

Chapter 2

Fundamentals

Abstract In this chapter, basic theories are described for interpreting and considering the experimental results obtained in this research. First, the Rashba effect is described because it has an important influence on the physical properties of the electronic state on the surface two-dimensional system. The latter part is devoted to fundamental matters of electron transport and superconductivity, which is the main issue of this research. The section of superconductivity contains the phenomenology, the BCS theory and the ideas of some non-BCS case arising from two-dimensionality.

Keywords Rashba effect · Superconductivity

2.1 Surface Electronic States and Spatial Inversion Symmetry

The surface can be regarded as bulk-cut plane. Hence, at the topmost surface of the covalent crystal, there are many lone pairs called dangling bonds. Dangling bonds are so energetically unstable that sometimes a reconstruction or a relaxation of atomic structure occurs so as to minimize the number of dangling bonds and the total cohesive energy. This makes the electronic structure also different one, which is called surface states that are two-dimensional and have wave functions localized at the surface. In particular, novel surface states can be created on semiconductor surfaces by metal adsorption, which rearranges surface structure. Such reconstructed semiconductor surfaces have been one of the main issues of surface science for three decades due to their diversity.

However, there is a so simple difference between surface and bulk; *Symmetry* has a dramatic effect on physical properties of surface. In the bulk material with space inversion symmetry (SIS), $\varepsilon(\mathbf{k}, \uparrow) = \varepsilon(-\mathbf{k}, \uparrow)$ is required. In addition, $\varepsilon(\mathbf{k}, \uparrow) = \varepsilon(-\mathbf{k}, \downarrow)$ holds in the presence of time reversal symmetry. These relations lead to $\varepsilon(\mathbf{k}, \uparrow) = \varepsilon(\mathbf{k}, \downarrow)$, namely, every electronic state should have spin degeneracy. In the system without space inversion symmetry, on the other hand, spin degeneracy can be lifted, i.e. $\varepsilon(\mathbf{k}, \uparrow) \neq \varepsilon(\mathbf{k}, \downarrow)$. Even for the crystals with centrosymmetry inside,

SIS is always broken on the surface. This is why we have spin-related phenomena such as Rashba effect on the surface.

2.1.1 Rashba Effect

Spin splitting arising from broken SIS is important in the system with strong SOC. Hamiltonian of free electron with SOC is described as:

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hat{\mathcal{H}}_{SO} = -\frac{\hbar^2}{2m^*} \nabla^2 + \frac{\hbar}{4m^{*2}c^2} \boldsymbol{\sigma} \cdot (\nabla V \times \mathbf{p}). \quad (2.1)$$

Here, $\boldsymbol{\sigma}$ is spin operator. In the presence of SIS, average of $\hat{\mathcal{H}}_{SO}$ is zero because $\nabla V = 0$. However, once SIS is broken, it effectively acts as magnetic field. For instance, when electron on surface 2DEG has in-plane momentum $\mathbf{p}$ and feels strong confinement potential normal to surface $\nabla V = (0, 0, E_\perp)$, the vector product $\nabla V \times \mathbf{p}$ is parallel to surface and perpendicular to momentum $\mathbf{p} = \hbar \mathbf{k}$ as shown in Fig. 2.1a. Hence, electron spin is quantized and parallel to the effective magnetic field (spin-momentum locking). The magnitude of spin splitting is proportional to $k = |\mathbf{k}|$ so that energy band splits into two branches depending on its spin state:

$$\varepsilon(k) = \frac{\hbar^2}{2m^*} k^2 \pm \frac{\hbar^2 E_\perp}{4m^{*2}c^2} k = \varepsilon_0(k) \pm \alpha_R k \quad (2.2)$$

Here, $\alpha_R = (\hbar^2 E_\perp)/(4m^{*2}c^2)$ is called Rashba parameter, which is used to indicate the phenomenological magnitude of spin splitting in each material system. Up and down spin states cross at $k = 0$, namely, they degenerate at $k = 0$ and the lower energy spin state is reversed depending on the sign of k (Fig. 2.1b).

The surface confinement potential of typical metal is ca. 1 eV, which corresponds to $\alpha_R \sim 10^{-6} \text{ eV}\text{\AA}$. However, actual crystal surfaces show much larger spin splitting. Au(111) is the first surface system which spin splitting by the Rashba effect is observed [1]. It has a 2D free electron like surface band in the projected bulk band

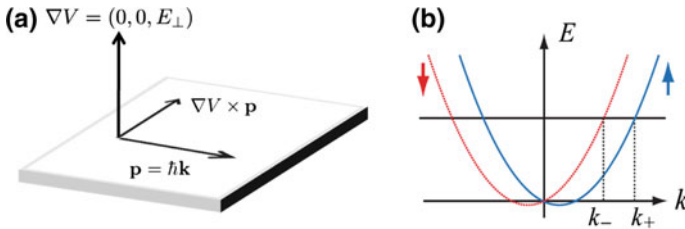


Fig. 2.1 Schematic drawing of (a) a free electron confined in a surface two-dimensional state and (b) the band dispersion of one-dimensional free electron with the Rashba effect

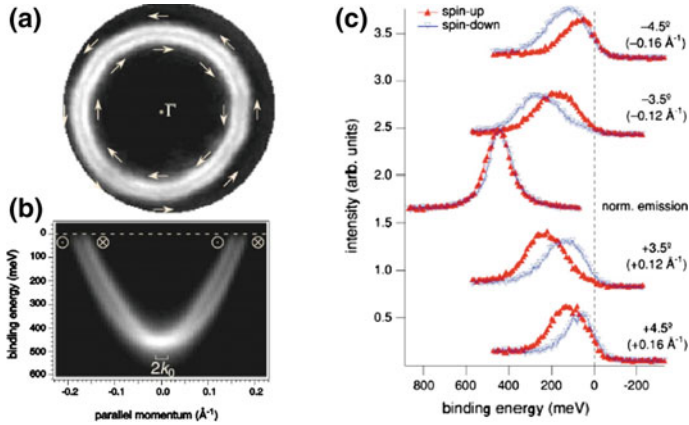


Fig. 2.2 Experimental evidences of the Rashba spin splitting on Au(111) surface provided by ARPES [2]. **a** The Fermi surface, **b** the band dispersion and **c** the spectra of spin-resolved ARPES. Reprinted with permission from Ref. [2]

gap at around $\bar{\Gamma}$ point. Owing to the resolutional improvement of ARPES, La Shell et al. found the surface band is split in accordance with the prediction of the model above. The Rashba parameter estimated by the experiment is $\alpha_R = 0.33 \text{ eV\AA}$, larger than the simple estimation above by over orders of magnitude. Since the surface bands of Au(111) is free-electron like, Rashba-type split states are two parabolas shifting in the wavenumber direction (Fig. 2.2b). Consequently, the Fermi contours are observed as two concentric circles as seen in Fig. 2.2a. Spin vector is predicted to rotate in the same direction as the motion along the circles but opposite for different branch. For the inner branch, the spin rotates in the clockwise direction, while for the outer branch they rotate in the counterclockwise direction. In fact, such spin texture is shown by Hoesch et al. from spin-resolved ARPES measurements (Fig. 2.2c) [2]. Now the idea of the Rashba effect is widely accepted and the surface of crystal is regarded as a model system for it.

Why can surfaces have such large Rashba spin splitting? Peterson et al. calculated the electronic state derived from $6p$ in the topmost layer of Au(111) surface by tight-binding method including SOC [3]. Their result showed that the Rashba effect is caused by not only breaking symmetry but SOC in the nucleus on surface. This is why magnitude of the Rashba effect depend on atomic numbers of surface elements. Nagano et al. performed *ab initio* calculations for various surfaces, indicating importance of concentration and asymmetry (or distortion) of wavefunction near the surface [4].

These theories tell us the intricate nature of the Rashba effect. Actually, the systems with especially large Rashba splits are surface alloys like Bi/Ag(111) [5], which have more complicated atomic structure than simple metals.

2.2 Electrical Transport

In this thesis, superconducting transport properties in two-dimensional systems with metallic state will be discussed. Although superconductivity is carried by Cooper paired electrons, it inherits normal state electronic properties e.g. coupling strength with phonon and mean free path. Such physical quantities are defined here by Drude and Boltzman formulas.

2.2.1 Drude Model

Carrier is driven by electrical field. When a constant force acts on electrons, they show Bloch oscillation in a perfect crystal while steady uniform motion in a natural crystal due to scattering by defects.

Drude constructed a model to describe electron motion in classical sense. In the Drude model, it is assumed that an electron travels for a time τ since its last collision, namely, scattering rate per unit of time is $1/\tau$ in average. The τ is called relaxation time. The equation of motion for an electron under electric field of $\mathbf{E}$ is

$$m^* \frac{d\mathbf{v}(t)}{dt} = e\mathbf{E} - m^* \frac{\mathbf{v}(t)}{\tau}, \quad (2.3)$$

where m^* is electron mass. Then, velocity of electron in steady state is

$$\mathbf{v} = \frac{e\tau}{m^*} \mathbf{E} = \mu \mathbf{E}. \quad (2.4)$$

$\mu = e\tau/m^*$ is called mobility. Current density of carriers with density of n is

$$\mathbf{j} = ne\mathbf{v} = \frac{ne^2\tau}{m^*} \mathbf{E} = ne\mu \mathbf{E}. \quad (2.5)$$

Electrical conductivity σ is defined by $\mathbf{j} = \sigma \mathbf{E}$. From Eq. (2.5),

$$\sigma = \frac{ne^2\tau}{m^*} = ne\mu. \quad (2.6)$$

2.2.2 Boltzmann Equation

Although the Drude model assumes independent motion of electrons in a classical way, the idea of the relaxation time and the mobility can be used to describe macroscopic properties of the real systems. However, in order to estimate conductivity by

quantum mechanical states in solids, we have to use the Boltzmann model. In equilibrium condition, electrons occupy states in energy bands $(1, 2, \dots, i, j, \dots)$ according to the Fermi distribution function, which is modified by application of the electrical field. By adopting the relaxation time approximation, the distribution function returns to equilibrium after time τ . Then, conductivity tensor σ_{ij} ($j_i = \sigma_{ij} E_j$) can be written as [6]

$$\sigma_{ij} = \frac{2e^2\tau}{(2\pi)^d\hbar} \int dS_F \frac{v_i v_j}{v}. \quad (2.7)$$

In two-dimensional case,

$$\sigma_{ij} = \frac{e^2\tau}{2\pi^2\hbar} \int dk_F \frac{v_i v_j}{v}. \quad (2.8)$$

If current is uniform and isotropic, $v_{i(j)}$ can be rewritten by the Fermi velocity v_F ;

$$\sigma = \frac{e^2\tau v_F}{4\pi^2\hbar} \int dk_F. \quad (2.9)$$

In 2D free electron, density of state at the Fermi surface per square unit is

$$N = \frac{1}{2\pi^2} \int \frac{dk_F}{\partial E / \partial k} = \frac{1}{2\pi^2\hbar} \int \frac{dk_F}{v_F} = \frac{m^*}{\pi\hbar^2}. \quad (2.10)$$

Here m^* is the effective mass. Therefore σ is simplified as

$$\sigma = \frac{e^2}{2} l v_F N = \frac{e^2\tau k_F^2}{2\pi m^*}, \quad (2.11)$$

where $l = \tau v_F$ is the mean free path. Using $m^* v_F = \hbar k_F$,

$$\sigma = \frac{e^2}{h} k_F l. \quad (2.12)$$

Hence, we can estimate mean free path from sheet resistivity $R_{\text{sheet}} = 1/\sigma$ as

$$l = \frac{1}{k_F} \cdot \frac{h/e^2}{R_{\text{sheet}}}. \quad (2.13)$$

Namely, the mean free path is proportional to the Fermi wavelength $1/k_F$ and $1/R_{\text{sheet}}$. $h/e^2 = 25.8\text{ k}\Omega$ is the quantized resistance of electron.

