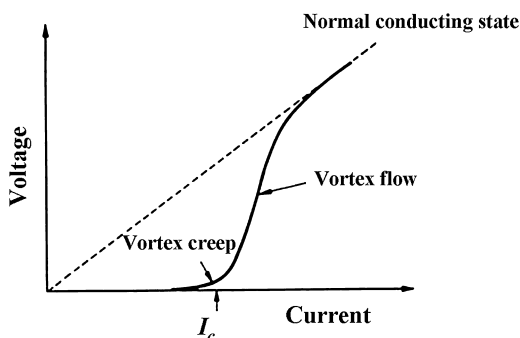


Figure 1.33 Current–voltage characteristics of superconductors. The critical current I_c is usually determined by the electrical resistivity standard such as $10^{-14} \Omega\text{m}$ or the electrical field standard such as $1 \mu\text{Vcm}^{-1}$.

$10^{-14} \Omega\text{m}$ and the electric field standard such as $1 \mu\text{Vcm}^{-1}$ are often used for the determination of I_c . The vicinity of I_c is an area where *vortex creep* (or the *flux creep*) described later becomes significant. The area of vortex flow (or flux flow) appears on the high current side; and the area where Ohm's law is obeyed appears by increasing the current. The low voltage area below the vortex flow region is represented by the power law as

$$E(I) \propto (I/I_c)^n, \quad (1.45)$$

where the power n is called the n value, which is the index that shows characteristics of superconducting material. It is thought that material with a large n value is homogeneous, and this is important for the applications.

1.4.1.2 Depairing Current Density

Next, the maximum critical current density in the superconductor is estimated. When the kinetic energy of Cooper pair becomes equal to energy gap 2Δ , the pair is destroyed and the maximum value is achieved. That is,

$$(1/2)m^*v_F^2 = 2\Delta, \quad (1.46)$$

where v_F is the Fermi velocity and $m^* = 2m$. A rough estimation is obtained by substituting v_F for $J = e^*n_s v_F$. More accurately by transforming Equation 1.31 derived by the GL theory, we obtain

$$J_d = \Phi_0 / (3\sqrt{3}\pi\mu_0\lambda^2\xi). \quad (1.47)$$

J_d is called the *depairing current density*. The result of calculating J_d of some superconducting materials is summarized in Table 1.4 [58]. Although the current density in a copper wire under conditions without a big energy loss is usually ca. $10^2 - 10^3 \text{ Acm}^{-2}$, superconductors can carry a maximum current density that is ca. $10^5 - 10^6$ times larger than that in copper without energy loss. However, the J_c of practical superconducting wires has not yet reached this theoretical limit. This is because the voltage generation in the current-voltage characteristic is decided by the strength of the vortex pinning.

Table 1.4 Depairing current density J_d and the observed J_c for typical superconductors.

Superconductor	T_c (K)	J_d (MA cm $^{-2}$)	J_c (MA cm $^{-2}$)	J_c/J_d
NbTi	9	36	~ 2 (4.2 K, 0 T)	6%
Nb $_3$ Sn	18	770	~ 2 (4.2 K, 0 T)	0.3%
MgB $_2$	39	77	~ 1 (4.2 K, 0 T)	1.3%
YBa $_2$ Cu $_3$ O $_{7-x}$	93	~ 300	~ 20 (4.2 K, 0 T)	7%
Bi $_2$ Sr $_2$ Ca $_2$ Cu $_3$ O $_{10}$	110	~ 300	~ 0.3 (4.2 K, 0 T)	0.1%

(MA cm $^{-2}$ = 10^6 A cm $^{-2}$).

1.4.2

Vortex Pinning**1.4.2.1 Elementary Pinning Force**

When a type II superconductor that does not contain crystal defects at all is in the mixed state and a current is applied to the superconductor, the vortex flow is induced by the Lorentz force. However, some crystal defects, which are actually contained in superconducting materials, exert pinning forces which stem the vortex flow against the Lorentz forces on the vortices. This is *vortex pinning* and these defects are called *pinning centers*. The pinning centers are classified as follows from their dimensions. That is,

- 1) point defect, oxygen vacancy, void, fine precipitate, etc.
- 2) dislocation, columnar defect, nanorod, etc.
- 3) grain boundary, planar precipitate, stacking fault, interface, etc.

