UNIT 12 SUPERCONDUCTIVITY

Structure

12.1 INTRODUCTION

In the preceding units of this block, you have studied how various properties of metals and semiconductors can be understood in terms of the motion of charge carriers (electrons and/or holes). You may recall from Unit 9 that at low temperatures electrical resistivity of metals saturates to a *residual* value (Matthiessen's rule). No matter how pure a metallic specimen, it always offers resistance to flow of current. Does this suggest that electric current can not flow without resistance in any material? Under normal conditions, the answer to this question is in the affirmative. However, in 1911, Kamerlingh Onnes showed that when mercury was cooled to liquid helium temperature, its resistance became too small to measure. At $T = 4.3$ K, the resistance of the sample was measured to be 0.125 Ω but when temperature was reduced below 4.2 K, it dropped to less than 10^{-5} Ω, the limit of sensitivity of his apparatus. That is, mercury practically lost all resistance below 4.2 K over a temperature interval of 0.1 K. From this, he concluded that an entirely new phenomenon – superconductivity; completely unknown in classical physics – had appeared!

From our course on Thermodynamics and Statistical Mechanics (PHE-06), you may recall that production of low temperatures requires a great deal of sophistication. But the interest has continued to grow in understanding the phenomenon of superconductivity because of its exciting scientific and technological applications. In particular, using cables made of such materials, electrical power can be transmitted without resistive losses (Joule heating) resulting in saving energy (and hence money!). Also, it can be used for fabrication of high field magnets, storage of electrical energy, microelectronics etc. Now we know of several materials becoming *superconductors* at transition temperatures as high as liquid nitrogen temperatures, the so called *high temperature superconductors*. As such, a complete understanding of superconductivity requires detailed knowledge of advanced quantum mechanics and higher mathematical techniques which are completely out of the scope of this course. For this reason, here we have discussed only some important physical properties of superconductors and their qualitative explanations.

Since not all metals become superconductors down to very, very low temperatures, in Sec. 12.2, you will learn what distinguishes a metal from a superconductor. You will also discover the consequences of treating superconductor as a *perfect* conductor; and find out that describing superconductor as a *perfect* diamagnetic material is more consistent with experimental observations. The first comprehensive microscopic theory was proposed by Bardeen, Cooper and Schrieffer (BCS) in 1957 – almost half a century after the discovery of the phenomenon. The BCS theory explains most of the properties of conventional superconductors. The complete BCS theory of conventional superconductors is beyond the scope of this course but we have discussed its essential elements in Sec. 12.3. In 1986, a new group of oxide superconductors was discovered whose transition temperatures were much higher in comparison with the then known (that is, conventional) superconductors. These **high temperature superconductors** differ from conventional superconductors with respect to transition temperature as well as the type of material. In Sec. 12.4, we briefly review the salient features of high temperature superconductors.

After the discovery of high temperature superconductor, a term **conventional superconductors** has been coined. It refers to those superconductors which require liquid helium for cooling below transition temperature and which do not contain copper as one of its ingradient.

Objectives

After studying this unit, you should be able to:

- distinguish a superconductor from a metal;
- explain the difference between a perfect conductor and a superconductor;
- describe Meissner effect;
- differentiate between type I and type II superconductors;
- discuss the essential elements of BCS theory; and
- state the characteristic features of high temperature superconductors.

12.2 WHAT IS A SUPERCONDUCTOR?

You may recall from Unit 9 that resistance to the flow of electric current in a metal arises due to scattering of electrons by lattice ions and impurities, and resistance decreases as temperature is lowered. Therefore, it is natural to expect that a pure metal specimen should not offer any resistance as temperature approaches absolute zero. However, no material – natural or fabricated – has absolutely perfect structure needed to permit complete absence of resistivity; resistivity saturates to a residual value as temperature is brought down to absolute zero. The residual resistivity is caused due to collision of electrons with impurity atoms and is independent of temperature. Temperature dependence of resistivities of an ideal metal and a real metal specimen is shown in Fig.12.1.

Till early 20th century, resistivity of metals near absolute zero could not be measured; it was just an interpolation of experimental curves supported by theoretical arguments. Such measurements became possible only after Kamerlingh Onnes was successful in liquefying helium in 1908 and obtain a temperature of 4.2K.

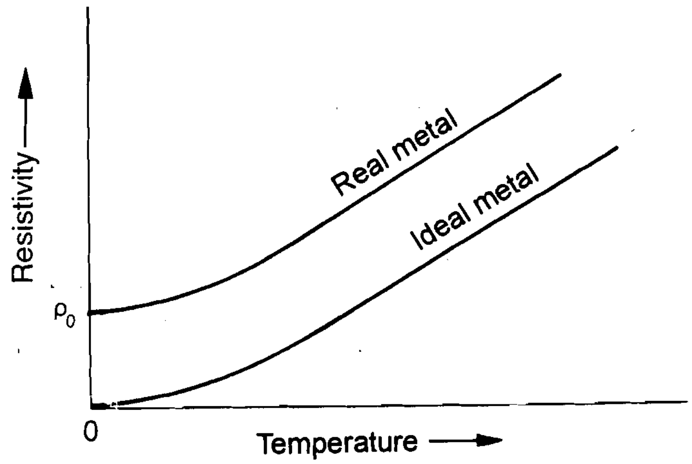

Fig.12.1: Variation of electrical resistivity with temperature for an ideal and a real metal

Superconductors are metals and alloys showing *superconductivity* when cooled below the critical or transition temperature. Thus, a substance is said to be in superconducting state when it exhibits superconductivity and is said to be in normal state when it is above the transition temperature and exhibit normal resistivity behaviour.

