12 Superconductivity in metals

In this chapter we focus on the phenomenon of superconductivity and the Bardeen–Cooper–Schrieffer (BCS) (BCS1957) theory behind it. Superconductivity obtains when a finite fraction of the conduction electrons in a metal condense into a quantum state characterized by a unique quantum-mechanical phase. The specific value of the quantum-mechanical phase varies from one superconductor to another. The locking in of the phase of a number of electrons on the order of Avogadro's number ensures the rigidity of the superconducting state. For example, electrons in the condensate find it impossible to move individually. Rather, the whole condensate moves from one end of the sample to the other as a single unit. Likewise, electron scattering events that tend to destroy the condensate must disrupt the phase of a macroscopic number of electrons for the superconducting state to be destroyed. Hence, phase rigidity implies collective motion as well as collective destruction of a superconducting condensate. The only other physical phenomenon that arises from a similar condensation of a macroscopic number of particles into a phase-locked state is that of Bose–Einstein condensation. There is a crucial difference between these effects, however. The particles that constitute the condensate in superconductivity are Cooper pairs, which do not obey Bose statistics. In fact, it is the Pauli principle acting on the electrons comprising a Cooper pair that prevents the complete mapping of the superconducting problem onto a simple one of Bose condensation. As we will see, it is the Pauli principle that makes BCS theory work so well. What do we mean by this? In BCS theory, it is assumed that electrons form Cooper pairs, and the pairs are strongly overlapping. Such a strong overlap would imply a strong correlation between pairs. In fact, it is the correlations between pairs that accounts for most of the observed properties of superconductors, for example the energy gap and the Meissner effect. In BCS theory, however, there is no explicit dynamical interaction between Cooper pairs. The only interaction, if it can be thought of in these terms, is that arising from the Pauli exclusion principle which precludes two Cooper pairs from occupying the same momentum state. That BCS theory works so well speaks volumes for the real nature of pair–pair correlations in metals. It would suggest that real pair–pair interactions in a metal arise primarily from the Pauli exclusion principle, rather than from some additional dynamical interaction. It is primarily for this reason that the simple pairing hypothesis of BCS has had such profound success.

12.1 Superconductivity: phenomenology

At the outset, we lay plain the experimental facts that any theory of superconductivity must explain.

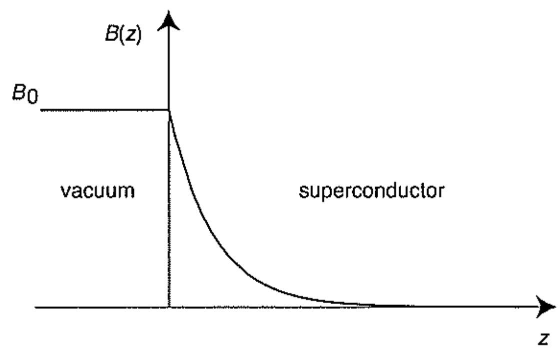

Fig. 12.1 Fall-off of the magnetic field in a Type I superconductor.

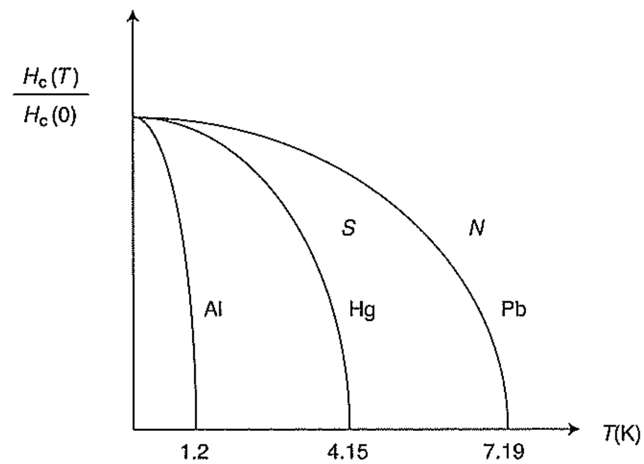

Fig. 12.2 The dependence of the critical field as a function of temperature. The temperatures indicated on the horizontal axis represent the superconducting transition temperatures for a series of metals.