The interaction between the defect and the vortex is generated through various mechanisms. For instance, suppose there is a small normal conductive precipitate and a single vortex that is apart from the precipitate in the superconductor, as shown in Figure 1.34. The superconductivity in the cylindrical normal core of the vortex is lost, and the order parameter ψ is zero at the core. Therefore, the total energy increases by the condensation energy of the core volume when the vortex stays in the superconducting region. But, if the vortex is located in the precipitate, the energy penalty which is proportional to the condensation energy of the intersection volume between the normal core and the precipitate is canceled. This energy difference gives the following pinning energy U_p

$$U_p = (1/2)\mu_0 H_c^2 \pi \xi^2 d, \quad (1.48)$$

where d is the length of the vortex that intersects with the precipitate. The *elementary pinning force* f_p exerted by the precipitate is given by the maximum value of the energy change by moving the vortex across the precipitate [4, 59, 60] and is approximated by

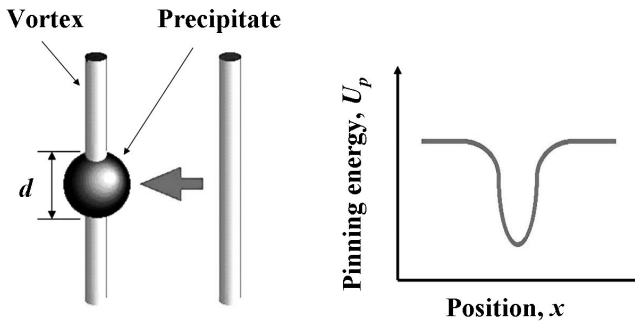


Figure 1.34 Flux pinning of vortex due to the normal conducting precipitate. The pinning energy U_p is estimated as $(1/2)\mu_0 H_c^2 \pi \xi^2 d$.

$$f_p \approx U_p / \xi = (1/2) \mu_0 H_c^2 \pi \xi d. \quad (1.49)$$

The grain boundary is the important pinning center other than the normal conducting precipitate. The electron is scattered in the vicinity of the grain boundary, and its mean free path l shortens. Because the coherence length ξ obeys the relationship $\xi \propto \sqrt{l}$, ξ becomes small as l decreases. This means that the size of the normal core is reduced and the area in which the superconductivity is lost becomes small, as the vortex approaches the grain boundary. When the vortex is located in the grain boundary, an energy gain is obtained, and this energy difference functions as the pinning energy [61, 62].

Though these are the core interactions that arise from the normal core of the vortex, there is also the magnetic interaction that stems from the change in the distribution of the superconducting current which flows in the circumference of the vortex. If there is a planar precipitate whose thickness is thinner than ξ in the superconductor, the distribution of the superconducting current that flows around the vortex changes as the vortex approaches the precipitate, and a *Josephson vortex* is formed. The core disappears in the Josephson vortex and only the shielding current flows, expanding along the planar precipitate to achieve the quantization of magnetic flux. Such a thin planar precipitate also gives the pinning interaction that nearly equals the core interaction, and the strong elementary pinning force is thought to be yielded [63].

1.4.2.2 Elasticity of Vortex Lattice

A triangular lattice of the quantized vortices is formed because of the repulsive interaction between the vortices under the influence of the magnetic field $H_{c1} < H < H_{c2}$ in type II superconductors. The elastic character of the vortex lattice can be treated by considering the vortex lattice to be an anisotropic continuous body as well as a usual crystal. Taking the z -axis to be parallel to the direction of the vortex, the x - y plane and the x - z plane will be normal to and parallel to the direction of the vortex, respectively. Here, as shown in Figure 1.35, C_{11} , C_{44} , and C_{66} correspond to the shear moduli for the uniaxial compression in the x - y plane, the bending in the x - z plane, and transverse shear in the x - y plane, respectively [5, 59]. From electromagnetism and thermodynamic considerations, the specific expressions for the elastic moduli of C_{11} , C_{44} , and C_{66} are obtained as