Availability of liquid helium made it possible to study variation of resistance with temperature at much lower temperatures. Onnes studied the behaviour of electrical resistance of mercury (Hg) at low temperatures. (The choice of mercury was guided by the fact that it could be easily obtained in a very pure form.) He discovered that mercury behaved in an unusual manner below *liquid helium temperature; its resistance suddenly droped to less than* $10^{-5}\Omega$ *which for all practical purposes is zero* (Fig.12.2). The resistivity above this temperature had a finite value and resistivity below this temperature was very, very small and could be taken to be zero. This phenomenon – absence of electrical resistance below a certain temperature – was named **superconductivity** by him. The temperature at which resistance becomes zero is called **critical temperature** or **transition temperature** (T_c) and the material below this temperature is said to be in *superconducting state* and above this temperature, it is said to be in *normal state.*

For taking measurement below the boiling point of liquid helium, the container with liquid helium is evacuated to low pressure. By doing so, data down to a few degrees below 4.2 K can be obtained. Low temperature measurements are also carried out now using nuclear cooling technique.

Superconductivity is, therefore, a state of matter exhibited by certain metals and alloys below the transition temperature. Subsequent to the discovery of superconductivity in mercury by Onnes, a large number of metallic elements such as Nb, Pb, Al, and alloys such as Nb_3Sn, V_3Ga, Nb_3Au have been found to exhibit superconductivity with varying transition temperatures. Some elemental and compound superconductors and their transition temperatures are given in Table 12.1.

Table 12.1: Some superconductors and their transition temperatures

Element	T_c (K)	Compound	T_c (K)
Hg	4.2	Nb_3Sn	18.1
Al	1.2	V_3Ga	16.5
Nb	9.3	Nb_3Al	17.5
In	3.4	Nb_3Au	11.5
Pb	7.2		

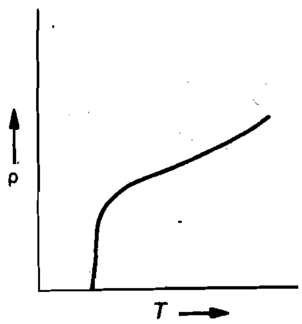

Fig.12.2: Plot of resistivity vs. temperature for a superconductor

It is interesting to note that metals like copper and iron, which are very good conductors at ordinary temperatures do not show superconductivity down to lowest possible temperatures.

On comparing Fig.12.1 and 12.2, you will note that:

a) resistivity at low temperatures becomes very, very small in metal as well as in superconductor; however, in superconductors, it is characterized by *sudden* transition to zero resistivity state at a particular temperature.
b) temperature independent residual resistivity is masked by superconducting transition in superconductors.
c) nature of transition to superconducting state at T_c is similar to phase transitions such as vapour to liquid at vapourisation point and ferromagnetic transition at the Curie point.

Impurities in a superconductor broaden the transition range to superconducting state (Fig.12.3).

In addition, Onnes observed that transition from normal to superconducting state is a **reversible process**, that is, if temperature is raised above the transition temperature, superconductor makes a reverse transition from superconducting to normal state.

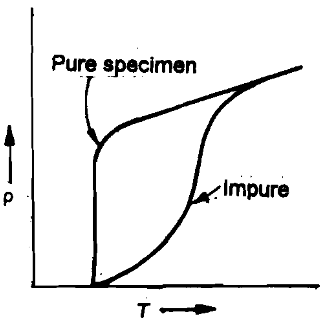

Fig.12.3: Effect of impurity on superconducting transition

You may now ask: Does the electrical resistance in superconducting state actually become zero or it has merely fallen to a very small value? Well, as such, it is impossible to prove that the resistance is indeed zero. Do you know why? It is because the value can be just less than the sensitivity of the measuring apparatus. However, it is possible to infer whether or not resistance is zero. To do so, all we have to do is to pass a current through a ring shaped superconducting specimen and observe whether or not the current decays with time. In one of such experiment, it was found that the decay was less than two percent in seven hours. So, you will agree that it is quite reasonable to treat superconducting specimen as resistanceless. In other words, superconductor is a perfect conductor. Next logical question is: How does unhindered motion of electrons in a perfect conductor influence its other physical properties? Let us first discover the effect on magnetic properties.

12.2.1 Trapped Magnetic Flux

Consider a ring shaped specimen of superconductor which is placed in a magnetic field $\mathbf{B}_a$ (Fig.12.4a). If area enclosed by the ring is A, and magnetic field is normal to it, the magnetic flux linked with the specimen is AB_a.

Transition temperature is one of the crucial parameters of a superconductor because it determines the nature of coolant to be used for observing superconductivity. To cool a superconductor below 10 K, we need liquid helium. If the transition temperature were higher, the applications of superconductors will be less expensive and less cumbersome it is to put superconductors to practical applications. Before the discovery of high temperature ($T_c \sim 90$K) superconductors in 1987, the highest T_c in elemental superconductor was in Nb (~ 9.3 K) and in alloys it was in Nb_3Ge (~ 23.2 K).

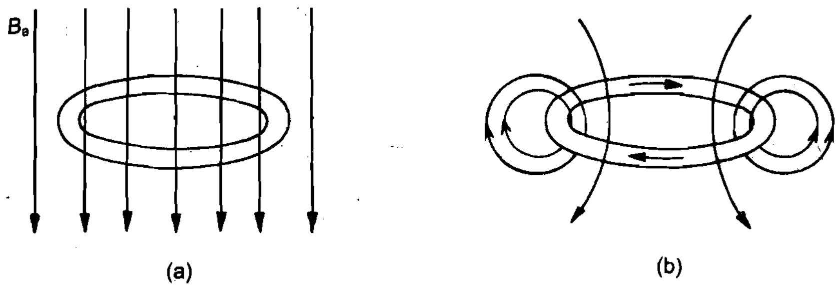

Fig.12.4: A superconducting ring in a) an applied magnetic field, B_a; and b) when field has been removed

Let the specimen be cooled below its transition temperature. Now, if we switch off the magnetic field, as per the Faraday's law of induction the changing field induces an emf which gives rise to a current in the specimen. The induced current generates its own magnetic field in the loop in such a way that the flux is same as before we switched off the field (Fig.12.4b). You can easily explain it by applying Lenz's law. In mathematical terms, we say that the changing magnetic field gives rise to an electromotive force $-A \dfrac{dB_a}{dt}$ and an induced current i, so that,

$$Ri + L\frac{di}{dt} = -A\frac{dB_a}{dt} \qquad (12.1)$$

where, R and L are the resistance and inductance of the specimen, respectively.

