CHAPTER I

A BRIEF INTRODUCTION
TO THE HISTORY OF SUPERCONDUCTIVITY

The Beginning-Zero Resistance

Superconductivity (London, 1961, Shoenberg, 1965 and Tinkham, 1965) is the name given to a combination of electric and magnetic properties which appears in certain metals when they are cooled to extremely low temperatures. Such very low temperatures first became available in 1908 when Kamerlingh Onnes at the University of Leiden succeeded in liquefying helium (Onnes, 1911). In 1911, when he was studying the variation with the temperature of the electrical resistance of mercury, he observed that the resistance dropped sharply to zero at a temperature of about 4.2 K as shown in figure 1. The same properties were later detected in some other metals. This new phenomenon was termed "*superconductivity*" and the corresponding materials were called "*superconductors*".

The temperature at which the resistance disappears is called the *critical temperature*, T_C; it is different in different superconductors. Among pure metals, this temperature varies from a maximum of 9.25 K for niobium to a minimum of 0.0154 K for tungsten (Abrikosov, 1988). Although these are both low temperatures, in fact the temperature range is very wide, since the extremes differ by about a factor of a thousand.

In what follows we shall also mention the practical applications of superconductors; even at this moment they are numerous. However, the recent discovery of so-called *high temperature superconductivity* (Bednorz and Müller, 1986, Wu *et al.*, 1987, Murphy *et al.*, 1987, Torardi *et al.*, 1988, Subramanian, 1988, and Tarascon, 1988) arouses hope for a further development of such applications. At the moment this thesis was written the highest confirmed

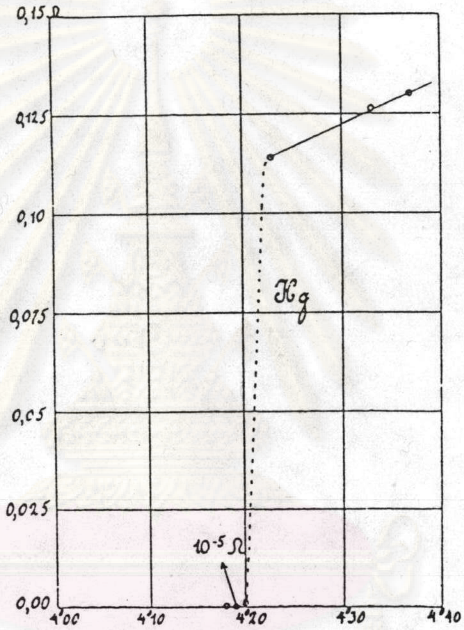

Fig.1.1 The discovery of superconductivity in 1911 by Kamerlingh Onnes. Resistance in ohms of a specimen of mercury versus absolute temperature (Kittel, 1986).

critical temperature was registered for a composition Tl -Ba-Ca-Cu-O (Sheng and Herman, 1988) and is equal to 127 K (Parkin *et al.*, 1988), but the discovery of even higher critical temperatures is not excluded. The importance of these discoveries is based on the fact that the superconductivity in such ceramics can be maintained in a cryostat with liquid nitrogen (boiling point 77.4 K).

Investigations of the properties of superconductors have shown that superconductivity can be destroyed not only by increasing the temperature but also by applying a sufficiently strong magnetic field (H_C) in which the superconductivity is destroyed. This critical field decreases with increasing temperature (Onnes, 1914). It has been established empirically that the dependence on temperature of $H_C(T)$ is described by the formula (Abrikosov, 1988).

$$H_c(T) = H_c(0)\left[1-\left(\frac{T}{T_c}\right)^2\right]$$

Where $H_C(0)$ is the critical magnetic field at 0 K. Superconductivity is also destroyed by a strong electric current (Abrikosov, 1988). If the superconductor is not too thin, the critical current at which resistance appears satisfies Silsbee's rule (Silsbee, 1916) : the magnetic field produced by the critical current at the surface of a superconductor is equal to H_C.

<u>The Meissner Effect</u>

In 1933, one of the basic properties of superconductors ,the so-called *Meissner effect*, was discovered by Meissner and Ochsenfeld (Meissner and Ochsenfeld,1933). If a metal is placed in a magnetic field smaller than H_C, then ,upon the transition into the superconducting state, the field is expelled from its interior, i.e.,the true field $B = 0$ in the superconductor. This is shown in Fig.1. 2.

In more detailed investigations it has been found that the magnetic field is equal to zero only in the bulk of a massive sample. In a thin surface layer the field gradually decreases from a given value at the surface to zero. The thickness of this layer which is called the *penetration depth* (λ), is usually of the order of 10^{-5} -10^{-6} cm (Abrikosov, 1988).

