Chapter-I

Introduction

In this chapter a general review of superconductivity is given. Occurrence of superconductivity, Meissner effect and para-Meissner effect has been reviewed. London penetration depth has been discussed. Concept of flux motion is reviewed. Low T_c as well as high T_c superconductors have been discussed.
One of the important properties of the materials is their electrical resistivity. Physicists have considerable interest to study the variation of electrical resistivity with temperature. It had been known for many years that the resistance of metals falls when they are cooled below room temperature but it was not known that what limiting value the resistance would approach if the temperature were reduced towards 0 K.

Kamerlingh Onnes [1] at the University of Leiden took such a study of the variation of electrical resistance of metals with temperature. He while experimenting with platinum and gold, found that resistance decreases when cooled but it depends on the purity of the specimen. So he took pure mercury as the sample. In 1911 surprisingly he observed that at a temperature about 4.2 K the resistance of mercury dropped abruptly to a value experimentally undetectable. Furthermore, this phenomenon occurred even if mercury was quite impure. He called this remarkable phenomenon as superconductivity and the temperature at which it occurred, the critical temperature \( T_c \).

This critical temperature (also called transition temperature) varies from metal to metal. Not only metals, a number of alloys also have been found to become superconducting at low temperatures. The materials which exhibit superconductivity, are called superconductors.

The disappearance of dc resistance within the critical temperature \( T_c \) can be understood by persistent current measurements in a superconducting ring. File and Mills [2] studied the decay of supercurrents in a solenoid by using precision nuclear magnetic resonance method. It can be concluded from the result that there will be no change in field produced by the supercurrent in \( 10^{10} \) years. Quinn and Ittner [3] have calculated the resistance of a superconducting thin film tube by measuring the time decay of the current circulating in the tube. They calculated the upper limit of dc resistivity as \( 3.6 \times 10^{-23} \) Ohm-cm.
Magnetic properties

Below the transition temperature $T_c$, superconducting behaviour can be quenched and normal conductivity restored by the application of strong external magnetic field. The field at which superconductivity is destroyed is called critical field ($H_c$). The value of the critical field decreases with increasing temperature. The approximate relation between $H_c$ and $T_c$ is

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

where $H_c(0) = H_c$ at $T=0K$. A diagram of magnetic field vs. temperature is called phase diagram. A phase diagram for a superconductor is shown in the figure.

Fig.1 Temperature dependence of critical magnetic field.

Meissner effect

In 1933 Meissner and Ochsenfeld [4] found that when a superconducting specimen cooled below the transition temperature ($T_c$) in the presence of an external magnetic field, the magnetic flux is expelled from the interior of the specimen. This phenomenon is called
Meissner effect. This phenomenon is true for the case when sample is cooled below $T_c$ in the absence of magnetic field and then if magnetic field is applied also. That is to say, inside a superconductor we always have

$$B = 0$$  \hspace{1cm} (2)

where $B$ is the magnetic flux density. Now we have the relation

$$B = H_a + 4\pi M$$  \hspace{1cm} (3)

where $H_a$ is the applied magnetic field and $M$ is the magnetization. Now according to the condition (2) equation (3) becomes

$$H_a = -4\pi M$$  \hspace{1cm} (4)

Therefore susceptibility becomes

$$\lambda = \frac{M}{H_a} = -\frac{1}{4\pi}$$  \hspace{1cm} (5)

Thus superconductors shows the property of perfect diamagnetism.

**Type-I and Type-II superconductors**

Pure specimen of many materials shows complete Meissner effect, that means below the critical temperature flux inside the superconducting specimen is zero. Thus there is only one value of critical field ($H_c$) available for a particular temperature $T$, ($T < T_c$). These materials are called Type-I superconductors.

Transition metals and alloys show different behaviour, there are two critical fields $H_{c1}$ and $H_{c2}$ available for a particular temperature $T$, ($T < T_c$). Between $H_{c1}$ and $H_{c2}$, Meissner effect is said to be incomplete, specimen is threaded by magnetic flux lines, these are called vortices. These superconductors are known as Type-II superconductors. Here one
point we can mention that all high-$T_c$ superconductors are Type-II superconductors.