Since the specimen is in superconducting state, we have $R = 0$ and Eq. (12.1) reduces to,

$$L\frac{di}{dt} = -A\frac{dB_a}{dt}$$

By integrating both sides, we get

$$iL + AB_a = \text{Constant} \qquad (12.2)$$

where LHS of Eq. (12.2) is the total flux threading the specimen. Thus, Eq. (12.2) shows that the total magnetic flux through the ring shaped specimen cannot change. That is, the **magnetic flux is trapped** (Fig.12.4b).

As the applied field changes, AB_a will change. However, this change is exactly compensated by the flux (iL) due to induced current. It means that **total flux** threading a superconducting circuit is constant. Further, since there is no resistance in the circuit, the induced current will flow continuously. Any decay in this current can be detected by measuring the magnetic field it generates. Such currents have been seen to persist for very very long time without any decay. *The important point to note here is that in a closed superconducting circuit, the magnetic flux remains constant.* An important application of this characteristic of superconducting coil is that it can be used for **magnetic shielding**.

The results arrived at in this section is based on the fact that a superconductor has no resistance. This was considered a hallmark of a superconductor for a long time. But a superconductor is actually more than just a perfect conductor. It is also a perfect diamagnet as observed by Meissner and Ochsenfeld during their careful experimentation. You will learn it now.

12.2.2 Perfect Diamagnet: The Meissner Effect

From PHE-07 course on Electric and Magnetic Phenomena, you may recall that for a diamagnetic substance, magnetic and electric fields vanish everywhere inside the specimen. However, in the preceding sub-section, you learnt that when a superconductor (which has been visualized as a conductor with zero resistance or as a *perfect conductor*) is placed in a magnetic field and its temperature is lowered below its transition temperature, the magnetic flux should persists even if the field has been removed. This inference drawn on the basis of perfect conductor model of a superconductor is incorrect and is not observed experimentally. Instead, when a superconductor is in superconducting state (that is, when it is below its transition temperature), the magnetic lines of induction is expelled suddenly and completely, so that $B = 0$ everywhere inside the specimen. This is called **Meissner effect**. Meissner and his co-workers also showed that when the temperature is raised from below T_c, the flux suddenly penetrates the specimen as it reaches the transition temperature and is in the normal state. This implies that this effect is reversible.

We can, therefore, say that a superconductor is characterized by

- zero resistance; and
- perfect diamagnetism.

Meissner effect is summarized as follows: *a material in superconducting state does not allow any flux inside even when it is cooled in the presence of magnetic field* (Fig.12.5). Mathematically, we can express Meissner effect as

$$B = 0 \tag{12.3}$$

Note that the condition $B = 0$ cannot be obtained from zero resistivity. From Ohm's law, $\varepsilon = \rho \mathbf{J}$, we find that if $\rho = 0$, ε must be zero if $\mathbf{J}$ has to be finite. Further, from Maxwell's relation,

$$-\frac{d\mathbf{B}}{dt} = \nabla \times \varepsilon$$

we get

$$\frac{d\mathbf{B}}{dt} = 0$$

which shows that flux threading a superconducting specimen cannot change.

When a material is placed in a magnetic field B_a, the magnetic induction inside it is given by $B = B_a + \mu_0 M$, where, M is called magnetization of the specimen. From Eq. (12.3), $B = 0$ for a superconductor, thus, we have $M/B_a = -1/\mu_0$. Thus, magnetization is equal (but for a constant factor $1/\mu_0$) and opposite to applied magnetic field. In other words, we can say that superconductor acts as a perfect diamagnet.

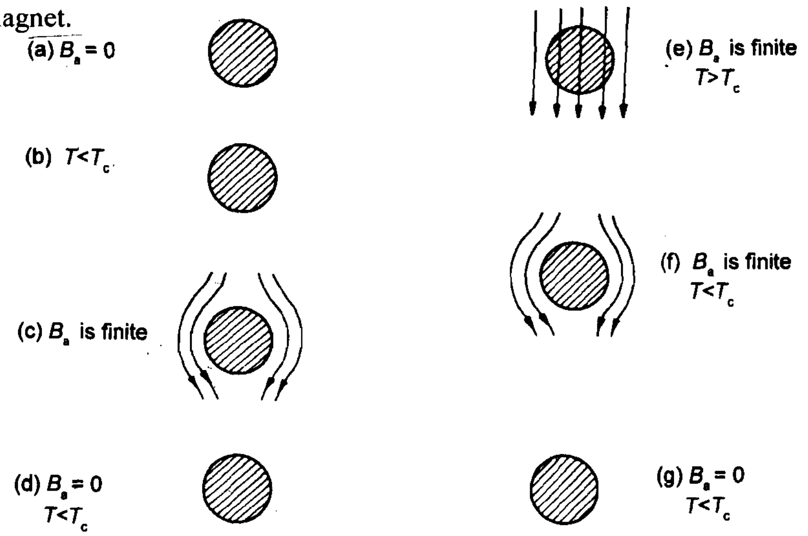

Fig.12.5: The Meissner effect; (a) to (d) shows the case when specimen is cooled in the absence of magnetic field; (e) to (g) shows the case when it is cooled in the presence of a magnetic field

Refer to Fig.12.5. Irrespective of the fact whether the specimen has been cooled below its transition temperature in the absence or in the presence of a magnetic field, the end results (Fig.12.5d and 12.5g) remains the same. *In other words, the state of* *magnetisation of a superconductor is not a function of the external conditions at the time of superconducting transition.* The discovery of Meissner effect established that:

a) perfect diamagnetism is a fundamental property of superconductors, and
b) principles of reversible thermodynamics can be applied to the phenomenon of superconductivity because the state of a superconductor can be described explicitly in terms of macroscopic variables (temperature, magnetisation etc.) and that it does not depend on the particular path followed in going from one set of values of the macroscopic variables to another.

Now, in order to fix your ideas about what you have learnt till now, you should answer the following SAQ.

SAQ 1

Spend 2 min.