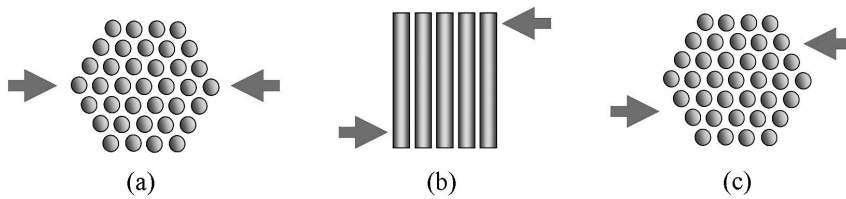


Figure 1.35 Elastic moduli of the vortex lattice for compression, bending, and shear: (a) C_{11} , (b) C_{44} , and (c) C_{66} .

$$C_{11} \approx C_{44} = B^2/\mu_0, \text{ and} \quad (1.50)$$

$$C_{66} \approx (B\Phi_0/16\pi\lambda^2\mu_0)(1-1/2\kappa^2)(1-h^2)(1-0.58h+0.29h^2), \quad (1.51)$$

where $h = H/H_{c2}$ and generally $C_{66} \ll C_{11}, C_{44}$ [64]. C_{11} and C_{44} increase with increase of the magnetic field and C_{66} decreases as the magnetic field approaches the vicinity of H_{c2} after it increases. That is, the vortex lattice is hard with respect to compression and bending with respect to high magnetic field, but is soft with respect to shearing. Such an elastic character of the vortex lattice is important in considering vortex pinning.

1.4.2.3 Global Pinning Force

The Lorentz force that is exerted on an individual vortex balances with the pinning force of the pinning center, and the vortex is pinned there until the Lorentz force exceeds f_p . The maximum pinning force per unit volume achieved with a large number of pinning center is called the *global pinning force* F_p , and is given by

$$F_p = J_c \times B. \quad (1.52)$$

F_p is also expressed as a function of the elementary pinning force f_p and the pin density N_p . The problem of obtaining F_p at a certain temperature and in a certain magnetic field is called a *summation problem* under the condition of given f_p and N_p [59, 60, 65]. This is a many-body problem where the elastic energy between vortices competes with the pinning energy. Furthermore, the thermal energy is added to this in the case of high- T_c superconductors and the problem becomes more complex.

Let us first consider the case in which the vortex lattice is not deformed by the pinning, since f_p is extremely small and the rigidity of the vortex lattice is relatively high. If the pinning centers exist at random, the vortex lattice receives small random forces. As a result, the resultant force is

$$F_p = |\mathbf{F}_p| = \sum f_p = 0. \quad (1.53)$$

Namely, J_c is zero. This is called the *weak pinning limit*. Figure 1.36 shows such a condition. In contrast, in the *strong pinning limit* in which f_p is extremely large and the vortex lattice is deformed freely, each vortices can be pinned by the strong pinning centers as shown also in Figure 1.36, and we obtain the relation of

$$F_p = |\mathbf{F}_p| = \sum f_p = N_p f_p. \quad (1.54)$$

This is the *direct summation*, where the maximum J_c which can be achieved by the pinning is given [60, 66]. But, F_p of actual superconductors is located in between these two limits. In addition, if f_p is so small that the vortex lattice behaves collectively, we can estimate the value of F_p on the basis of the *collective pinning model* [65]. This model is often applied to the interpretation of the vortex pinning in high- T_c superconductors.

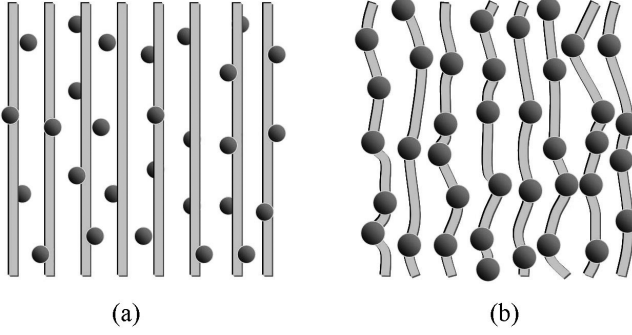


Figure 1.36 Comparison of configuration of vortices trapped by the pinning centers: (a) weak pinning centers, and (b) strong pinning centers.