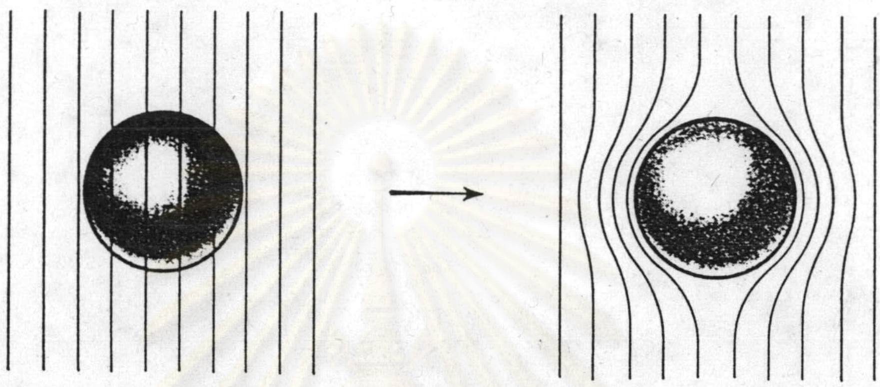

Fig. 1.2 The Meissner effect in a superconducting sphere cooled in a constant applied magnetic field; on passing below the transition temperature the lines of induction B are ejected from the sphere(Kittel, 1986).

The London Theory

In 1934 F. and H. London, motivated by the discovery of the Meissner effect, introduced the first phenomenological theory of superconductivity (London and London, 1935), which is known as the *London Theory*. The purpose of this theory was to express in mathematical form the basic experimental fact that a metal in the superconducting state permits no magnetic field in its interior: (the absence of resistance and the Meissner effect), without consideration of the microscopic factors responsible for superconductivity. The crucial assumption of this model is that in a superconductor at temperature $T < T_c$, only a fraction $n_s(T)/n$ of the total number of conduction electrons are capable of participating in the *supercurrent*. The quantity

$n_s(T)$ is known as the density of superconducting electrons. It approaches the full electron density n as T falls well below T_c, but it drops to zero as T rises to T_c.

If superconducting electrons do not undergo scattering, they are accelerated by an external electric field **E** and, hence

$$m\frac{dv_s}{dt} = eE \tag{1.1}$$

where $\mathbf{v}_s$ is the mean velocity of superconducting electrons. The current density carried by these electrons is $\mathbf{J} = n_s e \mathbf{v}_s$, where n_s is the superelectron density and e is the charge. Eq. (1.1) can be written as

$$\frac{d}{dt}(\Lambda \mathbf{J}) = \mathbf{E} \tag{1.2}$$

where $\Lambda = m/(n_s e^2)$. The partial derivative, which describes the variation at a given point of space is given by the relation (Abrikosov, 1988)

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{v}\cdot\nabla$$

Since the real current velocities **v** in a metal are small compared to the Fermi velocity, we can replace the total derivative by a partial derivative, then we have

$$\frac{\partial}{\partial t}(\Lambda \mathbf{J}) = \mathbf{E} \tag{1.3}$$

According to the Maxwell's equation (Jackson, 1962)

$$\nabla\times\mathbf{E} = -\frac{1}{c}\frac{\partial\mathbf{B}}{\partial t} \tag{1.4}$$

taking the curl of eq. (1.3) and substituting in eq.(1.4), we get

$$\frac{\partial}{\partial t}\left(\nabla\times\Lambda\mathbf{J} + \frac{1}{c}\mathbf{B}\right) = 0 \tag{1.5}$$

This is the relation between the current density and the magnetic field. This means that the quantity in parentheses does not change with time. Suppose that at a given time, the current density $\mathbf{J} = 0$ and the internal magnetic field $\mathbf{B} = 0$. Then the quantity in parentheses is always equal to zero, so that even if an external field is introduced

$$\nabla\times\mathbf{J} = -\frac{n_s e^2}{mc}\mathbf{B} \tag{1.6}$$

Let us consider the simplest problem: a bulk superconductor in an external magnetic field. According to the Maxwell equation (Jackson, 1962)

$$\nabla\times\mathbf{B} = \frac{4\pi}{c}\mathbf{J} \tag{1.7}$$

If we take the curl of this equation, then we have

$$\nabla\times\nabla\times\mathbf{B} = \nabla\left(\nabla\cdot\mathbf{B}\right) - \nabla^2\mathbf{B} = \frac{4\pi}{c}\nabla\times\mathbf{J} \tag{1.8}$$

Using the fact that $\nabla\cdot\mathbf{B} = 0$ and substituting for $\nabla\times\mathbf{J}$ using eq. (1.6), we obtain

$$\nabla^2 \mathbf{B} - \frac{1}{\lambda_L^2}\mathbf{B} = 0 \qquad (1.9)$$

and

$$\nabla^2 \mathbf{J} - \frac{1}{\lambda_L^2}\mathbf{J} = 0 \qquad (1.10)$$

where $\lambda_L = \sqrt{\frac{mc^2}{4\pi n_s e^2}}$ is called the *London penetration depth.*

These equations, in turn, predict that the currents and magnetic fields in superconductors can exist only within a layer of thickness λ_L of the surface. Thus the London equations can yield the Meissner effect. The currents that occur within a surface layer of thickness 10^2 - 10^3Å screen out the applied field (Ashcroft and Mermin, 1976). Within this same surface layer the field drops continuously to zero. These predictions are confirmed by the fact that the field penetration is not complete in superconducting films as thin as or thinner than the penetration depth.