Mark the following statements as True or False:

a) Resistance of a superconductor is immeasurably small.
b) Rate of change of magnetic flux passing through a superconductor is zero.
c) Magnetic flux passing through a superconductor is zero.
d) A superconductor is a perfect conductor but does not show diamagnetic behaviour in superconducting state.

Meissner effect is an experimentally observed phenomenon. To understand its theoretical basis, we can use analogy from electrostatics. You may recall that a conductor expels electric fields by moving electric charges to its surface which shields the interior from external field. Similarly, a superconductor expels magnetic fields by setting up electric currents at its surface. These surface currents produce a magnetic field which screens the interior of the superconductor from external applied field. When the temperature is lowered below transition temperature and the specimen attains superconducting state, these surface currents appears spontaneously. If we change the external field, these surface currents also change, and do not allow the applied field to penetrate the interior of a superconductor.

Soon after the discovery of the phenomenon of superconductivity, it was thought that a solenoid made of superconducting wire might be used to generate large magnetic fields if the wire could carry very large currents. However, it was found that sufficiently strong magnetic field could destroy superconductivity. This puts a limit on the amount of current that can flow in a superconductor. It means that apart from its transition temperature, a superconductor is characterized by a critical magnetic field. Let us learn about it now.

12.2.3 Critical Magnetic Fields

Experiments show that a superconductor in superconducting state makes a transition to normal state under the influence of an applied magnetic field. The magnetic field which destroys superconductivity in a specimen is called *critical magnetic field*, B_{ac}. Empirical evidences suggest that critical magnetic field is a function of the temperature of specimen: it is zero at T_c, increases as temperature decreases and attains a maximum value $B_{ac}(0)$ at absolute zero. Mathematically, we can express this experimental observation as

$$B_{ac}(T) = B_{ac}(0)\left[1 - \left(\frac{T}{T_c}\right)^2\right]. \tag{12.4}$$

Refer to Fig.12.6 which is called the **phase diagram** of a superconductor. On examining it closely, you will note that a specimen can be in superconducting state for any combination of the values of temperature and magnetic field within the superconducting region (shown by shaded region).

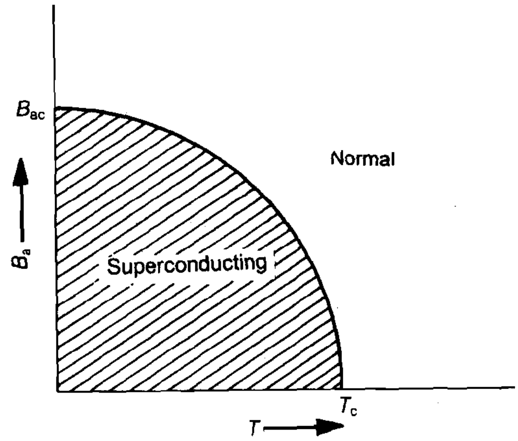

Fig.12.6: Temperature vs. critical magnetic field of a superconductor

You know that current passing through a wire produces magnetic field around it. And, when a conductor is placed in a changing magnetic field, the induced emf generate electric current. Similarly if current passing through a superconductor gives rise to a magnetic field that equals the critical magnetic field at a particular temperature, the specimen becomes normal. *The current density which changes a superconductor from superconducting to normal state is called critical current density.* We denote it by J_c. It is however important to note that if an external magnetic field is also present in addition to the current through superconducting specimen, J_c is the sum of current from the external source and the screening current.

You must have noted that Meissner effect emphasizes dependence of superconducting transition on thermodynamic variables of state, and the transition from normal to superconducting state is reversible. It suggests that we can apply principles of thermodynamics to understand the behaviour of superconductors. Let us learn about it now.

12.2.4 Thermodynamics of a Superconductor

Refer to Fig.12.7 which shows the variation of heat capacity with temperature of a specimen in superconducting and normal states. You will note that as the transition temperature is approached from below, there is a significant jump in the value of heat capacity of the superconducting specimen.

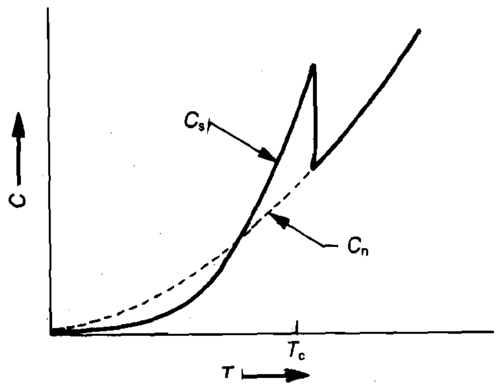

Fig.12.7: Variation of heat capacity with temperature for a specimen in superconducting (C_s) and normal (C_n) states

You may now ask: What does this behaviour of heat capacity suggest? First, it indicates the nature of phase transition. You know from Thermodynamics and Statistical Mechanics (PHE-06) course that a jump in heat capacity at the point of transition is indicative of a *second order phase transition*. Therefore, we may conclude that superconducting transition is a second-order phase transition.

Further, from Fig.12.7 we find that for $T < T_c$, heat capacity of superconducting state is less than that in the normal state. To understand its significance, you may recall that heat capacity of a metal is a combination of lattice and electronic heat capacities. Since lattice properties do not change due to superconducting transition, the change in the values of heat capacity must arise due to changes in the electronic contributions in normal and superconducting phases. The jump in the heat capacity curve at the transition temperature is indicative of an *energy gap for electrons in a superconductor*. You will learn about it in Sec. 12.3.

For a second order phase transition, another requirement is that there should not be any **latent heat** of transition. That is, no heat is supplied or taken away from the system to complete the transition. It has been observed that superconducting transition do not involve latent heat.