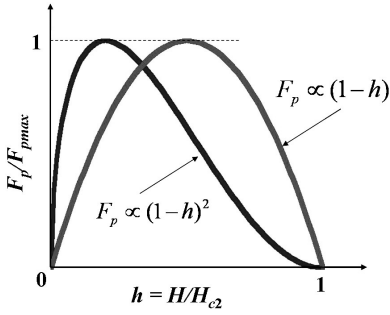


Figure 1.37 The typical magnetic field dependences of F_p for superconductors. $F_p \propto (1-h)^2$ is characteristic of saturation and $F_p \propto (1-h)$ nonsaturation, where $h = H/H_{c2}$.

1.4.2.4 Scaling Rule

The magnetic field and temperature dependences of F_p can be shown by using the following scaling rule

$$F_p = KH_{c2}^m h^p (1-h)^q, \quad (1.55)$$

where K , m , p , and q are the constants decided empirically, and $h = H/H_{c2}$ [15, 59, 60]. Typically $m \approx 1.5 - 2.5$ in a metallic superconductor. Moreover, it is known that $p \approx 0.5 - 1$ and $q \approx 1$ in practical Nb–Ti superconducting wires and $p \approx 0.5$ and $q \approx 2$ in typical superconducting wires such as Nb₃Sn.

Figure 1.37 shows an example of the magnetic field dependence of F_p . The relationship $F_p \propto (1-h)^2$ observed in Nb₃Sn, and so forth, is called a *saturation characteristic* [67]. In this case, the elastic coefficient C_{66} decreases according to the magnetic field dependence of $(1-h)^2$, although the vortex lattice is pinned.

Therefore, the shear deformation in the vortex lattice is partially caused by the Lorentz force, and J_c is limited by the flow of the vortices generated. On the other hand, the relationship $F_p \propto (1 - h)$ is called a *nonsaturated characteristic* [68], and this is important in the application of a superconducting coil, because it means that J_c is still high even in high magnetic fields. Such a tendency can be observed if f_p is comparatively large.

To discuss the scaling rule in the cuprate superconductors, the *irreversibility line* H_{irr} which shows the boundary between $J_c = 0$ and $J_c \neq 0$ is used instead of H_{c2} [69]. In the low-temperature and low-filled side below the H_{irr} curve, the flux pinning becomes effective and $J_c \neq 0$. In the case of metallic superconductors the H_{irr} curve is beneath its H_{c2} , but, in the case of the cuprate superconductors the H_{irr} is far below its H_{c2} . The quantized vortices move easily by thermal fluctuation in the cuprate superconductors, and, as a result, in the vicinity of H_{c2} the energy dissipation occurs easily and J_c becomes zero. However, it is known empirically that the behavior of F_p in a wide temperature and magnetic field range can also be described by the scaling rule which uses H_{irr} instead of H_{c2} .

1.4.3

Critical State and Thermal Fluctuation

1.4.3.1 Critical State Model

The quantized vortices invade the superconductors when a magnetic field of H_{c1} or more is applied to type II superconductors. Figure 1.38 shows the magnetic field distribution in the semi-infinite superconducting slab with different pinning forces. The magnetic field is uniform in the case of no pinning center, but, when the pinning centers exist, its distribution shows a certain gradient because the macroscopic shielding current proportional to J_c flows inside. That is, in the area where the magnetic field invades,

$$J_c = dH/dx \quad (1.56)$$

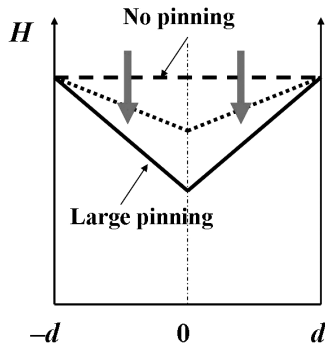


Figure 1.38 Comparison of the internal magnetic field distribution in a superconductor with slab geometry for the cases of no pinning and large pinning.

