CHAPTER II

THE HISTORY OF SUPERCONDUCTIVITY

The Era of Discovery

Superconductivity is a state of matter with a very remarkable behavior when materials are cooled on reaching a significant temperature. They suddenly loss all trace of electrical resistance [1]. The temperature at which the loss of resistivity occurs is called its superconducting transition temperature or critical temperature (denote by T_c). The first discovery was in 1911 by Heike Kammerlingh Onnes [31] in Leiden. Onnes discovered that mercury (Hg) lost all resistance to direct electric current flow when cooled to 4.3 K. This occurred soon after the successful liquefaction of helium (He) at 4.2 K, which allowed such very low temperatures to be reached. This famous discovery of superconductivity is shown in Fig. 1. Low temperature zero resistance is the key property of superconductors.

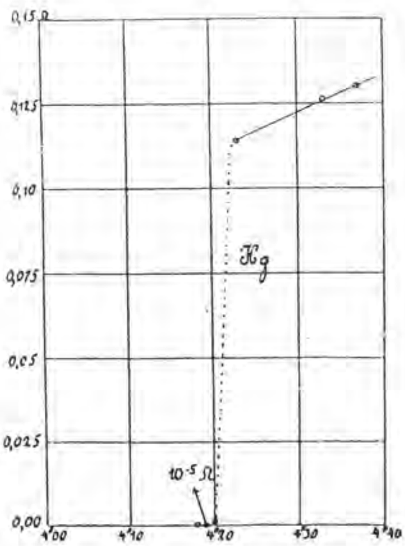


Fig. 1 Resistance in ohms of a specimen of mercury versus absolute temperature. This plot by Kammerlingh Onnes marked the discovery of superconductivity [31].

It turned out, however, that zero resistance is not a sufficient condition for superconductivity. In 1933 Meissner and Ochsenfeld [32] discovered that a magnetic field is expelled from a metal when it is in the superconducting state. This phenomena is called the Meissner effect, and suggest that the superconductor is a perfect diamagnet (see Fig. 2). The superconductivity will be destroyed in a sufficiently strong magnetic field.

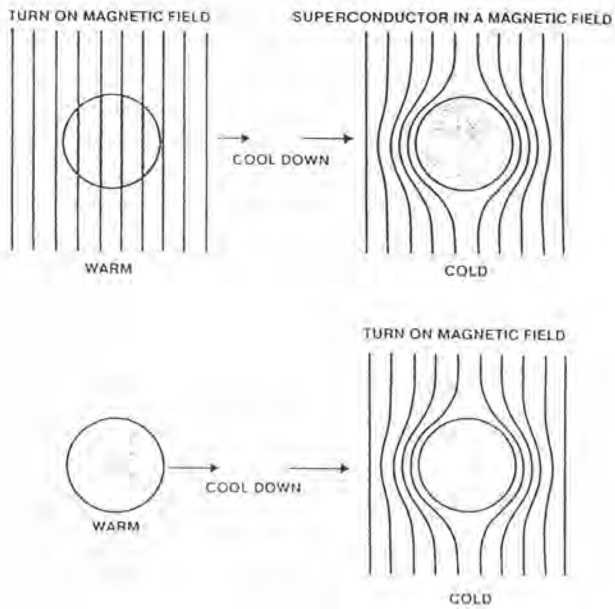
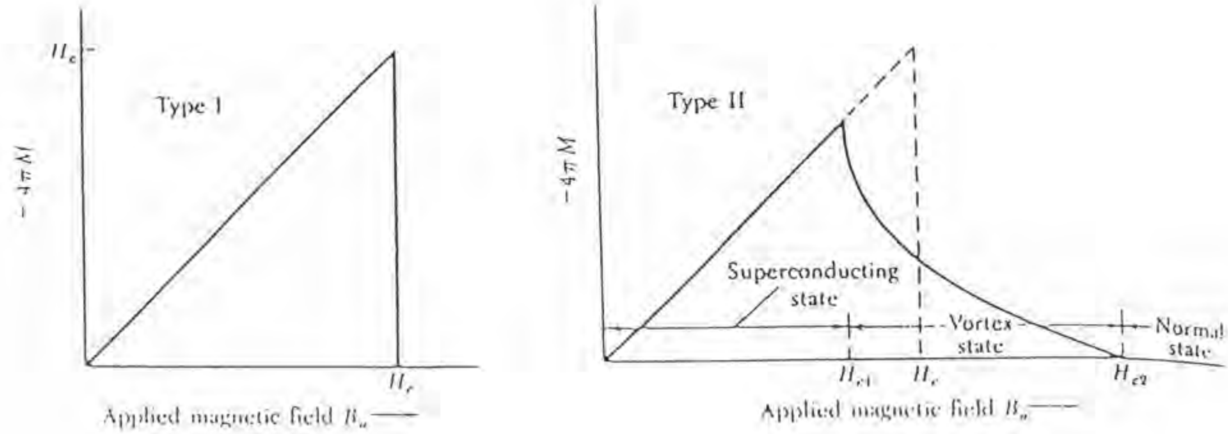