To obtain an expression for the energy gap, we consider the Gibb's free energy of the system. Suppose a specimen is cooled below the transition temperature. As a result, energy of the superconducting state will be lower than that of the normal state. Suppose, the Gibbs free energy of the normal and superconducting phases in the absence of magnetic field at temperature T be $g_n(T, O)$ and $g_s(T, O)$ respectively. Now, if magnetic field B_a be applied and the specimen acquires magnetisation M, the change in its energy is given by

$$\Delta g\,(B_a) = -\int_0^{B_a} M dB_a \tag{12.5}$$

The total heat capacity for a normal metal is given by

$$C_n = (C_{latt.})_n + (C_{el})_n$$

$$= A\left(\frac{T}{T_D}\right)^3 + \gamma T$$

where, A is a constant, T_D is Debye temperature and γ is Sommerfeld constant which is a measure of density of states at the Fermi level.

This equation implies that if magnetisation is positive, the free energy of the system is lowered. However, in superconducting specimen, negative magnetisation is produced. Therefore, free energy of the system is increased and we may write

$$g_s(T, B_a) = g_s(T, 0) + \int_0^{B_a} |M| dB.$$

Further, for superconductors, we have $|M| = \dfrac{B_a}{\mu_0}$ (see Eq. (12.3) and discussion below it). Thus we may write

$$g_s(T, B_a) = g_s(T, 0) + \frac{B_a^2}{2\mu_0} \tag{12.6}$$

That is, due to applied magnetic field, free energy of superconducting state increases. On the other hand, normal state of the specimen is non-magnetic and its free energy remains unaffected due to applied magnetic field. Therefore, if sufficiently strong magnetic field is applied, free energy of superconducting state will attain a value more than that of the normal state. In such a condition, the specimen cannot remain superconducting: it returns to normal state. Further, when the applied field attains critical value B_{ac}, we can write,

$$g_s(T, B_{ac}) - g_s(T, 0) = \frac{B_{ac}^2}{2\mu_0} \tag{12.7}$$

You may recall from our course on Thermodynamics and Statistical Mechanics (PHE-06) that the energy of a stable system is lowest. Further, Gibbs free energy enables us to compare the free energies of two phases – normal and superconducting – of a superconductor in applied magnetic field.

Eq. (12.7) gives the energy needed to change a specimen from superconducting state to normal state. Conversely, when a specimen makes a transition from normal to superconducting state, this much energy will be released. Thus, Eq. (12.7) gives us an estimate of **energy gap**. Before you proceed further, how about answering an SAQ!

Spend 3 min.

SAQ 2

What do you understand by critical magnetic field and critical current density of a superconductor?

12.2.5 Type I and Type II Superconductors

You have studied that when critical field B_{ac} is applied, the diamagnetic property disappears completely. *Superconductors exhibiting such sharp disappearance of diamagnetism* (Fig.12.6) *are called type I superconductors and most elemental superconductors belong to this type*. However, there is another group of superconductors which have two critical magnetic fields and are called type II superconductors.

It has been observed that for a group of superconductors, the Meissner effect begins to break down for the value of applied field much below its critical value. To appreciate the nature of flux penetration in these so called type-II superconductors, refer to Fig.12.8. As the value of applied magnetic field reaches a value B_{ac1}, magnetic flux begins to penetrate the specimen. The partial penetration of flux increases gradually till the field value is raised to B_{ac2}. Beyond B_{ac2}, the specimen turns normal. The values of magnetic fields B_{ac1} and B_{ac2} are called **lower critical field** and **upper critical field** respectively and B_{ac2} *is usually much higher than the critical field of type I superconductors*. Type II superconductors are, therefore, also called **hard superconductors**. In the field interval B_{ac1} and B_{ac2}, the substance is said to be a *mixed state*.

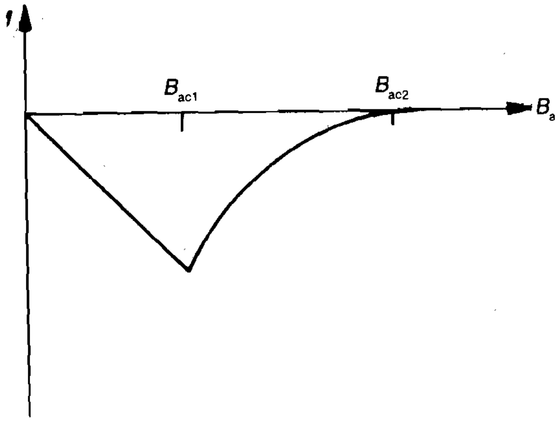

Fig.12.8: Critical magnetic fields of type II superconductors

Till now, you have learnt about superconductivity and its characteristic properties on the basis of electromagnetism and thermodynamics. However, a comprehensive theory of superconductivity was put forward in 1957 by Bardeen, Cooper and Schrieffer. Prior to this a number of phenomenological and microscopic theories were put forward. In the following, you will learn about some of them.

12.3 THEORIES OF SUPERCONDUCTIVITY

Early attempts to explain the phenomenon of superconductivity were partially successful because only a few properties could be explained. One such phenomenological theory, called *two-fluid model*, was proposed by Gorter and Casimir in 1934. It mainly addressed the thermodynamic properties of superconductors. Among the microscopic theories, there were three serious attempts. In 1935, London and London proposed a theory of infinite conductivity and that of Meissner effect. In 1950, Ginzburg and Landau proposed that superconductors can be explained if superconducting state can be considered as a bulk quantum system described by a single wave function. A comprehensive microscopic theory in terms of pairing of electrons was proposed by Bardeen, Cooper and Schrieffer (called BCS in short) in 1957.

A detailed discussion of these theories is beyond the scope of this course. However, in the following, we discuss the basic elements of the two-fluid model and the BCS theory.

12.3.1 Two-fluid Model

According to this model, conduction electrons in a superconductor below its transition temperature divide into two types: **super-electrons** and **normal electrons**. Super electrons can move in a superconductor without any resistance, whereas normal electrons behave in the usual fashion suffering collisions and thereby experience resistance. The number of super-electrons is a function of temperature and can be expressed as

$$n_s = n\left[1-\left(\frac{T}{T_c}\right)^4\right], \quad (12.8)$$

where n is the total number of conduction electrons.