(a) **Zero resistance** The typical signature of superconductivity is the vanishing of the electrical resistance below some critical temperature T_c. The superconducting state is a thermodynamically distinct state of matter. Below T_c, a current flows without any loss. Until the high-T_c materials were made, Nb held the highest transition temperature at 9.26 K.

(b) **Meissner effect** Another feature is the exclusion of magnetic fields, the Meissner effect. Materials in which the Meissner effect is complete are known as Type I superconductors. Consequently, the interior of a Type I superconductor is a perfect diamagnet. A magnetic field applied at the boundary of a Type I superconductor falls off exponentially with distance in the interior of the material, as illustrated in Fig. 12.1. The penetration depth, λ_L, is defined as the distance over which the magnetic field decreases by the factor $1/e$. Below T_c, the field needed to destroy superconductivity increases to some critical value $H_c(T)$, as illustrated in Fig. 12.2. Because the magnetic field inside a superconductor

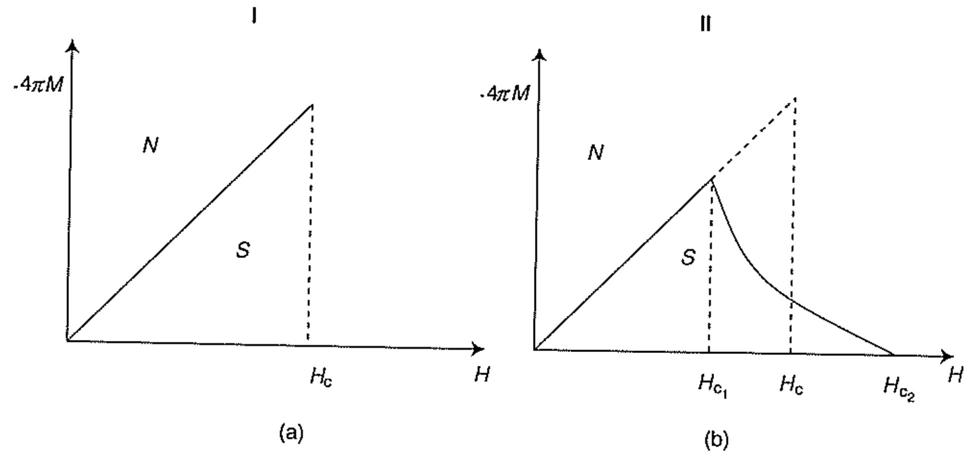

Fig. 12.3 (a) Magnetization vs applied field for a Type I superconductor. (b) Magnetization vs applied field for a Type II superconductor. Between H_{c_1} and H_{c_2}, magnetic field lines penetrate the superconductor but they do not destroy superconductivity. The field lines form a vortex lattice.

is zero,

$$B = 0 = H_{\text{appl}} + 4\pi M, \tag{12.1}$$

where H_{appl} is the applied field and M the magnetization. Solving this equation, we find that the magnetization is

$$M = -\frac{1}{4\pi} H_{\text{appl}}. \tag{12.2}$$

The negative value of M signals that the interior of a superconductor is diamagnetic. At any temperature less than T_c, the magnetization should be a linear function of the applied field. A material having a magnetization of this form is called a Type I superconductor. The normal state is indicated with an N and the superconducting state with an S. Above H_c, $B \neq 0$ and the magnetization no longer obeys Eq. (12.2).

In some materials, superconductivity is observed up to an upper critical field H_{c_2}, but an incomplete Meissner effect is seen between a lower critical field H_{c_1} and H_{c_2}. The resultant magnetization is shown in Fig. 12.3(b). Materials exhibiting a magnetization of this kind are known as Type II superconductors. Between H_{c_1} and H_{c_2}, the magnetic field penetrates the material but superconductivity is not destroyed. The field lines form a regular array known as the Abrikosov (A1957) vortex lattice. All high-T_c cuprate superconductors are Type II.