Note that the Boltzmann picture results in the Drude model [Eq. (2.6)] by adopting free electron approximation. First,

$$\int dk_F = 2\pi k_F \quad (2.14)$$

$$n = \frac{k_F^2}{2\pi}. \quad (2.15)$$

By using $v_F = \hbar k_F / m^*$, electrical conductivity

$$\sigma = \frac{e^2 \tau n}{m^*} = e \mu n. \quad (2.16)$$

Though the electrical transport occurs only near the Fermi surface, the conductivity involves the total number of electrons occupying the band from the bottom to the Fermi energy, same as the Drude formula.

Conductivity and band structure

Now we can get relations between transport properties and band dispersions based on the Boltzmann picture as follows.

From the Fermi wavenumber k_F and the gradient of band dispersion near the Fermi surface $\partial E / \partial k (k = k_F)$, The Fermi velocity is written as

$$v_F = \frac{1}{\hbar} \left(\frac{\partial E}{\partial k} \right)_{k_F}. \quad (2.17)$$

The effective mass:

$$m^* = \frac{\hbar k_F}{v_F} = \frac{\hbar^2 k_F}{\left(\frac{\partial E}{\partial k} \right)_{k_F}} \quad (2.18)$$

On the one hand, the career density n is estimated by

$$n = \frac{\text{spin degeneracy factor} \times \text{area of the Fermi surface}}{(2\pi)^2}. \quad (2.19)$$

2.2.3 Matthiessen's Low

In a solid, the electron repeatedly scatters off crystal defects, phonons, impurities, etc. According to the Matthiessen's low, the inverse of the relaxation time τ (scattering probability) is the sum of that from electron-phonon coupling, electron-electron interaction, and impurity scattering (τ_{e-p} , τ_{e-e} , τ_{imp}).

$$\frac{1}{\tau} = \frac{1}{\tau_{e-p}} + \frac{1}{\tau_{e-e}} + \frac{1}{\tau_{imp}}. \quad (2.20)$$

Here R_{sheet} is defined as the sheet resistance, the inverse of Eq. (2.11). Applying the Matthiessen's law,

$$R_{\text{sheet}} = \frac{2\pi m^*}{e^2 k_F^2} \left(\frac{1}{\tau_{e-p}} + \frac{1}{\tau_{e-e}} + \frac{1}{\tau_{\text{imp}}} \right). \quad (2.21)$$

At the temperature much lower than Debye temperature, the contributions from electron-electron interaction and impurity scattering are dominant. Since electron-electron scattering does not frequently occur in normal metals, resistance decrease with cooling, saturating in residual resistance due to impurity. Such monotonic behavior is broken by several reasons: Kondo effect, Mott transition and Anderson localization.

2.2.4 Ioffe-Regel Limit

Anderson localization is understood as the absence of diffusion of electrons in a crystal due to too many impurities. Namely, the Bloch picture itself is destroyed by strong randomness. Bloch wave spreads thorough the system when the mean free path is enough longer than the Fermi wavelength;

$$k_F l > 1. \quad (2.22)$$

Equation (2.13) gives us a relation

$$R_{\text{sheet}} < \frac{h}{e^2} = 25.8 \text{ (k}\Omega\text{)}. \quad (2.23)$$

This is what we call *Ioffe-Regel limit*, 25.8 k Ω . Namely, metallic behavior (*monotonic decrease of resistance*) is expected when $R_{\text{sheet}} < 25.8 \text{ k}\Omega$, unless insulating behavior (*increase of resistance*) or *metal-insulator transition* is predicted.

2.3 Basic Properties of Superconductivity

Many of the metals become superconductivity when cooled below a characteristic critical temperature T_c . There are two elementary properties of superconductors;

- Zero resistance: sustaining currents in superconducting rings with no power source.
- Perfect diamagnetism (Meissner effect): complete ejection of magnetic field lines from the interior of the superconductor.

A superconductor can be Type I, meaning that it has a single critical field H_{c1} , above which Meissner state is completely lost; or Type II, meaning that it has two critical

fields (H_{c1} and H_{c2}), between which it allows partial penetration of the magnetic field. $H_{c1} < H < H_{c2}$ is called mixed state where an increasing amount of magnetic flux penetrates the material, but there remains no resistance to the flow of electric current as long as the current is not too large. Elemental metals such as Hg, Sn and Al are classified in the former case: Type I, while most of the alloys and compounds are Type II.

2.3.1 London Equation

The first phenomenological theory of superconductivity was the London theory [7]. The London theory separates the conducting electrons within a superconductor into two fluids. According to this two-fluid model, one fluid consists of ‘normal’ electrons with number density n_n , which behave exactly in the same way as the free electrons in a normal metal. The current density $\mathbf{J}_n = n_n e \mathbf{v}_n$ due to flow of these electrons obeys Ohm’s law:

$$\mathbf{J}_n = \sigma_n \mathbf{E}. \quad (2.24)$$

The others are the superconducting electrons (or superelectrons), which form a fluid with number density n_s . The superconducting electrons are assumed to be freely accelerated by an electric field i.e. not scattered by impurities, defects or thermal vibrations. When the velocity and charge of a superconducting electron are $\mathbf{v}_s$ and e_s , then its equation of motion is written as

$$\frac{d\mathbf{v}_s}{dt} = -e_s \mathbf{E}. \quad (2.25)$$

Since the expression for the current density is $\mathbf{J}_s = n_s e_s \mathbf{v}_s$, we find that

$$\frac{d\mathbf{J}_s}{dt} = \frac{n_s e_s^2}{m_s} \mathbf{E}. \quad (2.26)$$

This is the first formula of London equation. If we consider a constant current flowing in the superconductor, then $d\mathbf{J}_s/dt = 0$, so $\mathbf{E} = 0$ i.e. no electric field or potential difference in the superconductor. This indicates *zero resistance* state.

To account for the Meissner effect in a superconductor, additional assumptions are needed;

$$\nabla \times \mathbf{J}_s = -\frac{n_s e_s^2}{m_s} \mathbf{h}. \quad (2.27)$$

This is the second formula of London equation. Displacement current and normal current decrease so rapidly that can be ignored to consider effect in steady condition. So the Ampère-Maxwell law can be written as $\nabla \times \mathbf{h} = \mu_0 \mathbf{J}_s$. Here, $\mathbf{h}$ is local magnetic field. Taking rotation of both side, we have

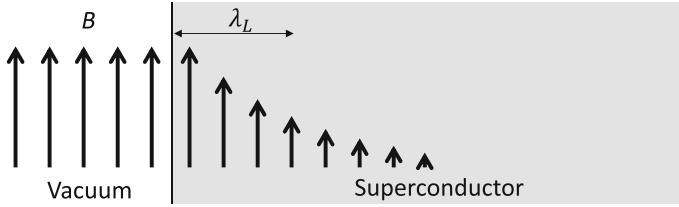


Fig. 2.3 Schematic illustration of the Meissner effect. The magnetic flux density parallel to the surface attenuated exponentially with distance below the surface of the superconductor. The inside of superconductor has perfect diamagnetism

$$\nabla \times (\nabla \times \mathbf{h}) = \mu_0 \nabla \times \mathbf{J}_s. \quad (2.28)$$

Inserting Eq. (2.27) gives us a second-order differential equation of $\mathbf{h}$.

$$\nabla^2 \mathbf{h} = \frac{1}{\lambda_L^2} \mathbf{h}. \quad (2.29)$$

Here, we define London penetration depth λ_L by

$$\lambda_L \equiv \sqrt{\frac{m_s}{\mu_0 n_s e_s^2}}. \quad (2.30)$$

By solving Eq. (2.29), we obtain

$$h_{\parallel} \propto \exp\left(-\frac{x}{\lambda_L}\right). \quad (2.31)$$

This indicates that the external magnetic field is attenuated exponentially with distance below the surface of the superconductor. $h_{\parallel} \rightarrow 0$ within the bulk; This is qualitative explanation of Meissner effect (see Fig. 2.3).

If Eq. (2.27) is rewritten by vector potential $\mathbf{A}$ instead of local magnetic field $\mathbf{h}$,

$$\mathbf{J}_s = -\frac{n_s e_s^2}{m_s} \mathbf{A}. \quad (2.32)$$

This is another expression of London equation, since Eq. (2.26) is obtained by temporal differentiation of Eq. (2.32). The laws of physics governing electricity and magnetism should be invariant under gauge transformation. Hence, Eq. (2.32) requires a specific gauge as $\mathbf{A}$, indicating that the gauge symmetry is broken accompanied with superconducting transition. In superconducting system, $\nabla \cdot \mathbf{J}_s = 0$. Therefore, we have to fix the gauge as following *Coulomb gauge*.

$$\nabla \cdot \mathbf{A} = 0. \quad (2.33)$$

2.3.2 GL Theory

The second order phase transition is accompanied by the spontaneous symmetry breaking. As mentioned above, London equation results in breaking of the gauge symmetry. Actually, superconducting phenomenon is explained as a second order phase transition in the Ginzburg-Landau (GL) theory.

The most typical example of the second order phase transition is magnetization in ferromagnetic materials. Above the Curie temperature, there is no order of spin direction (paramagnetism). Below the Curie temperature, every spin aim to be parallel in specific direction and the system has finite magnetization (ferromagnetism). Although the magnetic order has microscopic origin: exchange interaction with next neighbor spins, it can be described by macroscopic phenomenology using free energy $\mathcal{F}(M, T)$ without detailed mechanism. Here, M is magnetization: a kind of order parameter. In quantum statistical mechanics, Bose-Einstein condensate (BEC) is an example of the spontaneous phase transition. Then, a large fraction of bosons occupy the lowest quantum state called macroscopic wavefunction;

$$\Psi(\mathbf{r}) = |\Psi(\mathbf{r})|e^{-i\Phi}, \quad (2.34)$$

at which macroscopic quantum phenomena become apparent. Here, the gauge symmetry is broken: the phase of macroscopic wavefunction is ordered.