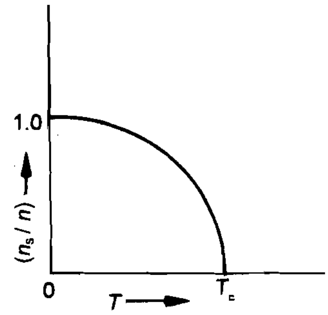

Fig.12.9: Temperature dependence of the number of super-electrons relative to normal electrons

Fig.12.9 shows the temperature variation of the fraction of super-electrons in a superconductor. Note that at absolute zero, all conduction electrons behave like super-electrons. As temperature increases, some of them start behaving like normal electrons and at the transition temperature, all the electrons become normal and superconductivity disappears.

In superconducting state below the transition temperature, current can be carried by normal as well as super-electrons. You may ask: Why then we do not observe any resistance? In fact, the super-electrons *short circuit* normal electrons and we observe zero resistance. A superconducting specimen essentially behaves like two conductors connected in parallel; one having a normal resistance and the other zero resistance.

This model could qualitatively explain zero resistance. But it failed to explain Meissner effect and other properties of superconductors. Moreover, this model is not based on basic principles.

London theory of superconductivity deals with the discussion on electromagnetic principles of superconductors and could explain the Meissner effect. It also used the two-fluid model and is semi-phenomenological as it uses an equation which at that time could not be derived from the first principles. The more comprehensive theory of superconductivity was proposed by BCS, which is capable of explaining all the observed phenomena relating to conventional superconductors. It starts with first principles and using quantum concepts, explains the occurrence of zero resistance, the Meissner effect, the observed temperature dependence of heat capacity and so on. Since meaningful discussion of BCS theory is possible only using advanced quantum mechanical concepts and mathematical techniques, for simplicity, we discuss it here only qualitatively.

12.3.2 BCS Theory

BCS focused on the behaviour of conduction electrons and noted that there must exist a unique kind of interaction among them. The nature of interaction should be such that the resulting superconducting state has lower energy than the normal state. As you know, conduction electrons in a metal do interact; but the *repulsive Coulomb interaction cannot account for the lowering of energy in superconducting state*. Further. even if Coulomb interactions were attractive, they are too strong and incommensurate with the observed energy gap (~ 10^{-4}eV) in a typical superconductor. Thus, it seemed necessary to formulate a *weak attractive interaction between electrons*. The question was: How to attain this?

Phonon mediated electron interaction

Phonons are quantised lattice vibrations. The frequency of phonons depends on the type of material including the mass of the atoms.

The clue to the possible solution of this problem of attractive interaction between electrons came from the discovery of **isotope effect** according to which transition temperature was related to the mass of the atoms of a superconductor. This led them to think that interaction between the electrons and the vibration of atoms (lattice vibrations) could play a decisive role. Further, BCS were guided by Frohlich's hypothesis that it is possible to visualise a direct interaction between two electrons in terms of electron-lattice interaction as a two step process. Firstly, as a result of electron-lattice interaction, a phonon is generated, and in the second step, this phonon is immediately captured by another electron. It means that interaction between the two electrons is due to exchange of phonons.

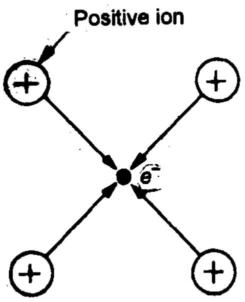

Fig.12.10: Positive ions attracted towar an electron crea a region of net positive charge

You will appreciate this concept by considering the situation shown in Fig.12.10. It depicts that attraction between an electron and positive ions in a lattice creates a region of net positive charge. As a result, the negative charge of electron is 'screened', and an electron passing by this region could be effectively attracted to it. This facilitates attraction between two electrons. Since both electrons are moving through the lattice, such deformations are quite dynamic and constitute a localized lattice vibration called phonon. So we can say that attraction between the two electrons is actually due to exchange of phonons. These two electrons having attractive interaction from a bound system called **Cooper pair**. One electron in a Cooper pair emits a phonon and the other electron absorbs it.

The phonon mediated interaction between electrons is shown in Fig.12.11. An electron with momentum p_1 emits a phonon of momentum q and is left with momentum p_1'. Thus, conservation of momentum requires that

$$p_1 = p_1' + q \tag{12.9}$$

It is observed that specimens of different isotopes of a given superconductor have different transition temperatures. In general, the transition temperature is inversely proportional to the square root of the isotopic mass. This is known as **isotope effect**. It suggests that lattice vibrations has a definite role in superconductivity.

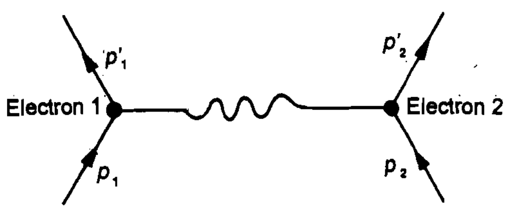

Fig.12.11: Phonon mediated electron interaction

Similarly, when the emitted phonon is absorbed by another electron with momentum p_2, we can write

$$p_2 + q = p_2' \tag{12.10}$$

By combining Eqs. (12.9) and (12.10), we have

$$p_1 + p_2 = p_1' + p_2' \tag{12.11}$$

That is, momentum of the Cooper pair is conserved.

Now you may ask: Is energy also conserved in this process? Well, energy is indeed conserved between initial and final states. *However, it may not be conserved between the initial and intermediate state or between the intermediate state and the final state.* Such processes can be understood only in terms of quantum mechanics and are known as *virtual processes*. In a virtual process, the initial and final energies of the first electron may be connected through the relation

Intermediate state refers to the situation when a phonon has been emitted due to electron-lattice interaction and is yet to be absorbed by another electron.

$$(E_1 - E_1') < h\nu_q \qquad (12.12)$$

where ν_q is the frequency of emitted phonon. *When this condition is satisfied, the phonon mediated interaction between electrons is attractive.* However, it is the strength of Coulomb interaction between electrons that ultimately determines the nature of interaction.