Fig. 2 The Meissner effect , a superconductivity in the magnetic field.

The critical value of the applied magnetic field for the destruction of superconductivity is called the critical field and denoted by H_c . It is a function of temperature. The magnetization curve expected for a superconductor under the condition of the Meissner experiment is sketched in Fig. 3a. A pure specimen of material exhibiting this behavior is called a type I superconductors . The values of H_c are always rather low in this type. Other materials exhibit a magnetization curve of the form of Fig. 3b and are known as type II superconductors, which have superconducting electrical properties up to the field denoted by H_{c2} . Between the lower critical field H_{c1} and the upper critical field H_{c2} the flux density is not zero and the Meissner effect is said to be incomplete and the superconductors are said to be in a vortex state.



3a. Type I superconductor 3b. Type II superconductor

Fig. 3 The magnetization curves of type I (3a), and type II (3b).

Over the years, more than 6,000 elements, compounds, and alloys have been found to be superconductors. But for many years no one understood how to find a superconductor at high temperatures in a high magnetic field up to a useful range. Many ideas have been conceived and tested making use of the unique characteristics of superconductivity-zero resistivity, quantum interference phenomena, and the Meissner effect. For example, powerful superconducting magnets and ultra sensitive devices have been constructed and used, sufficiently demonstrating the great technological potential of superconductivity. However, in spite of this successful demonstration, the full impact of superconductivity on technology has yet to be realized. This is mainly attributed to the low temperature below which superconductivity occurs in liquid helium which is hard to find and expensive. For the possibility to achieve useful technology, one searches for new superconducting materials with higher transition temperature, higher critical magnetic fields and use of other liquified materials such as liquid nitrogen (at 77 K) which is plentiful, cheap, efficient and easy to handle.

Search for Higher Transition Temperature Superconductors

The field of high temperature superconductivity was formally inaugurated by Matthias, Geballe, and Hulm due to their steady and persistent efforts on the so-called A15 [33], intermetallic compounds. A record T_c of 23.2 K in $NbGe_3$ was set by Gavaller and Testradi [34], and this record lasted until 1986. The unusual superconductivity in perovskite-based oxides can be traced back to the pioneering work [35-38] of Schooley, Hoster, and Cohen, on $SnTiO_{3-x}$ in 1964, Sweedler, Raub, and Matthias on Na_xWO_3 in 1965, Johnston, Prakash, Zachariasen, and Sleight, Gibson, and Bielseat on $Li_{1-x}Ti_{2-x}O_4$ in 1973 and Sleight, Gibson, and Bielstedt on $BaPb_{1-x}Bi_xO_3$ in 1975. $BaPb_{1-x}Bi_xO_3$ is particularly unusual because of its relativity high-T_c of about 13 K in spite of its extremely low density of states and absence of any transition metal elements. In fact, more than ten years ago this compound was initial investigations[39] for superconducting oxides in the long search for high temperature superconductors. However, the T_c was not advanced, but nevertheless, superconductivity had been observed in several complex oxides which evoked our special interest. An exciting report of the observation of superconductivity in the 30 K range in the ternary (LBCO), so-called 2-1-4 , compounds by Bednorz and Müller [2] was published in 1986.