Superconducting order parameter

To treat superconductivity in the same way, Ginzburg and Landau argued that the free energy, $\mathcal{F}$, of the superconductor near the superconducting transition can be expressed in terms of a complex order parameter field Ψ , which is nonzero below the phase transition into the superconducting state and is related to the density of the superconducting electron n_s ;

$$\Psi = \sqrt{n_s}e^{-i\Phi}. \quad (2.35)$$

Therefore,

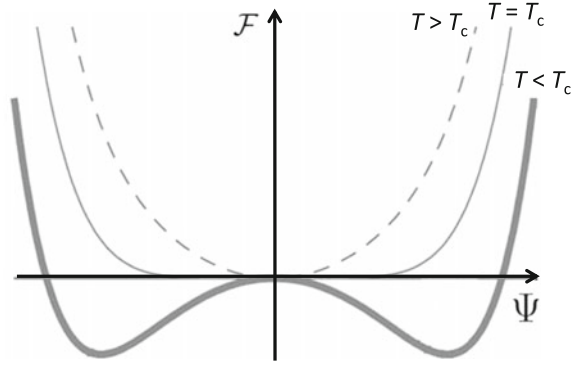
$$|\Psi|^2 = n_s. \quad (2.36)$$

Here, the spatial dependence is ignored for simplification. In the superconducting phase, the gauge symmetry is broken so that the phase of superconducting state has physical meaning. The charge flux density is written in the following form.

$$\mathbf{J}_s = \frac{ie_s\hbar}{2m_s}(\Psi\nabla\Psi^* - \Psi^*\nabla\Psi) = \frac{e_s\hbar}{m_s}n_s\nabla\Phi. \quad (2.37)$$

This equation indicates that *the superconducting current is driven by the phase of macroscopic wavefunction.*

Fig. 2.4 Temperature dependence of the free energy $\mathcal{F}(\Psi)$ in Ginzburg-Landau theory. There is an unique minimum at the origin when $T > T_c$, while there are two minima when $T < T_c$



According to the general discussion of the second order phase transition, the free energy has a form of the field theory using $|\Psi|^2$ as order parameter.

$$\mathcal{F}[\Psi] = \mathcal{F}_0 + \alpha|\Psi|^2 + \frac{\beta}{2}|\Psi|^4, \quad (2.38)$$

where $\alpha(T) = a(T - T_c)$ and a, β is positive constant. $\mathcal{F}_0$ indicates the free energy in normal state. This equation has a trivial solution: $|\Psi| = 0$. This corresponds to the normal state of the superconductor, that is for temperatures above the superconducting transition temperature, ($T > T_c$). Below the superconducting transition temperature, the above equation has non-trivial solutions:

$$|\Psi| = \pm \sqrt{\frac{a(T_c - T)}{\beta}}. \quad (2.39)$$

The temperature dependent behaviors of free energy is summarized in Fig. 2.4. This type is called *Higgs potential*. When $T > T_c$, there is a unique solution at the origin. On the other hand, when $T < T_c$, the minimums can be solution. This is so-called spontaneous symmetry breaking at $T = T_c$.

GL equation

Here, let us consider the spatial variation in amplitude of macroscopic wavefunction: $\Psi(\mathbf{r}) = |\Psi(\mathbf{r})|e^{-i\Phi}$. By minimizing the free energy with respect to variations in the order parameter and the vector potential, one arrives at the GL equations:

$$-\frac{\hbar^2}{2m_s} \left[\nabla - \frac{ie_s}{\hbar} \mathbf{A}(\mathbf{r}) \right]^2 \Psi(\mathbf{r}) + \alpha\Psi(\mathbf{r}) + \beta|\Psi(\mathbf{r})|^2\Psi(\mathbf{r}) = 0, \quad (2.40)$$

$$\mathbf{J}_s(\mathbf{r}) = \frac{-ie_s\hbar}{2m_s} [\Psi^*(\mathbf{r})\nabla\Psi(\mathbf{r}) - \Psi(\mathbf{r})\nabla\Psi^*(\mathbf{r})] - \frac{e_s^2}{m_s} |\Psi(\mathbf{r})|^2 \mathbf{A}(\mathbf{r}). \quad (2.41)$$

When $\mathbf{A}(\mathbf{r}) = 0$, easy solutions can be found: the minimums in Fig. 2.4. $[\nabla - (ie_s/\hbar)\mathbf{A}(\mathbf{r})]\Psi(\mathbf{r}) = 0$ in Eq. (2.40) also gives solutions with the same energy.

Next, by considering the spatial variation of phase $\Psi(\mathbf{r}) = |\Psi(\mathbf{r})|e^{-i\Phi(\mathbf{r})}$, we obtain the following equations.;

$$\nabla|\Psi(\mathbf{r})| = 0, \quad (2.42)$$

$$\nabla\Phi(\mathbf{r}) - \frac{e_s}{\hbar}\mathbf{A}(\mathbf{r}) = 0. \quad (2.43)$$

The former requires $|\Psi(\mathbf{r})|$ to be spatially constant. The latter gives a relation between vector potential $\mathbf{A}$ and $\Phi(\mathbf{r})$ as

$$\mathbf{A}(\mathbf{r}) = \frac{\hbar}{e_s}\nabla\Phi(\mathbf{r}). \quad (2.44)$$

Here, arbitrary $\mathbf{A}(\mathbf{r})$ satisfying the Eq. (2.33) (Coulomb gauge) is possible. Namely, *the solution of GL equation (2.40) infinitely degenerates* with respect to the phase of macroscopic wavefunction. The ground state Ψ is given by Higgs potential curve shown in Fig. 2.4. The phase degree of freedom of Ψ corresponds to rotation in complex plane $[\text{Re}(\Psi), \text{Im}(\Psi)]$ (indicated by the white arrow in Fig. 2.5). Therefore, Higgs potential form symmetrical upward dome with a trough circling the bottom in $[\text{Re}(\Psi), \text{Im}(\Psi), F]$ as shown in Fig. 2.5. At high temperature phase, the solution locates at the peak of this “Mexican hat”, and the system is rotational symmetric, corresponding to conservation of gauge symmetry. Phase transition from this symmetric state to low-temperature phase is regarded as rolling down the dome into the trough (indicated by the black arrow in Fig. 2.5), a point of the lowest energy. Afterward, the ball has come to a rest at some fixed point, namely, phase of macroscopic

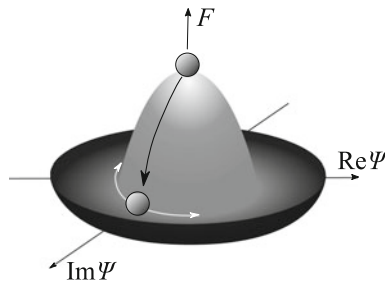


Fig. 2.5 Schematic illustration of the Higgs potential. At high temperature phase, the solution locates at the peak of the dome. Phase transition to low-temperature phase is indicated by the black arrow, rolling down the dome into the trough. The phase degree of freedom of Ψ corresponds to rotation in complex plane $[\text{Re}(\Psi), \text{Im}(\Psi)]$, which is indicated by the white arrow

wavefunction is determined. At the point, rotational symmetry is no longer conserved: gauge symmetry is *spontaneously* broken.

GL coherence length

Let us consider the spatial variation of macroscopic quantum state $|\Psi(\mathbf{r})|$ in a specific situation, in which a superconductor occupies $x > 0$ semi-infinite space. We solve the one dimensional GL equation (2.40)

$$-\frac{\hbar^2}{2m_s} \frac{d^2}{dx^2} \Psi(x) + \alpha \Psi(x) + \beta \Psi^3(x) = 0 \quad (2.45)$$

with a boundary condition $\Psi(0) = 0$. We can simplify this formula by defining

$$\xi_{\text{GL}}^2 \equiv \frac{\hbar^2}{2m_s |\alpha|} \quad (2.46)$$

and a normalization $\psi \equiv \Psi/\Psi_0$, $\Psi_0 = \sqrt{|\alpha|/\beta}$;

$$-\xi_{\text{GL}}^2 \frac{d^2}{dx^2} \psi(x) - \psi(x) + \psi^3(x) = 0. \quad (2.47)$$

This is rearranged to

$$\frac{d}{dx} \left[-\xi_{\text{GL}}^2 \left(\frac{d\psi(x)}{dx} \right)^2 - \psi(x)^2 + \frac{1}{2} \psi^4(x) \right] = 0. \quad (2.48)$$

Hence,

$$-\xi_{\text{GL}}^2 \left(\frac{d\psi(x)}{dx} \right)^2 - \psi(x)^2 + \frac{1}{2} \psi^4(x) = \text{const.} \quad (2.49)$$

At the interior of superconductor, $(x \rightarrow +\infty)$, $\Psi \rightarrow \Psi_0$. Then,

$$\xi_{\text{GL}}^2 \left(\frac{d\psi(x)}{dx} \right)^2 = \frac{1}{2} [1 - \psi^2(x)]^2, \quad (2.50)$$

leading to

$$\psi(x) = \tanh \left(\frac{x}{\sqrt{2}\xi_{\text{GL}}} \right). \quad (2.51)$$

Even though $\Psi(0, y, z) = 0$ at the interface, superconducting state recovers its equilibrium according to the characteristic exponent ξ_{GL} . It is called *GL coherence length*, which gives the length scale the variations of the density of superconducting component against small perturbations. Using $\alpha = a(T - T_c)$, we obtain

$$\xi_{GL}(T) = \left(\frac{\hbar^2}{2m_s a T_c} \right)^{1/2} \left(1 - \frac{T}{T_c} \right)^{-1/2}, \quad (2.52)$$

indicating that GL coherence length depends on temperature and diverges at T_c .

By replacing n_s with $|\Psi|^2$ in Eq. (2.30),

$$\lambda_L = \sqrt{\frac{m_s}{\mu_0 |\Psi|^2 e_s^2}} = \left(\frac{m_s \beta}{\mu_0 e_s^2 a T_c} \right)^{1/2} \left(1 - \frac{T}{T_c} \right)^{-1/2}. \quad (2.53)$$

Applying Eq. (2.51) gives us

$$\kappa \equiv \frac{\lambda_L}{\xi_{GL}} = \frac{m_s}{e_s \hbar} \sqrt{\frac{2\beta}{\mu_0}}. \quad (2.54)$$

Here defined κ is GL parameter which determines classification of superconductor as shown in Fig. 2.6; When $\kappa < 1/\sqrt{2}$, penetration of magnetic flux can be ignored so that the system is type-I. $\kappa > 1/\sqrt{2}$ means that the coherence length is smaller than the penetration depth. This manifests that magnetic flux passing through the material, which is the characteristic of type-II superconductor. Most of the compounds are classified to this case.

Quantum vortex

Magnetic flux penetrating to type-II superconductors is called *vortex*. At the center of vortex (vortex core), superconductivity is broken into normal state. The decay length ξ_{GL} gives diameter of vortex. Superconducting current circulates around the flux to cancel it (Fig. 2.7). Because the wavefunction must return to its same value after an integer number of turns around the vortex, circulation around vortex is quantised;

$$\oint_C \nabla \Phi \cdot d\mathbf{l} = 2\pi n, \quad (2.55)$$

where n is integer. Using Eq. (2.43),

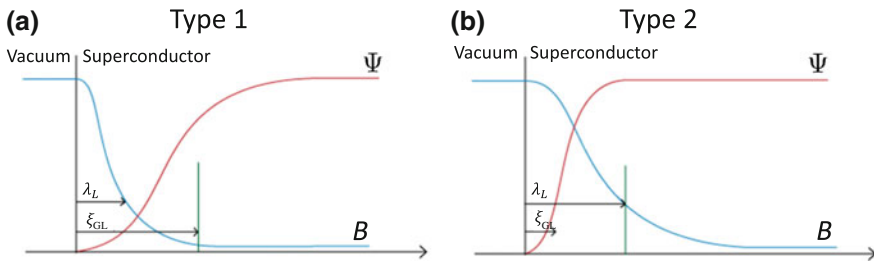
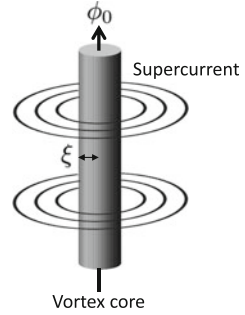


Fig. 2.6 a Schematically drawn coherence length and magnetic penetration length in a, type-I and b type-II superconductors

Fig. 2.7 Schematic picture of the vortex in type-II superconductor



$$\frac{e_s}{\hbar} \oint_C \mathbf{A} \cdot d\mathbf{l} = 2\pi n. \quad (2.56)$$

Here, circulation of vector potential equals to penetrating magnetic flux. Then

$$\oint_C \mathbf{A} \cdot d\mathbf{l} = \int_S \mathbf{B} \cdot d\mathbf{S} = \phi. \quad (2.57)$$

This results in *magnetic flux quantum*;

$$\phi = n \frac{h}{e_s} = n\phi_0. \quad (2.58)$$

Temperature dependence of upper critical field

Here we see the upper critical field H_{c2} of type-II superconductor. At the vicinity of H_{c2} , higher order term of Ψ can be ignored. Then we have linearized GL equation:

$$-\frac{\hbar^2}{2m_s} \left[\nabla - \frac{ie_s}{\hbar} \mathbf{A}(\mathbf{r}) \right]^2 \Psi(\mathbf{r}) + \alpha \Psi(\mathbf{r}) = 0. \quad (2.59)$$