To discuss the feasibility of attractive electron interaction, let us consider the free-electron model. Let k_F be the radius of the Fermi sphere. At absolute zero, all states below Fermi level in a normal metal will be occupied (Fig.12.12). What about states defined by $k > k_F$? All states outside the Fermi sphere will be unoccupied. With this distribution of occupied states, no phonon can be exchanged between any pair of electrons inside the Fermi surface because no state is vacant within the sphere. Do you know what forbids this? It is because of Pauli's exclusion principle. However, if we move a pair of electrons into states outside the Fermi surface ($k > k_F$), phonon exchange will be possible. The resulting attraction could offset the increase in kinetic energy ($\hbar^2k^2/2m$) required to take the pair outside the Fermi surface. This pair would then have a net energy $E < E_F$ forming a stable state. However, k should be near the Fermi surface so that the kinetic energy is as small as possible.

Non-conservation of energy arises due to uncertainty principle:

$$\Delta E \,.\, \Delta t \approx \hbar$$

Thus, if the life time of the intermediate state (Δt) is very short, there will be large uncertainty in its energy (ΔE). As a result, energy may not be conserved between initial and intermediate states or between intermediate and final states.

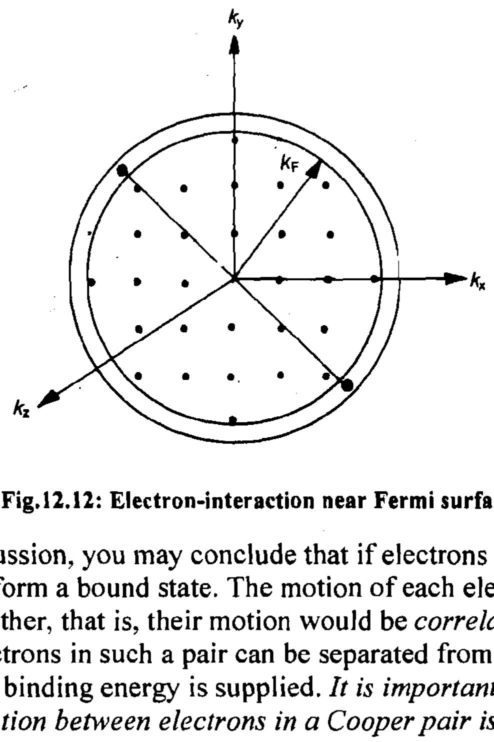

Fig.12.12: Electron-interaction near Fermi surface

From the above discussion, you may conclude that if electrons were close to Fermi surface, they would form a bound state. The motion of each electron in the pair would be influence by the other, that is, their motion would be *correlated* because they form a bound system. Electrons in such a pair can be separated from each other when energy equal to their binding energy is supplied. *It is important to mention here that the attractive interaction between electrons in a Cooper pair is stronger than the Coulomb repulsion when they have equal and opposite momenta and opposite spins.* Also note that Cooper pair is electron pair in *momentum space* rather than geometrical space. Such a pair would be about 2000 Å apart in geometric space! Compare this separation with interatomic separation (~ 2 to 3 Å).

The binding energy of electrons in Cooper pairs manifests itself as gap in the energy spectrum of electrons. Appearance of the energy gap alters the Fermi energy of a superconductor. This is shown in Fig.12.13. An energy gap equal to $2\Delta_0$ appears centred around the Fermi energy of the superconductor such that there is a sudden increase in the density of states near the gap edges. (These Cooper pairs are what we called super electrons in the two-fluid model).

Evidence for the existence of energy gap is provided by the absorption of electromagnetic radiation by a superconductor. It has been observed that superconductor absorbs photons which have an energy greater than its gap energy $2\Delta_0$. On absorbing such photons, Cooper pairs break apart. This effect provide a mechanism for measuring the gap energy in superconductors. Further evidence for the existence of energy gap in superconductors is observed in tunneling experiments. However, we shall not discuss any further details here.

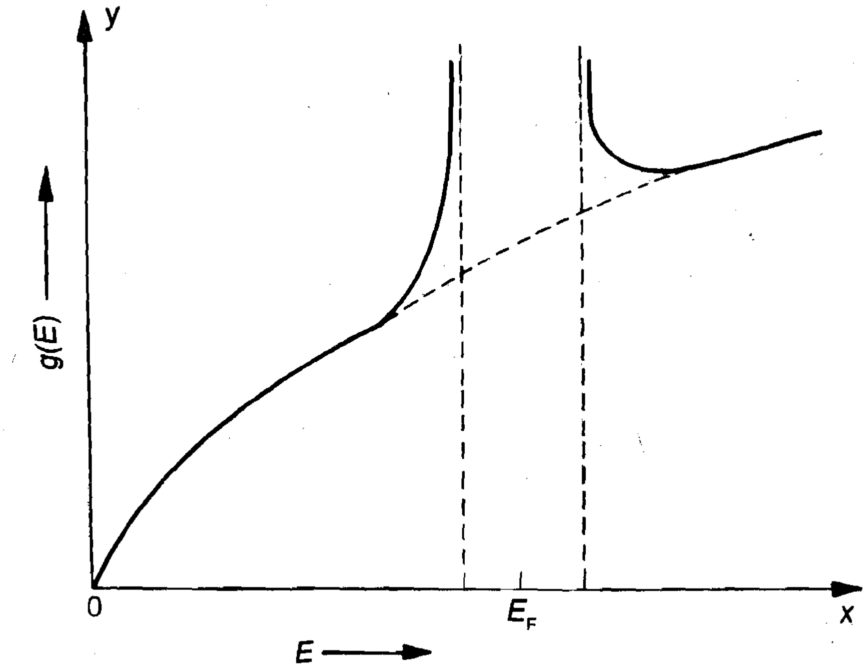

Fig.12.13: Energy variation of density of state of electrons in a superconductor

Till now in this sub-section, you learnt two main physical principles underlying the microscopic theory of superconductors proposed by BCS. As such, BCS theory includes much more and involves detailed quantum mechanical derivations which we have avoided for simplicity. Nevertheless, even with this qualitative description, it is possible to explain some of the properties of superconducting state.

As the transition temperature is approached from below, energy gap in a superconductor decreases and becomes zero at T_c.