We are concerned primarily with Type I materials. To understand the penetration depth in a superconductor, we resort to the London equations. First, we need the Maxwell equation for the curl of an electric field: $-\partial \mathbf{B}/\partial t = c\nabla \times \mathbf{E} = c\rho\nabla \times \mathbf{J}$, where ρ is the resistivity. In a perfect conductor $\rho = 0$ and, as a consequence, $\partial \mathbf{B}/\partial t = 0$. In a superconductor, $\rho = 0$ as well. However, it is an experimental fact that $B = 0$

inside a superconductor. This result cannot be deduced from the Maxwell equations. It is the Meissner effect that sets superconductivity apart from materials that just display perfect conductivity. Inside a superconductor, expulsion of magnetic flux is mediated by the current that flows. London proposed in 1935 that everywhere in a superconductor

$$\mathbf{J} = -\text{const.}\mathbf{A}, \tag{12.3}$$

where $\mathbf{A}$ is the vector potential and $\mathbf{B} = \nabla \times \mathbf{A}$. From this ansatz, London was able to show that a magnetic field decays exponentially inside a superconductor. Dimensionally, the constant has units of $1/(L \cdot \text{time})$. Let us write the constant as

$$\text{const.} = \frac{c}{4\pi\lambda_L^2}, \tag{12.4}$$

where c is the speed of light. If we take the curl of both sides of Eq. (12.3), we find that

$$\nabla \times \mathbf{J} = -\frac{c}{4\pi\lambda_L^2}\mathbf{B}. \tag{12.5}$$

From Ampère's law,

$$\nabla \times \mathbf{B} = \frac{4\pi}{c}\mathbf{j}, \tag{12.6}$$

we find that

$$\nabla \times (\nabla \times \mathbf{B}) = \frac{4\pi}{c}\nabla \times \mathbf{J}, \tag{12.7}$$

which implies that

$$\nabla^2\mathbf{B} = \frac{1}{\lambda_L^2}\mathbf{B}. \tag{12.8}$$

The solution to this equation,

$$B(r) = B(0)e^{-r/\lambda_L}, \tag{12.9}$$

is an exponentially decaying magnetic induction on a length scale λ_L. Exponential decay of the magnetic field into a superconductor is the Meissner effect. Let v_s, m^*, and e^*, respectively, be the velocity, mass, and charge of the current carriers in a superconductor. Then

$$m^*\dot{\mathbf{v}}_s = -e^*\mathbf{E}. \tag{12.10}$$

The current of these electrons is defined as $\mathbf{J} = -e^*\mathbf{v}_s n_s$, which, combined with Eq. (12.10), yields

$$\frac{\partial \mathbf{J}}{\partial t} = \frac{n_s e^{*2}}{m^*}E \tag{12.11}$$

for the time evolution of the current. Taking the curl of both sides, we find that

$$\begin{aligned} 0 &= \frac{\partial}{\partial t}(\nabla \times \mathbf{J}) - \frac{n_s e^2}{m^*}\nabla \times \mathbf{E} \\ &= \frac{\partial}{\partial t}\left(\nabla \times \mathbf{J} + \frac{n_s e^{*2}}{m^* c}\mathbf{B}\right). \end{aligned} \tag{12.12}$$

Comparing Eq. (12.12) with Eq. (12.5), we obtain that the penetration depth is

$$\lambda_L = \left(\frac{m^* c^2}{4\pi n_s e^{*2}}\right)^{1/2}. \tag{12.13}$$

We see then that as the superconducting density increases, λ_L decreases.