**Para-Meissner effect**

The field cooling Meissner effect of some ceramic high-$T_c$ samples was reported [5] to remain incomplete at $H \ll H_{c1}$. The flux expulsion for these samples is of the order of $\frac{1}{3}$ of a zero field cooling sample. This incompleteness was explained by flux pinning and anisotropy of the London penetration depth. It is quite common to find values of less than $-1/4\pi$ due to imperfections in the samples. Shrivastava and Braunisch et al. [6] reported that in certain Bi-based high-$T_c$ superconductors a paramagnetic magnetisation is found in the field-cooling mode, below a field of order 1 Oe. Since this magnetization appears spontaneously, this phenomenon is called as paramagnetic Meissner effect or Para-Meissner effect (PME).

**Fig.2** Zero field cooled (ZFC) and field cooled (FC) signals of a ceramic Bi-2:2:1:2 ($\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-x}$) sample exhibiting the para-Meissner effect [6].
Heinzel et al. [7] experimentally confirmed the occurrence of PME by the measurement of the second harmonic of the magnetic ac-susceptibility. This PME can be explained on the basis of $\pi$-junctions between the grains of the granular high-$T_c$ superconductors, which was thought to arise as a consequence of $d$-wave symmetry. Recently Araujo-Moreira et al. [8] reported the occurrence of PME without the presence of $\pi$-junctions. Our work on current loop sizes of PME is given in chapter-II.

The London Equations


According to this two fluid model, in a superconducting material a finite fraction of electrons condenses into 'superfluid' which extends all over the volume of the specimen. At absolute zero temperature the condensation is complete and all the electrons participate in forming the superfluid. As the temperature increases, fraction of electrons evaporate from the condensate and form normal fluid. As the temperature approaches critical value $T_c$, the fraction of electrons remaining in the superfluid tends to zero.

If $n_s$ and $n_n$ be the superelectron and normal electron densities respectively, then $n_s + n_n = n$, where $n$ is the average number of electrons per unit volume.

Below $T_c$, the supercurrent density $J_s$ can be written as

$$J_s = -en_s v_s$$  \hspace{1cm} (6)

where $v_s$ is the drift velocity of the super electrons and $e$ is the electronic charge.

when an electric field $E$ is applied, then the force equation can be written as

$$m \frac{dv_s}{dt} = -eE$$  \hspace{1cm} (7)
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Now from equation (6), with the help of equation (7) we can write,
\[ \frac{dJ_s}{dt} = \frac{e^2 n_s E}{m} \]  
(8)

This is known as first London equation. This equation shows steady current is possible in the absence of electric field.

Operating curl on both sides of equation (8) and with the help of Maxwell's equation we can get,
\[ \nabla \times J_s = -\frac{n_s e^2}{m c} B \]  
(9)

This is known as second London equation which explains Meissner effect. In terms of vector potential \( A \), equation (9) can be written as
\[ J_s = -\frac{c}{4\pi \lambda_L^2} A \]  
(10)

where \( \lambda_L = \left( \frac{mc^2}{4\pi n_s e^2} \right)^{\frac{1}{2}} \) is known as London penetration depth. It may be defined as the distance where the magnetic field reduces to \( \frac{1}{e} \) times its boundary value. The expression for \( \lambda_L \) can be written in more appealing form as
\[ \lambda_L = \left( \frac{mc^2}{4\pi n_s e^2} \right)^{\frac{1}{2}} \]  
(11)

Here \( e^* = 2e \) for superconducting state revealed from flux quantisation measurements. This \( \lambda_L \) plays an important role in characterizing a superconductor.

Temperature and magnetic field dependence of London penetration depth

According to the London theory \( \lambda \) (here \( \lambda \) denotes London penetration depth) is independent of temperature and magnetic field, but experimentally these dependence is found. The temperature and magnetic field dependence of \( \lambda \) is not well understood till today. Numbers of researchers are trying to find out exact dependence of \( \lambda \) with temperature as
well as with magnetic field.