The Ginzburg - Landau Theory

In 1950, a deeper idea than the London theory was proposed by Ginzburg and Landau as part of their general program of explaining phase transitions. The theory followed from the fact that the superconducting electrons are in a macroscopic quantum state. Ginzburg and Landau (Ginzburg and Landau, 1950) postulated the existence of a macroscopic wave function (or order parameter Ψ) to describe the behavior of the superconducting electrons. The London theory can be derived from this postulate. Thus, the Ginzburg-Landau theory accounted for zero resistance and the Meissner effect, but now in much more fundamental terms. The theory also accounted for the second order (or continuous) nature of the superconducting phase transition in zero magnetic field (Keesom and Kok, 1932, Fetter and Walecka, 1971).

The equations of motion follow from a variational analysis of the Ginzburg-Landau free energy (the details will be shown in the next chapter). In the details we show the correspondence between the Ginzburg-Landau wave function and the superconducting electron density and velocity that appear in the London theory. But the Ginzburg-Landau theory did more than just give a deeper meaning to the London theory. It provided a set of equations with which the superconducting macroscopic wave function could be calculated under many circumstances, in particular in the presence of applied currents and magnetic fields. The predictions of these equations so correctly describe the qualitative behavior of superconductors that they are the subject of continuing study to this very day.

The fact that superconductivity was a quantum phenomenon described by a macroscopic quantum wave function implied that there was a phase involved. This means that there is the possibility of quantization effects (e.g., flux quantization) and quantum interference, (London, 1950, Deaver and Fairbank 1961,and File and Mills, 1963) although these possibilities were not fully appreciated at the time. In any event, with the introduction of Ginzburg-Landau theory, the classical period of superconductivity of Onnes, Meissner, and the Londons came to a close, and the era of superconductivity as a macroscopic quantum phenomenon began. Still, like the London theory, the Ginzburg-Landau theory was a phenomenological theory, and its deeper origins in a microscopic theory were yet to be established. The details of the Ginzburg-Landau theory will be described carefully in the next chapter.

The BCS Theory

In 1957, a microscopic quantum theory of superconductivity was proposed by Bardeen, Cooper, and Schrieffer (1957). They produced their epoch-making pairing theory of superconductivity, in which it was shown that even a weak attractive interaction between electrons, such as that caused in the second order perturbation by the electron-phonon interaction, causes an instability of the ordinary Fermi-sea ground state of the electron gas with respect to formation of bound pairs of electrons occupying states with equal and opposite momenta and spins. These are the so-called *Cooper pairs* (Cooper, 1956). The resulting effective electron-phonon interaction, V, determines the critical temperature according to the following equation, for weak electron-phonon interactions (Fröhlich, 1950, Bardeen, 1950)

$$k_B T_c = 1.14\hbar\omega_D \exp\{-1/N(E_F)V\} \qquad (1.11)$$

where ω_D is the phonon frequency at the edge of the Debye sphere (Duzer and Turner, 1981) and $N(E_F)$ is the density of states at the Fermi level.

The consequence of the BCS theory is essential for our story. The prediction of the energy gap in the single particle density of states of superconductors, which depends on temperature, is given by the following expression near the critical temperature

$$\Delta(T) = 3.06\, T_c\, (1 - T/T_c)^{1/2} \qquad (1.12)$$

As far as the other superconducting phenomena are concerned, the BCS theory provides an underpinning to theories that already were successful in the past, none of which played an important role in identifying the mechanism of superconductivity. From the point of view of our history of superconductivity, the BCS theory is the most effective microscopic theory for conventional superconductors. Later, Gorkov (Gorkov, 1959), showed that one could derive the Ginzburg-Landau theory from the BCS theory. However, concerning the high-temperature oxide superconductors, there has been no generally accepted explanation of all the properties of these materials. Unconventional mechanisms have been advanced to describe the high-T_c values, especially above 90 K, in the oxide superconductors. The many theories proposed range from the phonon-based BCS theory to, those with a minor phonon role and the strong-coupling and weak-coupling theories. Generally, the proposed models follow two approaches to the superconducting pairing. One begins with free electrons plus a pairing interaction between them and the others start from a highly correlated or even localized electron system plus a proper interaction which is then delocalized into an itinerant superconducting state. In other words, electrons form superconducting pairs below T_c in one case, whereas they form non-superconducting pairs above T_c and then undergo a Bose-Einstein condensation at T_c to the superconducting state in the other case.

Although the concepts of the Ginzburg-Landau theory are only valid on the macroscopic scale, it is sufficient for use as a tool to study the superconductivity of many materials. This is the purpose of this thesis and the details are in the following chapters.