We can justify the main assumption in the London approach by appealing to the theory of Ginsburg and Landau (GL1950). The crucial ingredient in this phenomenological theory is that the difference in the free energy density between the superconducting and normal states can be written as a functional of an order parameter, $\psi(\mathbf{r})$, for the superconducting state. Physically, $|\psi(\mathbf{r})|^2$ is proportional to the charge density in the superconducting state, n_s. Consequently, we can interpret $\psi(\mathbf{r})$ as the wavefunction of the superconducting state. In BCS theory, $\psi(\mathbf{r})$ plays the role of the center-of-mass wavefunction for a Cooper pair. Near T_c, the superfluid density is small; hence $|\psi|^2 \ll n_e$. Consequently, Ginsburg and Landau expanded the free energy density for the superconducting state in the vicinity of T_c as a power series in $|\psi|^2$,

$$F = F_N + \int d\mathbf{r}\left(\frac{\hbar^2}{2m^*}|\nabla\psi|^2 + a(T)|\psi(\mathbf{r})|^2 + b(T)|\psi(\mathbf{r})|^4\right), \tag{12.14}$$

retaining the kinetic energy term, $|\nabla\psi|^2$, to account explicitly for spatial variations of the field $\psi(\mathbf{r})$. The free energy of the normal state is F_N. The coefficients $a(T)$ and $b(T)$ are real and temperature-dependent and, for stability, $b(T) > 0$.

To find the ground state of the system, we minimize the free energy density with respect to $\psi^*(\mathbf{r})$:

$$-\frac{\hbar^2}{2m^*}\nabla^2\psi(\mathbf{r}) + a(T)\psi(\mathbf{r}) + 2b(T)|\psi(\mathbf{r})|^2\psi(\mathbf{r}) = 0. \tag{12.15}$$

Because the free energy density contains the term $|\nabla\psi|^2$, which is always positive, the free energy is minimized by demanding that $\nabla\psi(\mathbf{r}) = 0$ or, equivalently, that ψ be uniform in space. Consequently, the solution to the saddle point equation is either $\psi = 0$ or

$$|\psi_0|^2 = -\frac{a(T)}{2b(T)} = n_s, \tag{12.16}$$

which implies that $a(T) < 0$. Should $a(T)$ exceed zero, $\psi = 0$, and the system would be in the normal state. Since superconductivity vanishes at T_c, we must have that $a(T_c) = 0$. A Taylor expansion of $a(T)$ around T_c to first order leads to the result that

$$a(T) = a_1(T - T_c) \tag{12.17}$$

with $a_1 > 0$.

We obtain the London conjecture by recalling that the current density in the presence of a vector potential, **A**, is

$$\mathbf{J} = \frac{e^*\hbar}{2im^*}(\psi^*\nabla\psi - \psi\nabla\psi^*) - \frac{e^{*2}}{m^*c}|\psi|^2\mathbf{A}. \tag{12.18}$$

If we assume that the magnetic field is sufficiently small that the equilibrium value of ψ_0 is unchanged, then substitution of ψ_0 into Eq. (12.18) yields the London result

$$\mathbf{J} = -\frac{e^{*2}n_s}{m^*c}\mathbf{A}. \tag{12.19}$$

Using Eq. (12.13), we find that this result is consistent with Eq. (12.4). Hence, from this simple phenomenological approach, we are able to justify the London ansatz for the current density. Indeed, as we will see, the key intellectual content of the BCS theory of superconductivity is the existence of an order parameter describing a charge $2e$ condensate with a well-defined phase, as in the Ginzburg–Landau theory. Such a condensate breaks the $U(1)$ gauge symmetry, as discussed in Chapter 1. In fact, the very existence of the Meissner effect implies the breaking of a continuous symmetry. The fact that a magnetic field cannot penetrate a superconductor tells us immediately that in a superconductor, the photon is massive. Consequently, it can no longer be assumed that the electrons are the propagating degrees of freedom. In fact, in a superconductor they are not. The charge is quantized in units of $2e$, implying that $U(1)$ symmetry is broken.