This equation has the same format as Schrödinger equation; $-\alpha$ corresponds to energy. When an uniform magnetic field is applied along z axis, by taking a vector potential $\mathbf{A} = (0, Bx, 0)$ we obtain

$$-\frac{\hbar^2}{2m_s} \left[\frac{\partial^2}{\partial x^2} + \left(\frac{\partial}{\partial y} - \frac{ie_s B}{\hbar} x \right)^2 + \frac{\partial^2}{\partial z^2} \right] \Psi = -\alpha \Psi, \quad (2.60)$$

which has the same format as the one to describe free electron motion in magnetic field. By separation of valuable $\Psi(x, y, z) = u_n(x)e^{ik_y y + ik_z z}$, this equation is arranged into:

$$\left[-\frac{\hbar^2}{2m_s} \frac{d^2}{dx^2} + \frac{1}{2} m_s \omega_c^2 (x - x_0)^2 \right] u_n(x) = \frac{\hbar^2}{2m_s} \left(\frac{1}{\xi_{GL}(T)^2} - k_z^2 \right) u_n(x). \quad (2.61)$$

Here, $\omega_c = e_s B / m_s$, $x_0 = \hbar k_y / e_s B$. This equation can be solved as harmonic oscillator.

$$\varepsilon_n = \left(n + \frac{1}{2} \right) \hbar \omega_c = \left(n + \frac{1}{2} \right) \hbar \left(\frac{e_s B}{m_s} \right), \quad (2.62)$$

where n is zero or positive integer. This equals to $(\hbar/2m_s)(\xi_{GL}(T)^{-2} - k_z^2)$, so

$$B = \frac{\phi_0}{2\pi(2n+1)} \left(\frac{1}{\xi_{GL}(T)^2} - k_z^2 \right). \quad (2.63)$$

H_{c2} is defined as the maximum of the field. Therefore, we obtain

$$\mu_0 H_{c2} = \frac{\phi_0}{2\pi \xi_{GL}(T)^2} = \frac{\phi_0}{2\pi \xi_{GL}(0)^2} \left(1 - \frac{T}{T_c} \right). \quad (2.64)$$

The temperature dependence of upper critical field can be acquired experimentally. We can estimate the GL coherence length at zero Kelvin by extrapolation.

2.3.3 BCS Theory

London and GL theory were postulated as phenomenological models which could describe macroscopic properties of superconductors. However, no one examined the microscopic origin *why macroscopic amount of career can be stored in one quantum state*. The superconducting state is fundamentally different than any possible normal metallic state; The free electron system without any impurity can have a perfect conductivity but not a Meissner state at zero-temperature limit, Thus, the transition from the normal metal state to the superconducting state must be a phase transition resulting from some many body effect.

However, direct coulomb interaction between electrons is repulsive so that it raises the total energy of systems. To reduce the energy requires some *attractive* force. We have seen the effect of phonon scattering to electrical resistance at the Sect. 2.2.3. An intuitive picture of electron-phonon interaction is described as follows; As an electron moves through the lattice, it attracts neighboring nucleus via a Coulomb interaction. The attraction leads to a local distortion of the lattice, cause the excess of the positive charge, which attracts another electron nearby. This process is taken into account to electron-electron interaction via lattice deformations, described by a phonon exchange (Fig. 2.8a). The net effect of the phonons is then to create an attractive interaction and generate quasiparticle states. This is in other words *bosonic* electron pairs, predicted to exhibit BEC.

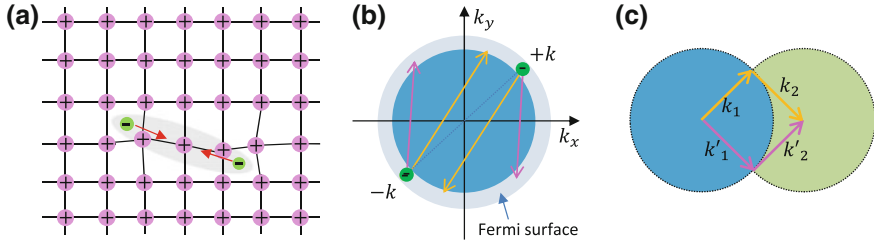


Fig. 2.8 Conceptual figures of Cooper pair formation in the BCS theory. **a** The attracting interaction between two electrons via lattice distortion. **b** The Cooper pair formation on a Fermi surface. The pink and yellow arrows indicate scattering paths which cause the attractive interaction. **c** The possible scattering paths to form Cooper pairs with nonzero center of mass of momentum. As the final state, k'_1 is forbidden except the crossing point of the spheres with the radius of $|k_1|$ centered on k_1

However, it is not easy to treat considerable amount of electron. Instead, Cooper considered to add electrons above a filled Fermi sphere as form in attracting pairs (Fig. 2.8b). Here, the total energy is minimized when two electrons with $(\mathbf{k}, -\mathbf{k})$ form bound state, namely, center of mass of a pair $\mathbf{K} = 0$. (Two electrons chase each other around the lattice.) If $\mathbf{K} = 0$, there are various scattering paths to cause attracting force conserving the total momentum as Fig. 2.8b. On the one hand, if $\mathbf{K} \neq 0$, such scattering paths are limited (Fig. 2.8c). Thus, Cooper quantified the superconducting ground state assuming $\mathbf{K} = 0$.

Cooper instability

A wavefunction of the two electrons above Fermi sphere can be written as

$$\Psi(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2) = \psi(\mathbf{r}_1, \mathbf{r}_2) \chi(\sigma_1, \sigma_2). \quad (2.65)$$

Here, ψ is spatial and χ is spin part. Since the pair in a zero center of mass state by the assumption, $\psi(\mathbf{r}_1, \mathbf{r}_2)$ is a function of $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$. By a Fourier expansion,

$$\psi(\mathbf{r}) = \frac{1}{L^3} \sum_{\mathbf{k}} g(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{r}}, \quad (2.66)$$

where $g(\mathbf{k})$ is probability amplitude to find the electron pair in $(\mathbf{k}, -\mathbf{k})$.

The spatial part must obey the Schrödinger equation of

$$\left[-\frac{\hbar^2}{2m^*} (\nabla_1^2 + \nabla_2^2) + V(\mathbf{r}) \right] \psi(\mathbf{r}) = (E + 2\varepsilon_F) \psi(\mathbf{r}). \quad (2.67)$$

Here $V(\mathbf{r})$ denotes attractive potential, E is a additional energy of two electrons and ε_F is Fermi energy. By substituting the Fourier-expanded wavefunction, we obtain

$$\frac{\hbar^2 \mathbf{k}^2}{m^*} g(\mathbf{k}) + \sum_{\mathbf{k}'} g(\mathbf{k}') V_{\mathbf{k}\mathbf{k}'} = (E + 2\varepsilon_F) g(\mathbf{k}). \quad (2.68)$$

Here,

$$V_{\mathbf{k}\mathbf{k}'} = \frac{1}{L^3} \int d\mathbf{r} V(\mathbf{r}) e^{-i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}} \quad (2.69)$$

is Fourier transform of $V(\mathbf{r})$.

$V_{\mathbf{k}\mathbf{k}'}$ indicates the attractive interaction via phonon exchange. However, the maximum energy which may be exchanged in this way is $\sim \hbar\omega_D$. (ω_D is the Debye frequency.) Thus the scattering in phase space is restricted in energy width

$$\varepsilon_F - \hbar\omega_D < \varepsilon_{\mathbf{k}} < \varepsilon_F + \hbar\omega_D, \quad (2.70)$$

where $\varepsilon_{\mathbf{k}} = \hbar^2 k^2 / 2m^*$. Since $\varepsilon_F \gg \omega_D$ in typical metal, this region is just a narrow shell on the Fermi sphere. Here, isotropic attractive interaction is described as

$$V_{\mathbf{k}\mathbf{k}'} = \begin{cases} -V_0 & (\varepsilon_F - \hbar\omega_D < \varepsilon_{\mathbf{k}} < \varepsilon_F + \hbar\omega_D) \\ 0 & (\text{otherwise}). \end{cases} \quad (2.71)$$

Then, Eq. (2.68) is simplified as

$$(-2\varepsilon_{\mathbf{k}} + E + 2\varepsilon_F) g(\mathbf{k}) = -V_0 \sum_{\mathbf{k}'} g(\mathbf{k}'). \quad (2.72)$$

Here, when spin part of wavefunction $\chi(\sigma_1, \sigma_2)$ is singlet (i.e. antisymmetric), spatial part is symmetric. Then, $g(\mathbf{k}) = g(-\mathbf{k})$ and

$$1 = V_0 \sum_{\mathbf{k}} \frac{1}{2\varepsilon_{\mathbf{k}} - E - 2\varepsilon_F} \quad (2.73)$$

$$= V_0 \int_0^{\hbar\omega_D} d\varepsilon N(\varepsilon_F + \varepsilon) \frac{1}{2\varepsilon - E} \quad (2.74)$$

$$= V_0 N(\varepsilon_F) \ln \frac{E - 2\hbar\omega_D}{E}, \quad (2.75)$$

where, $N(\varepsilon)$ is density of state, which is almost constant around Fermi energy. When $V_0 N(\varepsilon_F) \ll 1$,

$$E = -2\hbar\omega_D \exp\left(-\frac{2}{V_0 N(\varepsilon_F)}\right). \quad (2.76)$$

This indicates that the weak phonon-mediated attractive interaction $-V_0$ promote the formation of a spin-singlet pair ($k \uparrow, -k \downarrow$), which is called Cooper pair. No matter

how small attracting force is sufficient to destabilize the Fermi sea, and creates a new ground state.

On the other hand, when spin part is triplet, spatial part is antisymmetric. Then, $g(\mathbf{k}) = -g(-\mathbf{k})$, which make the right hand of Eq. (2.72) equals to zero and

$$E = 2(\varepsilon_{\mathbf{k}} - \varepsilon_F) > 0. \quad (2.77)$$

Therefore there is no instability of Fermi sphere.

From above discussion, following three assumptions are used in the BCS theory.

1. Cooper pairs take zero center-of-mass momentum.
2. Cooper pairs are spin singlet states.
3. Cooper pairs are created by isotropic attractive interaction.