is realized. This is called the *critical state model* [70]. The penetration field H^* where the front line of the flux of magnetic induction reaches the center of the superconductor is given by

$$H^* = J_c d, \quad (1.57)$$

where d is a half thickness of the superconducting slab. Then, the magnetization $M(H)$ when H is increased is given by the following expressions

$$\begin{aligned} M(H) &= -H + H^2/2J_c d & 0 < H < H^*, \\ M(H) &= -J_c d/2 & H^* < H. \end{aligned} \quad (1.58)$$

On the other hand, when H is decreased after the magnetic field of H_m ($>H^*$) is applied, we get the expressions

$$\begin{aligned} M(H) &= H_m - H - (H_m - H)^2/4J_c d - J_c d/2 & H_m - 2H^* < H < H_m, \\ M(H) &= J_c d/2 & -H_m < H < H_m - 2H^*. \end{aligned} \quad (1.59)$$

The change of the $M(H)$ curve in the increase and decrease processes of H is shown in Figure 1.39. By using the difference ΔM between both processes of H , J_c is expressed as

$$J_c = \Delta M/d. \quad (1.60)$$

When H is changed as a cycle of $0 \rightarrow H_m \rightarrow 0 \rightarrow -H_m \rightarrow 0$, the hysteresis loss Q per cycle is written

$$Q = \oint M(H) dH. \quad (1.61)$$

Thus, the hysteresis loss per second corresponds to Q multiplied by f when the alternating magnetic field with frequency f is applied.

1.4.3.2 Vortex Creep and TAFF

Even in the area of $J_c \neq 0$ below the H_{irr} curve, voltage generation occurs because of the thermal excitation. This is called vortex creep [71]. Suppose we have a one-

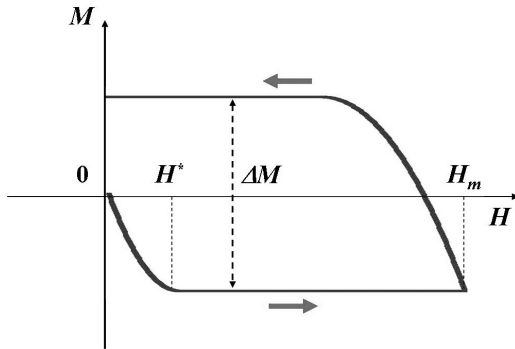


Figure 1.39 Calculated magnetization hysteresis loops of a superconductor with slab geometry. The critical state model is considered here.

dimensional superconductor which is located in the magnetic field. If the hopping probability ν of vortices from pinning centers by thermal excitation obeys the Boltzmann distribution, we have

$$\nu = \nu_0 \exp(-U_p/k_B T), \quad (1.62)$$

where ν_0 is the normalized factor, U_p is the pinning potential, and k_B is the Boltzmann constant. The pinning potential can be simply assumed with

$$U_p = U_0(1 - J/J_c), \quad (1.63)$$

because the effectiveness of vortex pinning is lost at $J = J_c$. By substituting Equation 1.63 in Equation 1.62, we get

$$J = J_c \left(1 - \frac{k_B T}{U_0} \ln \frac{\nu_0}{\nu} \right). \quad (1.64)$$

That is, the relaxation of J depending on the logarithm of time, which is the vortex creep, is derived.

Usually, though the electrical resistance of the superconductor vanishes sharply at T_c , the transition of the high- T_c superconductors becomes broad especially in magnetic fields. This behavior also relates closely to the vortex dynamics induced by thermal fluctuation. When the current density J is not induced in the superconductors, the hopping probabilities, ν^+ and ν^- , of vortices are equivalent to right and left. But the entire potential energy is inclined by the Lorentz force when the current is applied, as shown in Figure 1.40. Assuming that the inclination of this energy is W , the net hopping probability of vortices can be written as

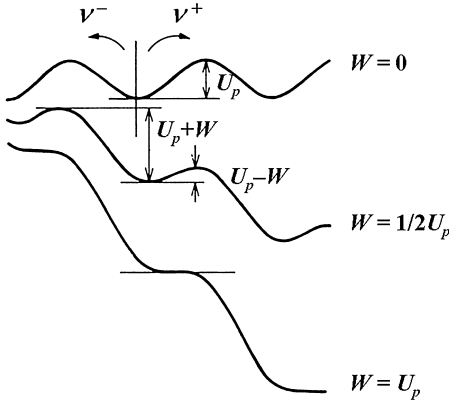


Figure 1.40 Variations of pinning potential when the Lorentz force is induced. W corresponds to the work induced by the hopping of the vortex bundle, and U_p is the pinning potential when the Lorentz force is zero.