(c) **Heat capacity** In the superconducting state, the entropy decreases continuously but dramatically, signaling the formation of a highly ordered state. This is depicted in Fig. 12.4(a). As a result, the temperature derivative of the entropy must be steeper on the superconducting side than on the normal side of the transition. Consequently, the heat capacity is discontinuous at T_c, and superconductivity is a second-order phase transition. As shown in Fig. 12.4(b), in the superconducting state, the heat capacity, c_s, falls off as $c_s \propto \exp -\Delta/k_BT$, where Δ is an energy scale. A heat capacity of this form is indicative of an energy gap in the excitation spectrum, with $\epsilon_p > \mu$. Let us verify this with the simple calculation:

$$c_V = \frac{\partial}{\partial T}\int \frac{\epsilon_p d\epsilon_p}{(e^{\beta(\epsilon_p-\mu)}+1)} \xrightarrow{T\to 0} \frac{\partial}{\partial T}\int \epsilon_p e^{-\beta(\epsilon_p-\mu)} d\epsilon_p. \tag{12.20}$$

If $(\epsilon_p - \mu) \approx \Delta$, then $c_V \sim \exp(-\Delta(T = 0)/k_BT)$. Consequently, in the superconducting state, we adopt the picture for the energy gap shown in Fig. 12.5.

The formation of a gap at the Fermi level in the superconducting state results in a lowering of the ground state energy of the system. The gap is actually 2Δ, not Δ. Hence, $\epsilon_p - \mu$ accounts for only half the gap. Experimentally, the gap can be measured by tunneling or ultrasound attenuation experiments. Thermodynamically, the gap gives rise to a discontinuity in the heat capacity. That is, $c_s(T_c^-) - c_N(T_c^+) \neq 0$. Across

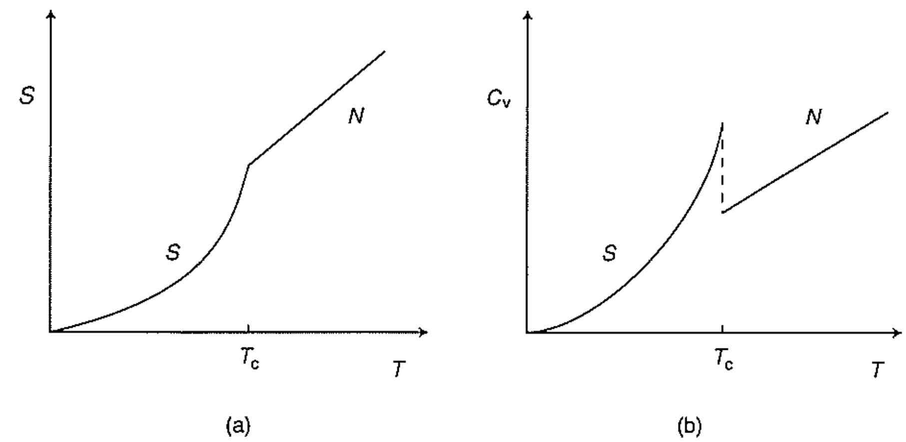

Fig. 12.4 (a) Behavior of the entropy across the superconducting transition. (b) Behavior of the heat capacity in the normal and superconducting states.

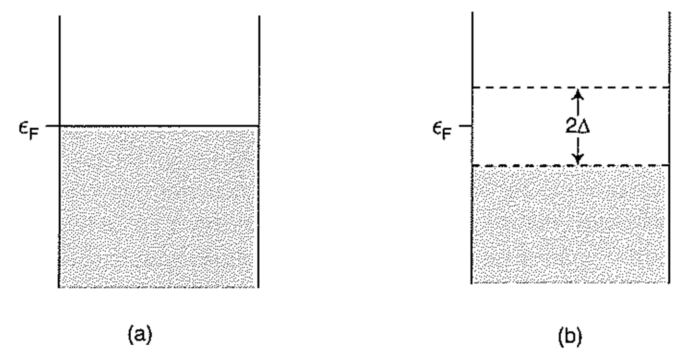

Fig. 12.5 (a) Filled energy levels in the normal state. (b) Formation of an energy gap in the superconducting state. The full gap is 2Δ, not Δ.