BCS ground state

As discussed in the preceding section, attractive interaction modifies distribution of electron in the ground state; All electrons are stored in Fermi sphere in free electronic ground state, while some of the electrons occupy the states above the Fermi surface as pairs in BCS one. Let us simplify the notations of pairing states; $|1\rangle_{\mathbf{k}} (|0\rangle_{\mathbf{k}})$ represents occupation (unoccupation) of $(\mathbf{k} \uparrow, -\mathbf{k} \downarrow)$, whose probability amplitude is defined as $v_{\mathbf{k}} (u_{\mathbf{k}})$. They satisfy

$$v_{\mathbf{k}}^2 + u_{\mathbf{k}}^2 = 1. \quad (2.78)$$

BCS wavefunction is written as

$$|\Psi\rangle = \prod_{\mathbf{k}} [u_{\mathbf{k}} |0\rangle_{\mathbf{k}} + v_{\mathbf{k}} |1\rangle_{\mathbf{k}}]. \quad (2.79)$$

Normal ground state is represented by

$$\begin{cases} v_{\mathbf{k}} = 1, & u_{\mathbf{k}} = 0 & (|\mathbf{k}| < k_F) \\ v_{\mathbf{k}} = 0, & u_{\mathbf{k}} = 1 & (|\mathbf{k}| > k_F). \end{cases} \quad (2.80)$$

Creation and annihilation operators for pairs are defined as $\eta_{\mathbf{k}}^{\dagger}$ and $\eta_{\mathbf{k}}$, respectively.

$$\eta_{\mathbf{k}}^{\dagger} |1\rangle_{\mathbf{k}} = 0 \quad (2.81)$$

$$\eta_{\mathbf{k}}^{\dagger} |0\rangle_{\mathbf{k}} = |1\rangle_{\mathbf{k}} \quad (2.82)$$

$$\eta_{\mathbf{k}} |1\rangle_{\mathbf{k}} = |0\rangle_{\mathbf{k}} \quad (2.83)$$

$$\eta_{\mathbf{k}} |0\rangle_{\mathbf{k}} = 0 \quad (2.84)$$

By using these operators, phonon mediated electron-electron scattering $(\mathbf{k} \uparrow, -\mathbf{k} \downarrow) \rightarrow (\mathbf{k}' \uparrow, -\mathbf{k}' \downarrow)$ is described as $\eta_{\mathbf{k}'}^{\dagger} \eta_{\mathbf{k}}$. Thus its Hamiltonian is

$$V = -V_0 \sum_{\mathbf{k}\mathbf{k}'} \eta_{\mathbf{k}'}^\dagger \eta_{\mathbf{k}}. \quad (2.85)$$

where V_0 is energy gain due to the interaction. Here $\mathbf{k}$ is limited by $\varepsilon_F - \hbar\omega_D < \varepsilon_{\mathbf{k}} < \varepsilon_F + \hbar\omega_D$. The expected value of the energy reduction is described as follows;

$$\langle \Psi | V | \Psi \rangle = -V_0 \left[\prod_p (u_p \langle 0 | p + v_p | 1 \rangle_p) \left(\sum_{\mathbf{k}\mathbf{k}'} \eta_{\mathbf{k}'}^\dagger \eta_{\mathbf{k}} \right) \prod_{p'} (u_{p'} \langle 0 | p' + v_{p'} | 1 \rangle_{p'}) \right]. \quad (2.86)$$

Since $\langle 1 | 1 \rangle_{\mathbf{k}\mathbf{k}'} = \delta_{\mathbf{k}\mathbf{k}'}$, $\langle 0 | 0 \rangle_{\mathbf{k}\mathbf{k}'} = \delta_{\mathbf{k}\mathbf{k}'}$, $\langle 0 | 1 \rangle_{\mathbf{k}\mathbf{k}'} = 0$,

$$\langle \Psi | V | \Psi \rangle = -V_0 \sum_{\mathbf{k}\mathbf{k}'} v_{\mathbf{k}} u_{\mathbf{k}'} u_{\mathbf{k}} v_{\mathbf{k}'}. \quad (2.87)$$

On the other hand, Cooper pair formation increases kinetic energy E_{kin} of the system.

$$E_{\text{kin}} = 2 \sum_{\mathbf{k}} \varepsilon_{\mathbf{k}} v_{\mathbf{k}}^2. \quad (2.88)$$

Here, $\varepsilon_{\mathbf{k}} = \varepsilon_{\mathbf{k}} - \varepsilon_F$. Thus, we obtain the expected value of total energy W as

$$W = 2 \sum_{\mathbf{k}} \varepsilon_{\mathbf{k}} v_{\mathbf{k}}^2 - V_0 \sum_{\mathbf{k}\mathbf{k}'} v_{\mathbf{k}} u_{\mathbf{k}'} u_{\mathbf{k}} v_{\mathbf{k}'}. \quad (2.89)$$

By minimizing W with respect to variations in $v_{\mathbf{k}}$, $u_{\mathbf{k}}$,

$$2\varepsilon_{\mathbf{k}} - V_0 \frac{1 - 2v_{\mathbf{k}}^2}{v_{\mathbf{k}} u_{\mathbf{k}}} \sum_{\mathbf{k}'} u_{\mathbf{k}'} v_{\mathbf{k}'} = 0. \quad (2.90)$$

Here we used $\partial W / \partial v_{\mathbf{k}}^2 = 0$. The summation about $\mathbf{k}'$ is constant so that we define a constant Δ by

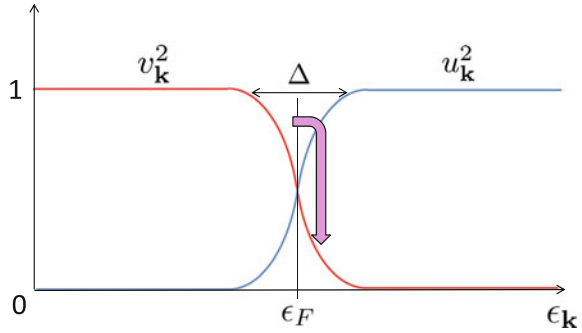
$$\Delta \equiv V_0 \sum_{\mathbf{k}'} u_{\mathbf{k}'} v_{\mathbf{k}'}. \quad (2.91)$$

Then,

$$\frac{v_{\mathbf{k}} u_{\mathbf{k}}}{1 - 2v_{\mathbf{k}}^2} = \frac{\Delta}{2\varepsilon_{\mathbf{k}}} \quad (2.92)$$

From Eq. (2.78), we obtain a quadratic

Fig. 2.9 Schematic drawing of the probability amplitude of the BCS ground state as a function of energy. The $v_{\mathbf{k}}$ is the probability amplitude as a Cooper pair. Electrons in an energy window $\varepsilon_F \pm \Delta$ are redistributed from the ground state of free electron model



$$v_{\mathbf{k}}^4 - v_{\mathbf{k}}^2 + \frac{\Delta^2}{4E_{\mathbf{k}}^2} = 0, \quad (2.93)$$

$$E_{\mathbf{k}} = \sqrt{\varepsilon_{\mathbf{k}}^2 + \Delta^2}, \quad (2.94)$$

which can be solved to yield

$$\begin{cases} u_{\mathbf{k}}^2 = \frac{1}{2} \left(1 + \frac{\varepsilon_{\mathbf{k}}}{E_{\mathbf{k}}} \right), \\ v_{\mathbf{k}}^2 = \frac{1}{2} \left(1 - \frac{\varepsilon_{\mathbf{k}}}{E_{\mathbf{k}}} \right). \end{cases} \quad (2.95)$$

This indicates that electrons slightly below the Fermi surface ($\varepsilon_F - \Delta < \varepsilon < \varepsilon_F$) redistribute above the Fermi surface ($\varepsilon_F < \varepsilon < \varepsilon_F + \Delta$) in the BCS ground state. (Fig. 2.9).

Superconducting gap

Subtracting Eqs. (2.91) to (2.95) leads to

$$\Delta = V_0 \sum_{\mathbf{k}} \left[\frac{1}{2} \left(1 - \frac{\varepsilon_{\mathbf{k}}}{E_{\mathbf{k}}} \right) \frac{1}{2} \left(1 + \frac{\varepsilon_{\mathbf{k}}}{E_{\mathbf{k}}} \right) \right]^{1/2} \quad (2.96)$$

$$= \frac{1}{2} V_0 \sum_{\mathbf{k}} \left(\frac{E_{\mathbf{k}}^2 - \varepsilon_{\mathbf{k}}^2}{E_{\mathbf{k}}^2} \right)^{1/2} \quad (2.97)$$

$$= \frac{\Delta}{2} V_0 \sum_{\mathbf{k}} \frac{1}{(\varepsilon_{\mathbf{k}}^2 + \Delta^2)^{1/2}}. \quad (2.98)$$

The summation about k' is able to be replaced by integral;

$$1 = \frac{N(\varepsilon_F)V_0}{2} \int_{-\hbar\omega_D}^{\hbar\omega_D} \frac{1}{(\varepsilon^2 + \Delta^2)^{1/2}} d\varepsilon \quad (2.99)$$

$$= N(\varepsilon_F)V_0 \int_0^{\hbar\omega_D} \frac{1}{(\varepsilon^2 + \Delta^2)^{1/2}} d\varepsilon \quad (2.100)$$

$$= N(\varepsilon_F)V_0 \sinh^{-1} \left(\frac{\hbar\omega_D}{\Delta} \right). \quad (2.101)$$

Hence

$$\frac{\hbar\omega_D}{\Delta} = \sinh \left(\frac{1}{N(\varepsilon_F)V_0} \right). \quad (2.102)$$

In weak coupling superconductor, $N(\varepsilon_F)V_0 \ll 1$. So

$$\Delta = 2\hbar\omega_D \exp \left(-\frac{1}{N(\varepsilon_F)V_0} \right) \quad (2.103)$$

$$= 2k_B\Theta_D \exp \left(-\frac{1}{N(\varepsilon_F)V_0} \right), \quad (2.104)$$

where Θ_D is the Debye temperature.

The approximation of $N(\varepsilon_F)V_0 \ll 1$ cannot be applied to strong coupled superconductors. Some of the results here are modified by analytical solution of electron-phonon coupling Hamiltonian (described later).

In the BCS ground state, electrons are above Fermi energy as pairs. Thus, elemental excitation (or *quesiparticle*) is half filling of a pair state. Then the system gets kinetic energy of an unpaired electron

$$\delta E = \varepsilon_{\mathbf{k}} - \left(2\varepsilon_{\mathbf{k}}v_{\mathbf{k}}^2 - 2V_0v_{\mathbf{k}}u_{\mathbf{k}} \sum_{\mathbf{k}'} v_{\mathbf{k}'}u_{\mathbf{k}'} \right). \quad (2.105)$$

Here Eq. (2.89) is used. From Eqs. (2.91) and (2.95), one can find that δE corresponds to $E_{\mathbf{k}}$ in Eq. (2.94). This leads to the dispersion relation of superconducting state;

$$E_{\mathbf{k}} = \sqrt{\varepsilon_{\mathbf{k}}^2 + \Delta^2}. \quad (2.106)$$

It has an energy gap of 2Δ as seen in Fig. 2.10a. Since normal electronic states turn into superconducting states one-to-one, the density of state in superconducting phase $N_s(E)$ has easy relationship with normal density of state $N_n(\varepsilon)$;

$$N_s(E)dE = N_n(\varepsilon)d\varepsilon. \quad (2.107)$$

Then,

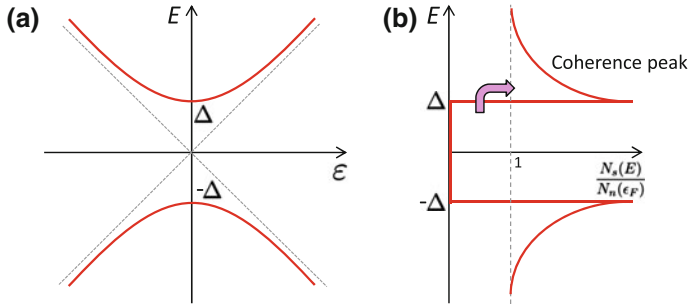


Fig. 2.10 Schematic pictures describing the BCS ground state. **a** The dispersion relationship of quasi particles. There opens a gap of 2Δ centering on ϵ_F . **b** The energy distribution of density of state. The states inside of the gap are moved and stacked to form coherence peaks at $E = \pm\Delta$ with Cooper pair generation

$$N_s(E) = N_n(\epsilon) \frac{d\epsilon}{dE} \quad (2.108)$$

$$= N_n(\epsilon) \frac{d}{dE} \sqrt{E^2 - \Delta^2}. \quad (2.109)$$

Around the Fermi energy, $N_n(\epsilon_F)$ is approximately constant. Then we obtain

$$\frac{N_s(E)}{N_n(\epsilon_F)} = \begin{cases} 0 & (|E| < \Delta), \\ \frac{|E|}{\sqrt{E^2 - \Delta^2}} & (|E| > \Delta). \end{cases} \quad (2.110)$$

As shown in Fig. 2.10b, the energy gap of 2Δ is clearly opened. The normal states within $\epsilon_F - \Delta < E < \epsilon_F + \Delta$ are stacked at $E = \pm\Delta$, resulting in sharp peaks (coherence peaks).