$$\begin{aligned}
v &= v^+ - v^- \\
&= v_0 \exp[-(U_p - W)/k_B T] - v_0 \exp[-(U_p + W)/k_B T] \\
&= 2v_0 \exp(-U_p/k_B T) \sinh(W/k_B T).
\end{aligned} \tag{1.65}$$

W corresponds to the work induced by the hopping of the vortex bundle and is given by

$$W = JB V_c r, \tag{1.66}$$

where V_c is the volume of vortex bundle and r is the distance the bundle hops. If the vortices move, the voltage is generated by $\mathbf{E} = \mathbf{B} \times \mathbf{v}_L$. Since $v_L = r(v^+ - v^-)$, we obtain

$$\begin{aligned}
E &= Br(v^+ - v^-) \\
&= 2v_0 Br \exp(-U_p/k_B T) \sinh(JB V_c r/k_B T).
\end{aligned} \tag{1.67}$$

Then, the resistivity is given by

$$\begin{aligned}
\rho &= E/J = Brv/J \\
&= (2Brv_0/J) \exp(-U_p/k_B T) \sinh(JB V_c r/k_B T).
\end{aligned} \tag{1.68}$$

In the limit of small J , using $\sinh x \approx x$ ($x \ll 1$), we get

$$\rho = (2v_0 B^2 V_c r^2 / k_B T) \exp(-U_p/k_B T). \tag{1.69}$$

Thus, the finite ohmic resistance remains, and the result contrasts with the case of vortex glass. This is called the *thermally assisted flux flow* (TAFF) [72].

1.4.3.3 Thermal Fluctuation

The self energy per unit length of vortices is expressed by the following [2]

$$\varepsilon = (1/2) \mu_0 H_c^2 4\pi \xi^2 \ln \kappa \propto H_c^2 \xi^2 \quad (\kappa \gg 1) \tag{1.70}$$

where $\varepsilon \propto 1/T_c$ because there are the relations of $H_c^2 \propto T_c$ and $\xi \propto 1/T_c$. That is, the higher T_c leads to the smaller self energy. Comparing high- T_c superconductors with conventional ones, it is found that the ε of high- T_c superconductors is quite small even if the different $\ln \kappa$ is considered. Therefore, the vortices in high- T_c superconductors bend by thermal fluctuation like spaghetti and may wander constantly.

Let us consider the straight vortex whose length is L and the bending vortex which is formed by thermal fluctuation, as shown in Figure 1.41. The extra length ΔL of the vortex that becomes longer by bending is written as

$$\Delta L = 2[(L/2)^2 + \Lambda^2]^{1/2} - L \tag{1.71}$$

where Λ is the displacement of the vortex to the vertical direction of the vortex, and its extra self energy becomes $\varepsilon \Delta L$. Λ can be estimated by assuming the relation $\varepsilon \Delta L \approx k_B T$, and it becomes $\Lambda \approx (k_B T L / 2\varepsilon)^{1/2}$ when $L \gg \Lambda$. Supposing $\mu_0 H_{c1} = \mu_0 \varepsilon / \Phi_0 = 0.007$ T, $T = 77$ K, and $L = 100 \mu\text{m}$, we obtain $\Lambda \approx 70$ nm. This value is relatively large, so that the thermal fluctuation has a big influence on the

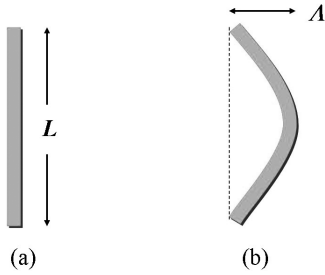


Figure 1.41 The bending of the vortex induced by thermal fluctuation: (a) straight vortex, and (b) bending vortex. The displacement of the vortex Λ is very large in the case of high- T_c superconductors.

vortex lattice of high- T_c superconductors. In the typical magnetic phase diagram of high- T_c superconductors, the area of vortices liquid phase extends widely below the H_{c2} curve as shown in Figure 1.31. This means that the vortex lattice melts easily by thermal fluctuation, and J_c becomes zero in this area since the pinning is not so effective. Besides, since there is the vortex glass phase below the vortex liquid phase, the magnetic phase diagram of high- T_c superconductors is greatly different from that of conventional superconductors.