the superconducting transition, both first derivatives of the free energy vanish. Hence, no latent heat is associated with the superconducting transition. Above T_c, $\Delta = 0$, and at $T = 0$, Δ has its largest value. A typical plot of $\Delta(T)/\Delta(T = 0)$ is shown in Fig. 12.6. A weak-coupling superconductor has a ratio of $2\Delta(T = 0)/k_B T_c$ in the range 1 to 3. Strong coupling corresponds to $2\Delta(T = 0)/k_B T_c > 4$. The basic energy scale for the creation of an electron–hole pair in a superconductor is 2Δ.

(d) **Microwave and infrared properties** As a result of the gap, photons possessing energies less than 2Δ are not absorbed: all such photons are reflected. Perfect reflection occurs for $\omega < 2\Delta(T = 0)/\hbar$. When this condition is true, photons see a completely resistanceless surface. As $\omega > 2\Delta(T = 0)/\hbar$ at absolute zero, the resistance begins to approach that of the normal state. We estimate this energy by assuming a weak-coupling description is valid for the superconductor. Then $\Delta \sim 2k_B T_c$, and $\omega \sim 4k_B T_c/\hbar$. For a T_c of 5 K, $\omega \sim 10^{12}\ \mathrm{s}^{-1}$. This frequency is in the infrared. Infrared radiation can then penetrate a superconductor and scatter the electrons.

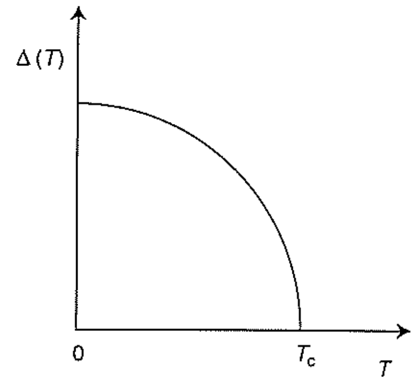

Fig. 12.6 The behavior of the superconducting gap, Δ, as $T \to T_c$.

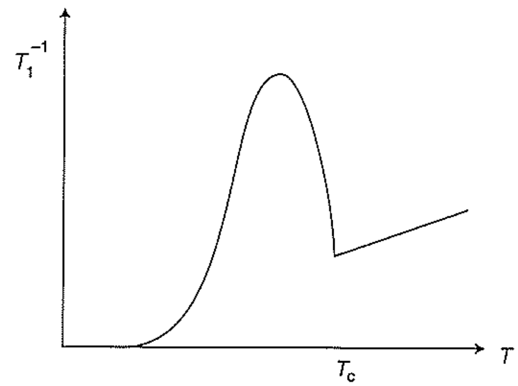

Fig. 12.7 Behavior of the spin-lattice relaxation time at and below T_c. The enhancement in $1/T_1$ is a signature that the spins in a superconductor are acting in consort.

(e) **Ultrasonic attenuation** No damping of an impinging beam of phonons is observed if $\omega_q < 2\Delta/\hbar$. As in the microwave absorption case, ω_q must exceed the energy needed to create an electron–hole pair.

(f) **Nuclear-spin relaxation** Consider a set of nuclei that have been forced to align with a magnetic field. The rate at which the equilibrium magnetization is recovered is the spin lattice relaxation rate, $1/T_1$. In a superconductor, $(1/T_1)_S > (1/T_1)_N$ just below T_c. That is, there is an enhancement in the relaxation rate that is brought on by the formation of the superconducting state. Hebel and Slichter (HS1959) were the first to see this effect experimentally. The peak in the relaxation rate just below T_c is known as the Hebel–Slichter peak.

(g) **Isotope effect** Experimentally, it is observed that if the mass of the ions is changed isotopically, T_c changes accordingly:

$$T_c \propto \frac{1}{\sqrt{M}} \propto \omega_D. \tag{12.21}$$