Superconducting gap at finite temperature

At finite temperature, thermal energy breaks Cooper pairs and creates quasi particles with the dispersion Eq. (2.106). Then, Δ decreases by heating the system and vanishes at T_c .

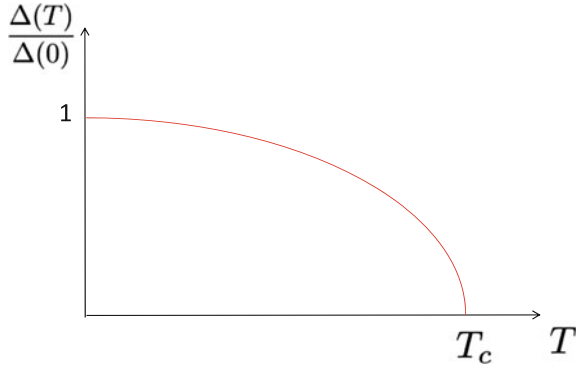
The quasi particles obey Fermi distribution.

$$f(E_{\mathbf{k}}) = \frac{1}{\exp(E_{\mathbf{k}}/k_B T) + 1}. \quad (2.111)$$

Hence, the occupation probability of Cooper-paired states is described as $1 - 2f(E_{\mathbf{k}})$ at finite temperature. In order to obtain temperature-dependency of superconducting gap $\Delta(T)$, we consider the occupation probability in Eq. (2.100).

$$1 = N(\epsilon_F) V_0 \int_0^{\hbar\omega_D} \frac{1 - 2f(E_{\mathbf{k}})}{(\epsilon^2 + \Delta^2)^{1/2}} d\epsilon. \quad (2.112)$$

Fig. 2.11 Schematically drawn temperature dependence of superconducting gap in the BCS theory



In Fig. 2.11, numerically obtained $\Delta(T)$ is displayed. Around the T_c , approximately

$$\frac{\Delta(T)}{\Delta(0)} \sim 1.74 \sqrt{1 - \frac{T}{T_c}}, \quad (2.113)$$

indicating rapid destruction of Cooper pairs.

Furthermore, from $\Delta(T_c) = 0$,

$$1 = N(\varepsilon_F) V_0 \int_0^{\hbar\omega_D} \frac{\tanh(\varepsilon/2k_B T_c)}{\varepsilon} d\varepsilon. \quad (2.114)$$

This leads to

$$k_B T_c = 1.14 \hbar\omega_D \exp\left(-\frac{1}{N(\varepsilon_F) V_0}\right). \quad (2.115)$$

In weak coupling superconductor, comparison between this equation and Eq. (2.104) give us an universal relation:

$$\frac{\Delta(0)}{k_B T_c} = 1.76. \quad (2.116)$$

Connection to phenomenology

Once the BCS theory had been established [8], the phenomenologies by London, Ginzburg and Landau was confirmed, starting from the microscopic origin [9–11]. That is, what is called *superelectron* in London theory is actually Cooper pair with charge of $e_s = 2e$ and effective mass of $m_s = 2m^*$. Here I summarize the important results from the phenomenologies.

$$\text{Penetration length } \lambda_L = \left(\frac{m^* \beta}{2\mu_0 e^2 a T_c} \right)^{1/2} \left(1 - \frac{T}{T_c} \right)^{-1/2} \quad (2.117)$$

$$\text{Quantized magnetic flux } \phi_0 = \frac{h}{2e} = 2.07 \times 10^{-15} (\text{Wb}) \quad (2.118)$$

$$\text{GL coherence length } \xi_{\text{GL}}(T) = \left(\frac{\hbar^2}{4m^* a T_c} \right)^{1/2} \left(1 - \frac{T}{T_c} \right)^{-1/2} \quad (2.119)$$

$$\text{GL parameter } \kappa \equiv \frac{\lambda_L}{\xi_{\text{GL}}} = \frac{m^*}{e\hbar} \sqrt{\frac{2\beta}{\mu_0}} \quad (2.120)$$

$$\text{Upper critical field } \mu_0 H_{c2}(T) = \frac{\phi_0}{2\pi \xi_{\text{GL}}(0)^2} \left(1 - \frac{T}{T_c} \right) \quad (2.121)$$

What is microscopic picture of magnetic decoupling of Cooper pairs? Since paired two electrons have opposite momentum each other, their binding is broken by Lorentz force. This is called *orbital pair breaking*. In ordinal superconductor, orbital breaking occurs at small magnetic field and determines the upper critical field. However, when it is suppressed by some reason, Cooper pair survives until spin-singlet component becomes unstable by Zeeman effect. This is called *paramagnetic effect*. The BCS theory predicts that this effect occurs at $\mu_0 H_p(T) = 1.86 T_c(\text{K})$ at 0 K (Pauli limit).

The BCS theory also gives microscopic interpretations of coherence length. In the real space, the length scale corresponding to superconducting gap is given by the uncertainty principle:

$$\xi_0 = \frac{\hbar v_F}{\pi \Delta(0)}. \quad (2.122)$$

This is called Pippard's coherence length and regarded as *characteristic size of Cooper pair*. Namely, an electron feels the interaction from another one at the distance of ξ_0 or less and forms a bound state. This is why macroscopic superconducting state cannot vary within coherence length.

It should be noted that, since ξ_0 is ideal coherence length, the effective coherence length ξ is suppressed by impurity scattering as

$$\frac{1}{\xi} = \frac{1}{\xi_0} + \frac{1}{l}, \quad (2.123)$$

where l is mean free path of normal electrons. $\xi_0 \ll l$ is called clean limit while $\xi_0 \gg l$ is dirty limit. In dirty limit,

$$\xi = 0.85\sqrt{\xi_0 l}. \quad (2.124)$$

In usual case, the effective coherence length coincides to experimental obtained GL coherence length.

2.3.4 Josephson Effect and Critical Current

Let us consider two superconducting materials described by macroscopic wavefunctions: $\Psi_i = \Delta_i(0)e^{i\Phi_i}$ ($i = 1, 2$). When the two superconductors are coupled by a weak link (e.g. a thin insulating barrier), a current flows indefinitely long without any voltage applied, due to the difference in phase of the wavefunction. This is called *Josephson effect*. Current density driven by a Josephson junction (JJ) is given as

$$J = J_c \sin(\Phi_2 - \Phi_1), \quad (2.125)$$

$$J_c \equiv \gamma \frac{e\hbar}{m^*} \Delta_1(0) \Delta_2(0). \quad (2.126)$$

[12]. Here γ is strength of the coupling and J_c is the maximum current density. Sometimes JJ is naturally formed by defects and impurities. In superconducting thin films, superconducting regions tend to be patched and connected via JJs each other. It is pointed that even atomic steps on the surface act as JJs in superconducting surface systems on semiconductors [13]. If the current through JJ is applied more than Eq. (2.126), superconductivity is broken down [13–15]. Such threshold is called critical current I_c , which relates with normal state resistance R_n as follows.

$$I_c(T) = \frac{\pi \Delta(T)}{2eR_n} \tanh\left(\frac{\Delta(T)}{2k_B T}\right) \quad (2.127)$$

For the interior of cleaner superconductor, on the other hand, I_c is determined by pair breaking current [16]; When superconducting current is flowing with group velocity v_s , the center-of-mass of Cooper pair's momentum $\mathbf{K}$ is non-zero and the energy of quasi particle is $\hbar k_F v_s$. The pair is broken when this shift reaches to $\Delta(T)$. Thus critical current is proportional to $\Delta(T)$;

$$I_s(T) \propto \left[1 - \left(\frac{T}{T_c}\right)^2\right]^{3/2}. \quad (2.128)$$

2.4 Special Cases of Superconductivity

2.4.1 Strong Coupled Superconductor

$\lambda \equiv N(\varepsilon_F)V_0$ in Eq. (2.115) indicates how strongly electrons feel attractive interaction. If it is mediated by phonon, λ is called electron-phonon coupling constant. In the BCS theory above, it has been assumed that $\lambda \equiv N(\varepsilon_F)V_0 \sim 0$. Eliashberg expanded the discussion to strong coupling case and McMillan and Allen-Dynes calculated the critical temperature at $\lambda \sim 1$ [17, 18].

$$T_c = \frac{\hbar\omega_D}{1.45k_B} \exp \left[-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)} \right], \quad (2.129)$$

where μ^* is a parameter of the direct repulsive interaction between electrons. Typically it is 0.1–0.15. Equation (2.129) is rewritten using the Debye temperature Θ_D as

$$T_c = \frac{\Theta_D}{1.45} \exp \left[-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)} \right]. \quad (2.130)$$

Then, Eq. (2.116)

$$a \equiv \frac{\Delta(0)}{k_B T_c} = 1.76 \quad (2.131)$$

is also need to be modified. Experimentally, the constant a is enhanced. In typical example of bulk Pb with $\lambda = 1.2 - 1.7$ [19], $a = 2.19$ [20]. Since materials in this study also have large electron-phonon coupling, I considered the possible enhancement of a to convert T_c to the superconducting gap. Namely, the gap is estimated by

$$\Delta(0) = a k_B T_c, \quad (2.132)$$

where a is ranged from 1.76 to 2.2.

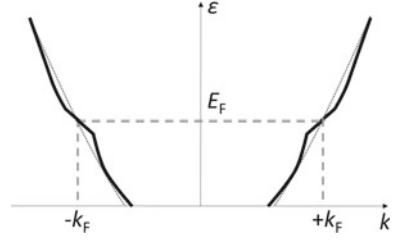
One can see the effect of strong electron-phonon coupling in enhancement of the effective mass of normal state electron as;

$$\lambda = \frac{m' - m^*}{m^*}. \quad (2.133)$$

m^* is effective mass without electron-phonon coupling while m' is enhanced one.

Since Fermi energy in metal is $\sim 10^5$ K while Debye temperature is in the order of several hundred Kelvin, the enhancement of effective mass occurs at only the neighborhood of Fermi surface. Thus, there appear *kink* structure in the band dispersion near Fermi surface (Fig. 2.12), which is a sign of strong electron-phonon

Fig. 2.12 Schematic picture of a kink structure in an electronic band dispersion, which induced by the electron-phonon interaction



interaction observed in recent studies on superconductivity by ARPES [21, 22]. The spectral function $A(\mathbf{k}, \omega)$ measured by ARPES [23] provides information on both the single-particle electronic dispersion $\varepsilon_0(\mathbf{k})$ and the quasi particle self-energy $\Sigma(\mathbf{k}, \omega) = \Sigma'(\mathbf{k}, \omega) + i\Sigma''(\mathbf{k}, \omega)$. The real and imaginary parts account for the renormalization of electron energy and lifetime due to many-body interactions e.g. electron-phonon coupling. Both of them are directly obtained by fitting with a Lorentzian, the ARPES intensity profiles at constant energy (momentum distribution curve, MDC); The real and imaginary parts of self-energy can be determined by peak position and peak width, respectively. Here we define Eliashberg function $F(\omega)$, which is the phonon density of states weighted by the electron-phonon coupling strength;

$$\lambda \equiv 2 \int_0^\infty \frac{d\omega}{\omega} \alpha(\omega)^2 F(\omega) \quad (2.134)$$

Then Σ'' is described by the following equation.

$$\Sigma'' = \pi h \int_0^{\omega_D} d\omega' \alpha(\omega')^2 F(\omega') [1 - f(\omega - \omega') + f_B(\omega') + f(\omega + \omega')] + W_0. \quad (2.135)$$

Here, ω_D is the Debye frequency and W_0 is a constant. $f_B(\omega)$ and $f(\omega)$ are distribution function of phonon (boson) and electron (fermion), respectively. Therefore, the momentum resolved $\alpha(\omega)^2 F(\omega)$ function can be extracted from the $\Sigma''(\mathbf{k}, \omega)$ probed by ARPES by the integral inversion procedure, resulting in calculation of total electron-phonon coupling λ .