The Breakthrough of the New Copper Oxide Superconductors

The breakthrough in higher transition temperatures resulted from Bednorz and Müller 's discovery [2] (IBM Zurich Research Laboratory) in the copper oxide system. They were convinced that it was necessary to move beyond the standard high -T_c classes to obtain a real breakthrough. They chose to work on transition metal oxides, because they were different and because they often display polaronic effects typical of extremely strong electron-phonon interactions. In 1986 they found evidence of a superconducting transition occurring near 30 K in the La-Ba-Cu-O system [2], a result that was rapidly confirmed and refined by a number of laboratories in U.S.A., Japan, and Europe. It was established that T_c in the range 20-40 K occurs for $La_{2-x}M_xCuO_{4-y}$ where M is the alkaline-earth (Ba, Sr, Ca) and that application of pressure leads to a large pressure coefficient of T_c and drives T_c higher in the Sr system. The crystal structure was identified, and it has since become clear that the high temperature superconductivity is the most astounding of a number of unusual properties of this system (to shorten notation somewhat, we shall refer to this class of materials generically as La214 and to the individual members by widely used acronyms LSCO, LBCO and LCCO).

Since pressure was so effective in increasing T_c in La124, Paul Chu and Maw Kuen Wu [3] simulated "chemical pressure" by replacing the smaller ion of Y^{3+} for the larger ion La^{3+} in LBCO in early 1987. This produced the first type of superconducting compound with a transition temperature above the boiling point of liquid nitrogen, a 90 K superconductor, later identified as $YBa_2Cu_3O_{7-\delta}$ (to be denoted Y123 or YBCO). Like the initial system, this material was prepared by ceramic processing techniques. High temperature annealing in an oxygen-containing atmosphere was necessary to give a high-T_c. Although other growth techniques have now been found that result in a high-T_c phase, it was clear already from preparation considerations that the new copper oxides were completely different from the previous high temperature superconductors.

Although there were numerous reports of resistive and magnetic anomalies at much higher temperatures, the next breakthrough came in early 1988 with the discovery by Maeda and Chu [4, 5] of the superconductors with T_c above 100 K $Bi_2Sr_2CaCu_2O_{8-\delta}$ (denoted by Bi2212 or BSCCO). These Bi-based compounds not only showed onset around 110 K, but also contain no rare-earth elements. There were also distinguished by a highly micaceous nature, indicating more layering than its predecessor. This breakthrough was followed rapidly by the discovery by Allen Hermann, and Zhengzhi Sheng [6] of onset at 115 K in the Tl-Sr-Ca-Cu-O system. The superconducting phase was identified as $Tl_2Ba_2CaCu_2O_{8-\delta}$ (denoted by Tl2212 or TBCCO), and this was soon improved to be above 120 K by several groups. At this writing the Tl compound $Tl_2Ba_2Ca_2Cu_3O_{10}$ (Tl2223) has the highest reproducible transition temperature at 125 K. The crystal structure of this system was identified and found to share certain features in common with the LMCO and YBCO materials, particularly the existence of square Cu-O layers separated by more-or-less ionic regions.

This period of rapid discovery (see Fig.4) may well continue for sometime. While it is certainly early to review any aspect of these novel materials, intense effort has been turned towards the understanding of their electronic structure and properties, and it is useful to collect the results and contemplate their implications. Developing a clear understanding of the electronic structure of these high-T_c materials is necessary to identifying the pairing mechanism, and also to describing the other essential and often unusual properties displayed by these materials.