If we take the temperature dependence of super-electron density then from Gorter-Casimir model [10] we can write,

$$n_s(T) = n \left[ 1 - \left( \frac{T}{T_c} \right)^4 \right]$$  \hspace{1cm} (12)

so that temperature dependence of $\lambda$ comes as

$$\lambda(T) = \lambda(0) \left[ 1 - \left( \frac{T}{T_c} \right)^4 \right]^{-\frac{1}{2}}$$  \hspace{1cm} (13)

![Graph](image)

**Fig.3** Temperature dependence of the superconducting penetration depth according to Gorter-Casimir two fluid model [11].

Annett et al. [12] have shown that all the possible non s-wave singlet pairing states of a superconductor with tetragonal or orthorhombic symmetry and a Fermi surface that has spherical or cylindrical topology have line nodes in the gap that give rise to a linear
temperature dependence in the penetration depth, $\Delta \lambda(T) \propto T$ unless scattering or Fermi-liquid corrections are important. Where $\Delta \lambda(T) = \lambda(T) - \lambda(0)$. They predicted that kinetic measurements can give a quadratic temperature dependence. In s-wave BCS theory [13] for a spherical Fermi surface the temperature dependence is given by,

$$\frac{\Delta \lambda(T)}{\lambda(0)} \sim 3.33 \left( \frac{T_c}{T} \right) \frac{1}{2} \exp\left(-1.76 \frac{T_c}{T} \right)$$

The exponential term is a consequence of the energy gap $\Delta$, which takes on the value $\Delta/k_B T_c = 1.76$ in weak coupling BCS theory. Prohammer and Carbotte [14] calculated the London penetration depth for d-wave superconductors stabilized by antiferromagnetic spin fluctuations. They found $\lambda(T) \sim T$ at low temperatures, but impurity scattering as in the case of p-wave order parameters changes $T$ to $T^2$ dependence.

Hardy et al. [15] have observed a linear temperature dependence of $\Delta \lambda(T)$ below 20 K in single crystal YBa$_2$Cu$_3$O$_{6.95}$ which is very different from that expected for s-wave BCS superconductivity. They predicted that the strong linear dependence to be the characteristic of the pure system and that its apparent absence in thin films and some crystals is due to the presence of defects.

Kosztin and Legget [16] have shown that at very low temperatures nonlocality may play an important role in the electromagnetic response of a d-wave (unconventional) superconductor, which leads to $\Delta \lambda(T) \propto T^2$ dependence. They predicted that this $T^2$ dependence can be observable experimentally in nominally clean high-$T_c$ superconductors below a crossover temperature $T^* \sim 1K$ but above this crossover temperature $T^*$ and below $T_c$, $\lambda(T)$ has the well known linear $T$ dependence. The penetration depth in a mixed wave superconductor has been calculated [17] and it was shown that at low temperature the ground state has $d_{x^2-y^2}$ symmetry which at higher temperature becomes s-wave type.
It was thought that, the penetration depth $\lambda$, of a magnetic field into a superconductor should be regarded not as independent of field strength at constant temperature but rather as increasing with field. Pippard [18] while studying experimentally the magnetic field variation of superconducting penetration depth found that the variation is considerably small. The result of the experiment suggested the existence of long-range order in the superconducting state over a distance of $10^{-4}$ cm or more.

Our work on variation of penetration depth with magnetic field is given in different chapters of the thesis.
Flux motion

It is known that for high-\(T_c\) superconductors \(H_{c2}\) can be as high as \(10^6\) Oe or higher. The basic criteria for making a superconducting magnet is that superconducting material must not only have a critical field substantially higher than the field to be produced but it must be able to carry high current in that field without resistance. The resistanceless current in a homogeneous type-II superconductor is limited to that value which just produces the field \(H_{c1}\) of the superconductor at its surface. For a wire of radius \(a\) this condition is given by Silsbee’s rule

\[
\frac{2I}{a} = H_{c1}
\]  

(15)

At \(H_{c1}\) the superconductor enters into the mixed state and sample contains both the transport current and the magnetic flux threading through the bulk of the superconductor. Due to their coexistence magnetic flux exerts Lorentz force on the current carriers. This force per unit volume is given by,

\[
F = J \times \frac{B}{c}
\]  