1.4.4

Grain Boundary Problem

Though the cuprate superconductors under development are advantageous since the T_c values are very high compared with those of conventional superconductors, features such as the crystalline anisotropy and the short coherence length ξ must be considered. These give a big problem in practical use. Figure 1.42 shows the grain boundary of the superconductor on an atomic scale. For instance, the spatial distribution of the order parameters ψ in the interface of grain 1 and grain 2 should be considered. Though both the order parameters in the grains decrease at the grain boundary, a ψ of sufficient size remains by overlapping both in the boundary if ξ is 5 nm, for instance. However, ψ in the grain boundary is almost lost if ξ is short (e.g. 1 nm) and the superconducting characteristic deteriorates. Therefore, the superconducting current flowing in the grain boundary becomes extremely small in the cuprate superconductors [73].

Figure 1.43 shows the relationship between the J_c at the grain boundary and the misorientation angle θ of the adjacent crystal grain in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ bicrystal film [74]. If the misorientation angle θ is five degrees or so, the J_c is not so badly affected, but if the angle becomes larger, the J_c decreases rapidly. This is because the number density of dislocations, which is an insulator, increases at the grain boundary as θ increases. In the polycrystalline $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ where the crystal grains in various azimuths exist together, the superconducting current through

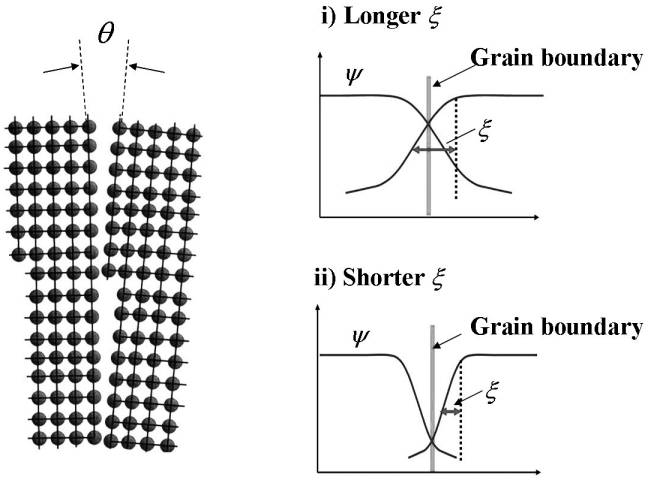


Figure 1.42 Schematic picture of a grain boundary with misorientation angle θ in the superconductors. The order parameter ψ is reduced at the grain boundary if the ξ is short.

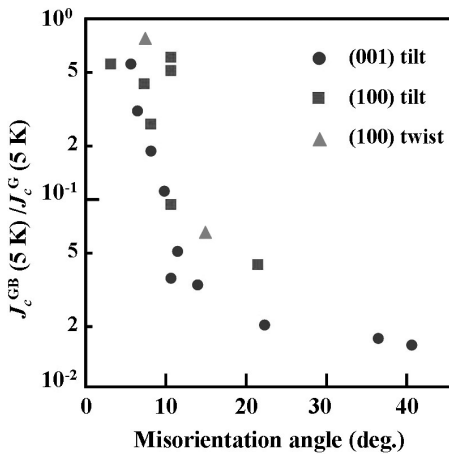


Figure 1.43 Experimental results of J_c deterioration as a function of misorientation angle in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ bicrystal film. J_c decreases exponentially as the misorientation angle increases.

the many grain boundaries becomes very small. Such a grain boundary problem has for some time seriously obstructed the development of high- T_c superconductors, but after at least 20 years of effort since the discovery of the cuprate superconductors in 1986, researchers have now succeeded in producing practicable high- T_c superconducting wires and tapes. The history of the solution of this problem is one of the important themes in this book.

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