At temperature sufficiently higher than Debye temperature, Eq.(2.135) can be simplified as:

$$\Sigma'' = \pi \lambda k_B T + W_0. \quad (2.136)$$

This indicates that we can extract λ from temperature-dependent ARPES spectrum.

2.4.2 Two-Dimensional Superconductivity

As a general sense, the term “two-dimensional superconductor” does not necessarily mean true 2D system—it does mean that the thickness of superconducting electron/hole system is thinner than coherence length $\xi_{GL}(0)$. The first notable property of 2DSC is anisotropy in upper critical field [24–27]. Since the out-of-plane electron motion is prohibited, orbital breaking of Cooper pair is no longer dominant when magnetic field is applied for the in-plane direction. Instead, Pauli paramagnetic effect may determine the upper critical field. This is an experimental advantage to probe spin-related superconducting phenomena, which are predicted in exotic 2DSC systems introduced later.

The next point to be consider is effect of *fluctuation*. As is schematically shown in Fig. 2.13a, when a d -dimensional system is in normal conducting state, the superconducting condensation energy per unit volume required for the first pair is $\mu_0 H_{c2}^{\parallel}/2$. On the one hand, at finite temperature, a system has thermal fluctuation $k_B T$ due to the Fermi distribution function. The fluctuation promote the formation of Cooper pair, which cause gradual decrement of resistance from slightly above the critical temperature. On the other hand, when the system is in superconducting state, the thermal fluctuation create the vortex pairs, which induce residual resistance below T_c (Fig. 2.13b). These effects arise from amplitude and phase part of order parameter, respectively. They cannot be negligible when

$$k_B T \sim \xi^d \frac{\mu_0 H_{c2}^{\parallel}}{2}, \quad (2.137)$$

where the diameter of a Cooper pair ξ^d is considered. Equation (2.137) indicate that the required thermal energy is smaller in lower dimension. This is why we have to consider the thermal fluctuation in low-dimensional superconductors.

Amplitude fluctuation

The correction due to fluctuation in amplitude of order parameter near T_c is described as follows. [28, 29].

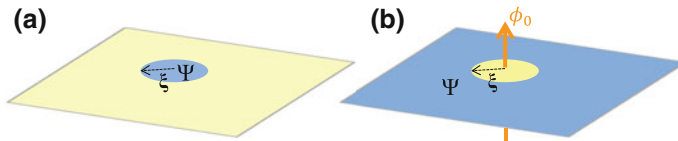


Fig. 2.13 Conceptual illustrations describing the effect of thermal fluctuation on the superconductivity. The yellow (blue) region indicates normal (superconducting) state. **a** amplitude fluctuation, where a Cooper pair is generated by thermal fluctuation even in $T > T_c$. **b** Phase fluctuation, where a vortex is generated by thermal fluctuation even in $T < T_c$

$$\rho = \frac{1}{\sigma_0 + \sigma_{\text{AL}} + \sigma_{\text{MT}}}, \quad (2.138)$$

$$\sigma_{\text{AL}} = \frac{e^2}{16\hbar} \cdot \frac{T_c}{T - T_c}, \quad (2.139)$$

$$\sigma_{\text{MT}} = \frac{e^2}{8\hbar} \cdot \frac{T_c}{T - (1 + \delta)T_c} \ln \frac{T - T_c}{\delta T_c}. \quad (2.140)$$

σ_{AL} is called Aslamazov-Larkin (AL) term, corresponding to excess conductivity carried by thermally created Cooper pairs. σ_{MT} is Maki-Thompson (MT) term, which is contribution due to the coherent scattering of electrons forming a Cooper pair on the same elastic impurity. It includes material-dependent pair-breaking parameter δ , whose typical value is ca. 0.1. Particularly, the MT term is important in clean two-dimensional superconducting systems.

Phase fluctuation

The idea of phase fluctuation is originated from Berezinskii-Kosterlitz-Thouless transition (BKT transition). The BKT transition can be found in 2D condensed matter systems that are approximated by XY model. The XY model is a two-dimensional vector spin model, which is not expected to possess a long-range order except absolute zero-temperature because of transverse fluctuations (Mermin-Wagner theorem). At finite temperature, one finds a quasi-ordered phase called *topological order*, where spin waves with long wavelength are excited and the spin angle varies over long distance as shown in Fig. 2.14. Vortices, where the sum of angle changes along an arbitrary closed curve around it is kept $2\pi n$ (n is integer) are topologically stable configurations. Here, generation of a single free vortex takes much higher energy than bound vortex-antivortex pairs (see Fig. 2.14b) because of topology. This bound antiparallel vortex pairs is dissociated thermodynamically into unbound vortices above a characteristic temperature T_{BKT} . This kind of transition is called BKT transition.

It is noted that the 2D XY models can be applied to many cases of real 2DSC systems, where patched superconducting areas are connected each other by JJs and each area has own phase of order parameter. Since in type-II superconductor, penetrating magnetic flux gives additional phase of 2π surrounding superconducting order parameter, it directly means *vortex* as a topological defect. When fluctuation-induced free vortices are moved by external current in the transverse direction, the motion gives rise to a voltage drop in the longitudinal direction, resulting in finite energy dissipation. However, for $T < T_{\text{BKT}}$, vortices appear as only bound pair states due to the topological order, namely, no free vortices exist, resulting in the true zero-resistance state. For $T_{\text{BKT}} < T < T_c$, more and more free vortices start to be generated and cause resistance described by Halperin-Nelson equation as follows [30]:

$$R \propto \exp \left[-2b \left(\frac{T_c - T_{\text{BKT}}}{T - T_{\text{BKT}}} \right)^{1/2} \right]. \quad (2.141)$$

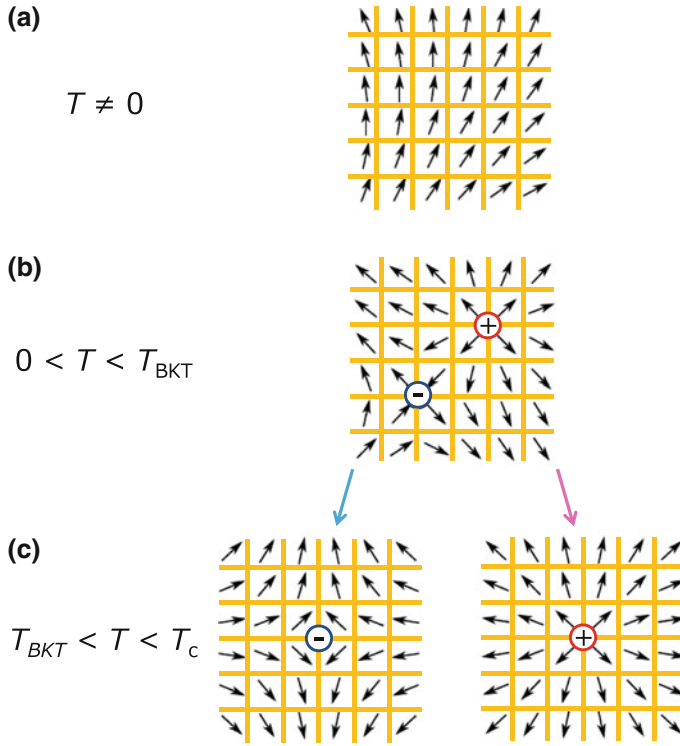


Fig. 2.14 Analogical explanation of the BKT transition in the two-dimensional spin system. **a** Topological order, which is conserved in pure two-dimensional system at $T \neq 0$ despite of long-range spin wave. **b** and **c** Vortex as a defect of topological order. The pairs are excited by low energy, while depaired vortices move freely at higher temperature than T_{BKT}

In the dirty limit 2D superconductor, following equation is also used to estimate T_{BKT} [31];

$$\frac{T_{\text{BKT}}}{T_c} \sim \frac{1}{1 + 0.17 \frac{R_n}{R_c}}. \quad (2.142)$$

Here, R_n is normal state resistance and $R_c = \hbar/e^2 = 4.11 \text{ k}\Omega$.

The vortex-antivortex pairs become unbound under finite external current. This unbinding occurs progressively as the current is increased, leading to a current-voltage ($I - V$) characteristics of power law dependence. As temperature is lowered from above T_{BKT} , exponent n jumps universally from 1 to 3 at $T = T_{\text{BKT}}$ and increases further at lower temperatures, which is one of the hallmarks of the BKT transition. Since 1980's, current-voltage characteristics in superconducting thin films have been intensively studied in terms of BKT physics [25, 32–38]. However, no

results reproduced the theoretical prediction completely. It is still open question whether we can find BKT transition in quasi-2D systems.

2.4.3 Disorder-Induced Superconductor-Insulator Transition

In 2D superconductor, it is known that disorder plays important role. The most significant and general phenomena is disorder-induced SIT; 2D systems is transit from superconducting phase to insulating directly by introduction of disorder. This is in clear contrast to the 3D case where superconductivity is robust against disorder.

As mentioned in Sect. 2.2.4, a normal metal transits into an insulator due to the Anderson localization when its resistance exceeds the quantized resistance of single electron;

$$\frac{h}{e^2} = 25.8 \text{ (k}\Omega\text{)}. \quad (2.143)$$

The disorder-induced SIT also occurs with respect to resistance at the quantized value of Cooper pair [39]

$$R_c = \frac{h}{4e^2} = 6.45 \text{ (k}\Omega\text{)}, \quad (2.144)$$

which is called *quantum critical*.

Close to the SIT, i.e., at $x = x_c$ and $T = 0$, where x is a control parameter, the linear response and the nonlinear response of the system are governed by the divergence of the correlation length ξ [40]. In the critical regime, the divergence of ξ is cut off by a length scale l_T , which is determined by the temperature as $l_T \sim T^{-1/z}$. One can derive a scaling relation for resistance R with temperature and a control parameter near x_c :

$$R(x, T) = F\left(\frac{|x - x_c|}{T^{z\nu}}\right), \quad (2.145)$$

where $F\left(\frac{|x - x_c|}{T^{z\nu}}\right)$ is an arbitrary scaling function. Scaling of the zero bias resistance with T and x determines the product $z\nu$. Experimentally, one can replot $R(x, T)$ as a function of the scaling variable $\frac{|x - x_c|}{T^{z\nu}}$, and adjust the power $z\nu$ to obtain the best visual coincidence of the data [40]. Generally speaking, the value of $z\nu$ relates to universality class of the system. For example, $z\nu = 4/3$ and $2/3$ correspond to the classical percolation and the 3D XY models, respectively. The most famous experimental demonstration of disorder-induced SIT was given by Goldman et al., where superconducting and insulating phases are clearly separated at 6.5 k Ω [41]. Even if a superconductor has slightly lower resistance than quantum critical, perpendicular magnetic field causes SIT (B-SIT) [42]. The transition field of B-SIT (B_c) appears as a crossing point of $R - B$ curves measured at various temperatures (see Fig. 2.15a).