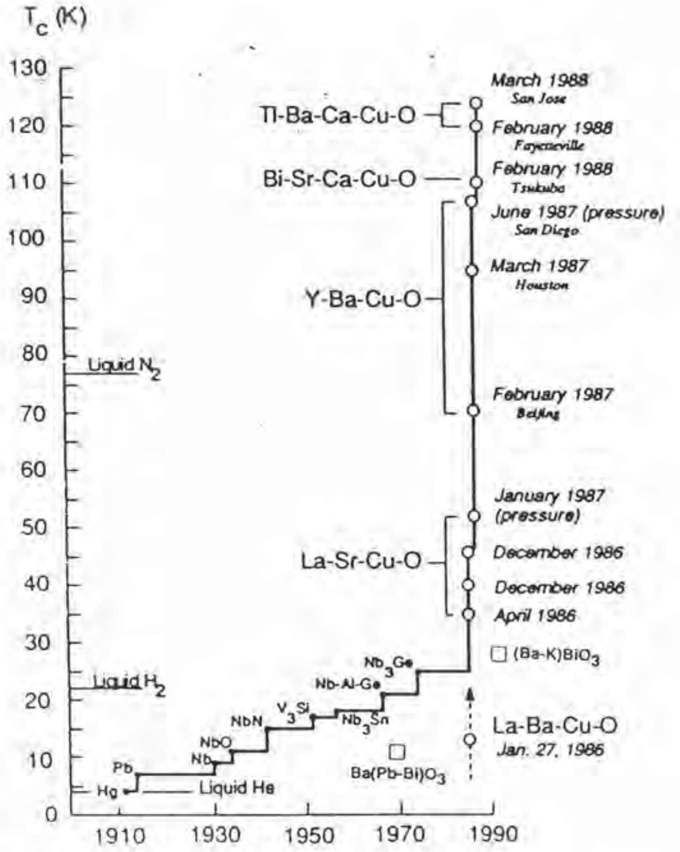


Fig. 4 The period of the search for superconductors, the conventional and also high temperature superconductors.

<u>Theoretical Survey</u>

Theoretical understanding of the phenomena associated with superconductivity has been reached in several ways. Certain results follow directly from thermodynamics. Many important results can be described by phenomenological equations; the London theory [40] and the Ginzburg-Landau theory [41], with the Abrikosov formulation [42] . A successful quantum theory of superconductivity was given by Bardeen, Cooper, and Schrieffer [43] and has provided the basis for subsequent work. The Eliashberg formalism [44], confirmed the microscopic theory of superconductors and other novel mechanisms. This review gives only the basic ideas and not the particulars.

The London Theory

Given a knowledge of the Meissner effect, F. and H. London introduced the first phenomenological theory of superconductivity in 1934 [40]. Appropriately it is known as the London theory. In brief, the Londons conceived of a set of equations that accounted for the observed properties of zero resistance and perfect diamagnetism. The physics embodied in these equations was that of a classical charged fluid flow in which there was no friction and in which the flow was basically irrotational, i.e., with no vortacity. The solutions of the equations yielded the Meissner effect and gave an explicit expression for the magnetic penetration depth of the superconductor .

While the London equations accounted for zero resistance and perfect diamagnetism, they were not explicitly based on fundamental concepts. Phenomenological theories of this sort play a tremendously important role in the advancement of science. They contain the distillate or essence of a collection of experimental facts and reduce them to a deeper set of questions. The work of the Londons was the first that happened in the conceptual development of superconductivity. Eventually the London theory was extended to include the two-fluid concept, the idea that a superconductor consists of two interpenetrating fluids, a normal fluid that exhibits resistance and a superconducting fluid that obeys the London equations. To think for a moment in electrical engineering terms, the two-fluid concept can be represented by a parallel circuit with the normal electron current J_n behaving as a normal resistor and the superconducting electron current $\mathbf{J}_s$ behaving like a perfect conductor. This conductance is associated with the kinetic energy of the superconducting electrons and is known as the kinetic inductance of the superconductor. F. and H. London suggested that in the superconducting state these superelectrons encounter no resistance to their motion and the supercurrent density is

$$\mathbf{J}_s = -(1/\mu_o \lambda_L^2)\,\mathbf{A} \tag{2.1}$$

where λ_L is a constant with the dimensions of length and A is the vector potential. From (2.1) we see that

$$\nabla \times \mathbf{J}_s = -(1/\mu_o \lambda_L^2)\,\mathbf{B} \tag{2.2}$$

The relation equation between the magnetic flux and the current density is

$$\nabla \times \mathbf{B} = \mu_o \mathbf{J}_s \qquad (2.3).$$

We can take the curl of both sides to obtain

$$\nabla \times (\nabla \times \mathbf{B}) = \mu_o (\nabla \times \mathbf{J}_s) \qquad (2.4).$$

From (2.2) and (2.4) we have

$$\nabla^2\mathbf{B} = (1/\lambda_L^2)\,\mathbf{B} \qquad (2.5).$$

or

$$\mathbf{B}(x) = \mathbf{B}(0)\exp(-x/\lambda_L) \qquad (2.6).$$

The expression (2.6) is the prediction of the London theory that shows the behavior of the superconductor in the magnetic field which can be passed through the material within the characteristic length λ_L which is called the London penetration depth. Even today this approach to superconductivity is useful in engineering applications of superconductivity.