(16)

where \(J\) is the current density and \(B\) is the average magnetic induction. To this force there is an equal and opposite reacting force which acts on magnetic flux lines referred to as Lorentz driving force. This driving force which acts on a single vortex can be written as

\[
f_L = J \times \frac{\phi_0}{c}
\]  

(17)

where \(\phi_0\) is the flux quantum. Because of this force, flux lines tend to move transverse to the current. In a homogeneous medium there is no counteracting force which results in which the vortex lines are driven into motion. This vortex motion gives rise to resistance which is not of practical interest.
Clearly to carry high current without resistance the vortex lines must be pinned so that their motion is inhibited. This can be done by introducing in the material various types of inhomogeneities, which may include lattice defects such as dislocations, precipitates, grain boundaries etc. In hard superconductors inhomogeneities offer pinning force counteracting the driving force and a static non-uniform vortex distribution becomes permissible, provided $f_L < f_p$, where $f_p$ is the maximum pinning force acting on each vortex. Thus no flux motion is to be expected until $f_L > f_p$. Anderson [19] pointed out that this would be so only at 0 K. At any finite temperature $T < T_c$, thermal activation aided by the driving force may cause the pinned vortices to overcome the barrier and move, even when $f_L < f_p$. This behaviour is given the name flux creep.

When $f_L > f_p$ the creep-like motion of vortex lines changes to a highly dissipative one characterized by a viscous flow. The motion of the vortices limited by viscous drag referred as flux flow. If the vortex line move with a velocity $v_L$, the force equation can be written as

$$J \frac{\phi_0}{c} = \eta v_L$$

where $\eta$ is the coefficient of viscosity. This flux flow usually gives a flow resistivity $\rho_f$,

$$\rho_f = \frac{E}{J} = B \frac{\phi_0}{\eta c^2}$$

A general model of this problem has developed by Bardeen and Stephen [20]. Our work on pinning frequency is given in different chapter.

**Progress of high-$T_c$**

Since 1911, when K. Onnes discovered superconductivity in mercury at 4.2 K, the highest observed values of $T_c$ gradually moved upward. But this increment was not so considerable. In 1973 Gavaler [21] observed that sputtered films of Nb$_3$Ge began to become...
superconducting at 22.3 K and this was soon pushed up to 23.2 K by altering the sputtering conditions slightly. Inspite of great efforts to increase this limit further, it stood as the record until 1986. The breakthrough of high temperature superconductivity came when Bednorz and Müller [22] reported that a lanthanum barium copper oxide began its superconducting transition as it was cooled below 35 K. All of the subsequent work proved that there were high temperature superconductors.

In rapid succession and in many laboratories the barium was substituted by strontium and calcium and the transition temperature was raised to nearly 40 K for the material La$_{1.85}$Sr$_{0.15}$CuO$_4$. Subsequent effort to raise $T_c$ was carried out by many scientist. M.K.Wu et al.[23] reported first the material capable of becoming superconducting in liquid nitrogen; it turned out to be YBa$_2$Cu$_3$O$_{7-6}$ with $T_c$ about 93 K. Thus with the discovery of high-$T_c$ superconductors they can be operated with liquid nitrogen which is much less expensive and easy to handle compared to expensive liquid helium. The highest $T_c$ for these series of compounds (Oxide superconductors) known today is 148 K.

Applications
The most useful application of superconductors is to make superconducting magnets (solenoid) which can supply steady fields of over 100,000 G without dissipation of energy because of the resistanceless persistent current. A comparable field produced by a water-cooled copper solenoid which dissipate several megawatts of power, with attendant cooling problems and it would not have the essentially infinite stability of the superconducting magnet. Superconducting magnets find applications in many areas in technology. Beside this, superconductors used in making memories, logic gates in computers: voltage standard, radiation detectors; and in biomedical, geophysical applications.
References

[1] Kamerlingh Onnes H., Leiden comm. 120b, 122b, 124c (1911)


REFERENCES