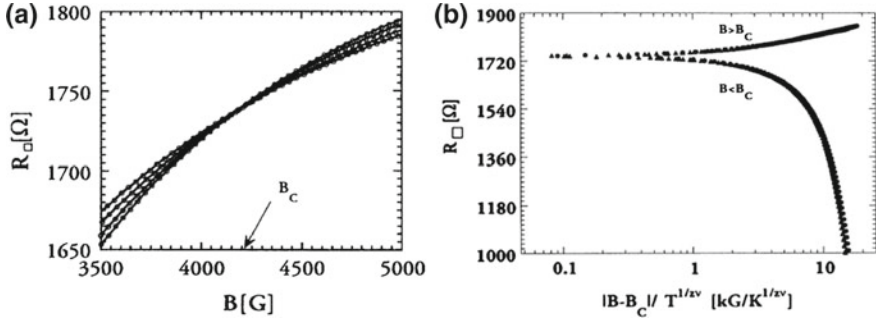


Fig. 2.15 Electrical transport properties of the amorphous MoGe thin film [42]. **a** Magnetic field dependence of sheet resistivity, where the curves cross at one point. **b** Scaling of sheet resistivity as a function of magnetic field and temperature. Reprinted with permission from Ref. [42]

Figure 2.15b shows a result of scaling procedure onto the B-SIT. The resistance curves collapse into two branches: insulator on the high field side ($B > B_c$) and superconductor on low field side ($B < B_c$).

2.4.4 Superconductivity Without Spatial Inversion Symmetry

Since the discovery of high- T_c cuprates, *exotic superconductors* has been intensively studied in the solid state physics community. Here “exotic” means “deviation from BCS theory”. Namely, (at least) one of the following assumptions violates in it:

1. Cooper pairs take zero center-of-mass momentum.
2. Cooper pairs are spin singlet states.
3. Cooper pairs are created by isotropic attractive interaction.

From the third assumption, the superconducting gap $\Delta(0)$ obtained by the BCS theory is isotropic. Such isotropic superconducting state is named *s-wave* after the analogy to the hydrogen atomic model. When the attractive interaction is not isotropic, anisotropic superconducting states (*p*, *d*, *f*, ...-wave) are possible, which have different parity.

Let us consider a Cooper pair originates from two electrons denoted by $(\mathbf{r}_{1,2}, \sigma_{1,2})$: $\Psi(\mathbf{r}, \sigma_1, \sigma_2) = \psi(\mathbf{r})\chi(\sigma_1, \sigma_2)$ ($\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$: relative coordinate). Its orbital and spin parts are classified by their parities as follows;

$$\text{Even function } \psi_{\text{even}}(-\mathbf{r}) = \psi_{\text{even}}(\mathbf{r}), \quad (2.146)$$

$$\text{Odd function } \psi_{\text{odd}}(-\mathbf{r}) = -\psi_{\text{odd}}(\mathbf{r}), \quad (2.147)$$

$$\text{Singlet } \chi_s(\sigma_2, \sigma_1) = -\chi_s(\sigma_1, \sigma_2), \quad (2.148)$$

$$\text{Triplet } \chi_t(\sigma_2, \sigma_1) = \chi_t(\sigma_1, \sigma_2). \quad (2.149)$$

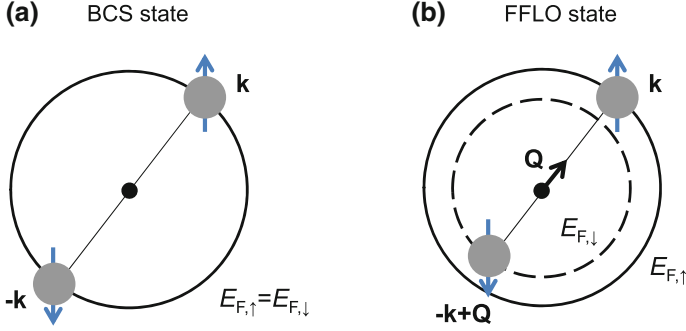


Fig. 2.16 **a** Conceptual illustration of the Cooper pair in **a**, BCS state and **b** FFLO state

According the Pauli exclusion principle, total wavefunction must be antisymmetric against the exchange of two electrons;

$$\Psi(-\mathbf{r}, \sigma_2, \sigma_1) = -\Psi(\mathbf{r}, \sigma_1, \sigma_2). \quad (2.150)$$

Hence, only two combinations below are allowed as pair states.

$$\Psi_{\text{even},s}(\mathbf{r}, \sigma_1, \sigma_2) = \psi_{\text{even}}(\mathbf{r}) \chi_s(\sigma_1, \sigma_2) \quad (2.151)$$

$$\Psi_{\text{odd},t}(\mathbf{r}, \sigma_1, \sigma_2) = \psi_{\text{odd}}(\mathbf{r}) \chi_t(\sigma_1, \sigma_2) \quad (2.152)$$

The latter case is known as spin-triplet superconductor.

The first assumption violates when the system has Zeeman-type spin splitting. As mentioned in Sect. 2.3.3, spin-singlet and zero center-of-mass momentum pair is the most favorable on a spin-degenerate Fermi surface as shown in Fig. 2.16a. On the other hand, on a spin-splitting Fermi surface, spin singlet pair has nonzero center-of-mass momentum. Figure 2.16b shows such a state. This results in spatial variation of order parameter in macroscopic scale, called Fulde-Ferrell-Larkin-Ovchinnikov (FFLO) phase [43, 44].

When the spatial inversion symmetry (SIS) of the system is broken, Rashba-type spin split is expected. This cause another exotic phenomena as mentioned below.

Mixing of singlet and triplet

The first thing to be predicted in superconductors without SIS is generation of Cooper pairs with mixed state of singlet and triplet components [45, 46].

Here we define spatial inversion operator P . If the SIS is conserved, the wavefunction is eigenstate of P i.e. $P\Psi = \pm\Psi$. Actually, the operator P acts on the orbital factor as $P\psi_{\text{even}} = \psi_{\text{even}}$ or $P\psi_{\text{odd}} = -\psi_{\text{odd}}$. Then spatial inversion of a mixed state $\Psi = \psi_{\text{even},s} + a\psi_{\text{odd},t}$ is converted as

$$P\Psi = \psi_{\text{even},s} - a\psi_{\text{odd},t} \neq \pm\Psi. \quad (2.153)$$

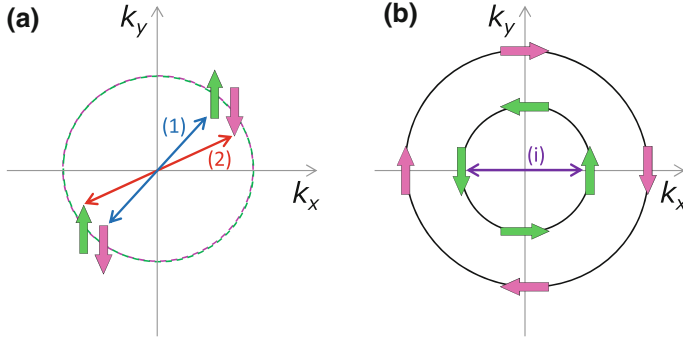


Fig. 2.17 **a** Schematic diagram of the Cooper pairing on a, a spin-degenerate Fermi circle and **b** a spin-split Fermi surface by Rashba effect

This indicates that parity is not conserved in the presence of SIS. However, once SIS is broken, mixed state becomes possible if the system has strong spin-orbit coupling.

In an usual spin-degenerate system, singlet Cooper pairs are formed at the Fermi level as

$$\frac{1}{\sqrt{2}} \left(\underbrace{|\mathbf{k}, \uparrow\rangle |-\mathbf{k}, \downarrow\rangle}_{(1)} - \underbrace{|\mathbf{k}, \downarrow\rangle |-\mathbf{k}, \uparrow\rangle}_{(2)} \right). \quad (2.154)$$

The term (1) and (2) are allowed to be taken from the spin-degenerate two states as shown in Fig. 2.17a. When the Rashba effect occurs, Fermi contour splits into two circles where spin rotates in opposite direction. Let us denote up spin as $\sigma_{\uparrow}$ and down spin as $\sigma_{\downarrow}$ when the spin quantization axis is parallel to $(-k_y, k_x, 0)$. Then, an electron pair with opposite momentums (i) $|\mathbf{k}, \sigma_{\uparrow}\rangle |-\mathbf{k}, \sigma_{\downarrow}\rangle$ (denoted as (i) in Fig. 2.17b) can be considered but the superposition with the counterpart state $|\sigma_{\downarrow}\rangle |\sigma_{\uparrow}\rangle$ is impossible when the energy separation due to Rashba effect E_{SO} is sufficiently large. Of course, the state (i) is not allowed actually because these are neither symmetric nor anti-symmetric with respect to exchange of the two electrons, namely, parity is broken. In order to avoid this problem, we divide (i) $|\mathbf{k}, \sigma_{\uparrow}\rangle |-\mathbf{k}, \sigma_{\downarrow}\rangle$ into two term and add virtual states: $(-|\mathbf{k}, \sigma_{\downarrow}\rangle |-\mathbf{k}, \sigma_{\uparrow}\rangle + |\mathbf{k}, \sigma_{\downarrow}\rangle |-\mathbf{k}, \sigma_{\uparrow}\rangle)/2 \equiv 0$, leading to the pairing state of an admixture of a spin singlet state and a spin triplet state:

$$\underbrace{|\mathbf{k}, \sigma_{\uparrow}\rangle |-\mathbf{k}, \sigma_{\downarrow}\rangle}_{(i)} = \frac{1}{2} \left(\underbrace{|\mathbf{k}, \sigma_{\uparrow}\rangle |-\mathbf{k}, \sigma_{\downarrow}\rangle - |\mathbf{k}, \sigma_{\downarrow}\rangle |-\mathbf{k}, \sigma_{\uparrow}\rangle}_{\text{singlet}} \right) \quad (2.155)$$

$$+ \frac{1}{2} \left(\underbrace{|\mathbf{k}, \sigma_{\uparrow}\rangle |-\mathbf{k}, \sigma_{\downarrow}\rangle + |\mathbf{k}, \sigma_{\downarrow}\rangle |-\mathbf{k}, \sigma_{\uparrow}\rangle}_{\text{triplet}} \right). \quad (2.156)$$

The first line in right hand is spin-singlet, while the second is a spin triplet state with with an in-plane spin projection equal to zero. If the quantization axis is redefined parallel to the z -axis, it corresponds to $|\mathbf{k}, \uparrow\rangle|-\mathbf{k}, \uparrow\rangle$ or $|\mathbf{k}, \downarrow\rangle|-\mathbf{k}, \downarrow\rangle$. So far, superconductivities have been found in several bulk materials with non-centrosymmetric crystal structures [47–51]. Though symmetry of the Cooper pair is discussed by nuclear magnetic resonance etc., there have is no clear evidence proving the mixing of singlet and triplet component.

Electromagnetic responses

Here we consider application of magnetic field to superconductors with strong Rashba effect. When the asymmetric potential gradient is parallel to the z -axis, for magnetic fields in same direction, Cooper pairs between electrons with the momenta $\mathbf{k}$ and $-\mathbf{k}$ are always possible, because the spins in a branch of Fermi contour tilt to same direction as shown in Fig. 2.17a. This implies the suppression of the paramagnetic depairing effect. [52] However, this effect may not been observed because in most cases, orbital effect is dominant for perpendicular magnetic field.

For magnetic fields parallel to the xy -plane, on the other hand, the orbital pair breaking is prohibited in ultrathin 2D superconductors. The Fermi surfaces are deformed into asymmetric shapes as shown in Fig. 2.17b, resulting in the spatially non-uniform order parameter similar to the FFLO state called *stripe or helical phase* [53, 54]. Experimentally, the huge upper critical field observed in the Pb extreme thin film on GaAs seems to be originated from the helical phase [26].

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