The Ginzburg - Landau Theory

In the years following the introduction of the London theory, there articulated a deeper idea in that the theory followed somehow from the fact that the superconducting electrons were in a macroscopic quantum state. However, it was not until Ginzburg and Landau introduced their famous phenomenological theory of superconductivity [41] that this idea was firmly embodied in a formal theory. Ginzburg and Landau postulated the existence of a macroscopic complex pseudowavefunction $\Psi(r)$ as an order parameter for the superconducting electrons to describe the behavior of the superconducting electrons. The London theory follows directly from this postulate. The Ginzburg-Landau theory also accounts for zero resistance and the Meissner effect, but in much more fundamental terms.

One of the most significant insights provided by Ginzburg-Landau theory concerns the difference between type I and II superconductors as exhibited in their contrasting responses to external magnetic fields. The Ginzburg-Landau theory separates the two-types of superconductors by a parameter κ (kappa) which is the ratio of the penetration depth λ, and coherence length ξ, characterizing $\Psi(r)$. Schematic diagrams of the variation in $\Psi(r)$ and the magnetic field, $h(x)$ for each type of superconductor are shown in Fig. 5. For the typical pure superconductors, kappa < 1 refers to type I superconductor and in the case of kappa > 1 refers to type II superconductor.

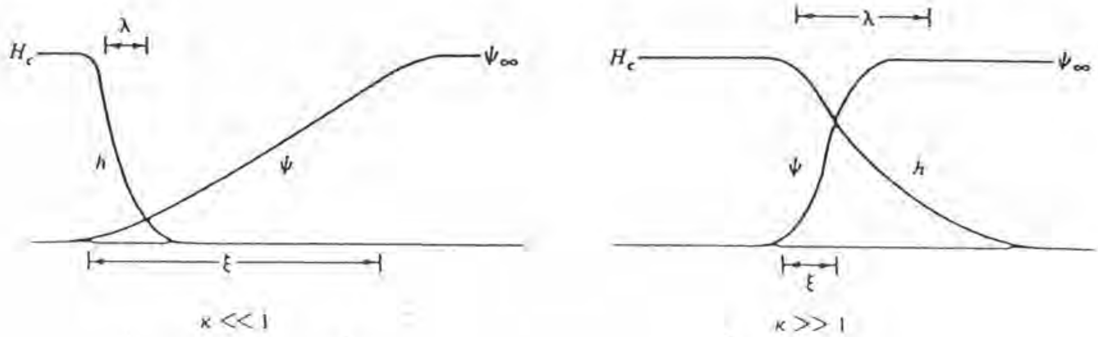


Fig. 5 Schematic diagram of variation of $\Psi(x)$ and h(x). For type I and type II superconductors.

The fact that superconductivity is 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 a quantization effect (e.g. flux quantization) and quantum interference, although these possibilities were not fully appreciated at the time. In any event, with the introduction of the Ginzburg-Landau theory, the classical period of superconductivity with 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 is a phenomenological theory, and its deeper origins in a microscopic theory were yet to be established.

The BCS Theory

In 1957 , the microscopic quantum nature of superconductivity was laid by the classic paper of Bardeen, Cooper, and Schrieffer [43]. 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 second order 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 momentum and spin. These are the so-called Cooper pair. The resulting effective electron-phonon interaction, V, determines the critical temperature according to the following equation, for the weak electron-phonon interaction,

$$k_B T_c = 1.14\, \hbar\omega_D \exp\left[-1 / N(E_F)V \right]. \quad (2.7)$$

Here ω_D is a limiting phonon frequency and $N(E_F)$ is the density of states at the Fermi level. The BCS theory explained the isotope effect in superconductivity well, since the phonon frequency which appears in Eq. (2.7) varies with the ionic mass according to $M^{-1/2}$ (see also chapter IV).

One final 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 expansion near the critical temperature

$$\Delta(T) = 3.06\, T_c(1 - T / T_c)^{1/2} \quad (2.8)$$

As far as the other superconducting phenomena are concerned, the BCS theory provides an underpinning to the theories that already were successful in the past, none of which played a 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 the conventional superconductor. Later, the work of Gorkov[45] and Josephson[46] was able to make an explicit connection between BCS theory and the macroscopic quantum nature of superconductivity.

For the high temperature oxide superconductors , there has been an explosion of recital work aimed at explaining the properties of these materials. Unconventional mechanisms have therefore been advanced to describe the high-T_c materials, especially above 90 K, in the oxide superconductors. Many theories proposed range from the phonon-based BCS theory, those with 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 nonsuperconducting pairs above T_c and then undergo a Bose-Einstein condensation at T_c to the superconducting state in the other case.