Firstly, let us take the case of zero resistance in superconducting state. You know that resistance is due to scattering of electrons with lattice vibrations and impurities. BCS theory does not rule out scattering; however, instead of single electron, Cooper pairs are scattered as a single entity. For electrical resistance to appear, scattering process must supply energy equal to gap energy so that the pairs break and we have free electrons. However, at low temperatures ($\leq T_c$), energy supplied to Cooper pairs is less than $2\Delta_0$ because only low energy phonons are excited. This explains why Cooper pairs drift along without encountering any resistance in the superconducting state.

The existence of transition temperature is explained by the BCS theory in terms of breaking of Cooper pairs. As temperature is increased above absolute zero, some Cooper pairs begin to break up due to thermal agitation. Simultaneously, the gap energy decreases. As $T \rightarrow T_c$, all the Cooper pairs are broken up and the gap energy vanishes completely. The BCS theory predicts that gap energy is connected to transition temperature through the relation

$$E_g = 2\Delta_0 = 3.5\, k_B T_c \tag{12.13}$$

It suggests that materials with larger gap energy will maintain superconductivity upto higher temperatures. The heat capacity curve (Fig.12.7) of a superconductor can be understood in terms of Cooper pairs. Near the transition temperature, there are large number of Cooper pairs ready to break up. Thus, substantial amount of energy is needed, making the heat capacity larger as manifested by jump in the curve (Fig.12.7). Moreover, at the transition temperature, the gap energy vanishes; and total energy of electrons as T approaches T_c from below is exactly the same as T approaches T_c from above. Therefore, there is no latent heat involved in superconducting transition and the phase transition is of second order.

Further, the long-range order exhibited by superelectrons is obvious from the formation of Cooper pairs in momentum space. Lastly, you may ask: Why do not all metals exhibit superconductivity when cooled to sufficiently low temperatures? According to the BCS theory, whether or not a metal shows superconductivity depends on the fact that the net interaction between electrons – Coulomb repulsion and phonon-mediated attraction – must be attractive. It is perhaps for this reason that good normal conductors which have weak electron – phonon interaction do not exhibit superconductivity.

You may now like to solve an SAQ.

SAQ 3

Spend 5 min.

The transition temperature for Al, Hg and Pb are 1.80 K, 4.153 K and 7.193 K respectively. Calculate the gap energy for these materials. Take $k_B = 1.38\times10^{-23}$ JK^{-1}.

On working out this SAQ, you will find that for these materials, BCS theory gives values of gap energies which compare well with experimental value of 0.34×10^{-3} eV, 1.65×10^{-3} eV and 2.73×10^{-3} eV.

Ever since the discovery of superconductivity by Onnes, efforts have been made to increase the transition temperature. These researches led to discovery of many new superconductors. The maximum transition temperature that could be achieved was 23 K till early ninety eighties. A major breakthrough was, however, achieved in 1986 when Bednorz and Muller discovered that lanthanum barium copper oxide exhibited superconductivity with $T_c \approx 30$ K. This breakthrough aroused great interest in superconductivity research and acted as a catalyst for the discovery of oxide superconductors with higher and higher transition temperatures. These *oxide* (or *cuprate*) superconductors are collectively called *high* T_c superconductor. You will learn about them now.

12.4 HIGH TEMPERATURE SUPERCONDUCTORS

The discovery of superconductivity in lanthanum barium copper oxide (La-Ba-Cu-O) system is significant for two reasons:

a) There is a jump in the transition temperature from 23 K to 30 K.
b) Superconductivity is observed in a *new* type of material. It raised the possibilities of discovering newer materials with still higher value of T_c and ultimately, may be, leading to *room temperature* superconductors!

La-Ba-Cu-O system refers to the fact that among the variety of chemical compounds which could be formed by taking different proportions of each of the four elements, only one or a few more stichiometric compositions exhibit superconductivity. Bednorz and Muller discovered superconductivity in a compound with stichiometric formula $(La_{2-x}Ba_x)\,CuO_4$.

Soon after this landmark discovery, Paul Chu and co-workers discovered a cuprate of Y-Ba-Cu-O system with a transition temperature of 90 K. This discovery had tremendous potential for practical applications because T_c is much above the boiling point (77K) of nitrogen — a coolant much more cheaper than liquid helium required for *conventional* superconductors.

These and subsequently discovered copper oxide superconductors are called *high* T_c *superconductors* because their discovery meant breaking theoretical upper limit on T_c of 30 K set by BCS theory. The speed with which materials with higher and higher T_c were being discovered during this period was unprecedented — in the interval of just one year, T_c had been increased from 30 K to 90 K! This was indeed a remarkable achievement in comparison to rate of increase of T_c in the preceding years (see Fig.12.14).

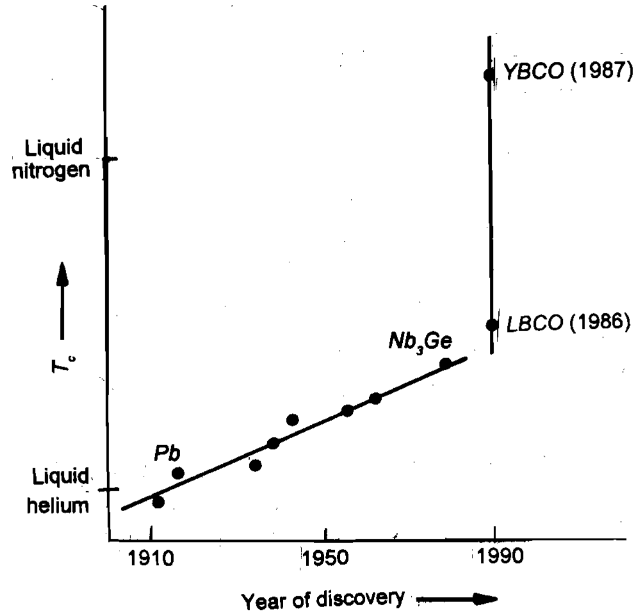

Fig.12.14: Transition temperature vs. year of discovery

High T_c superconductors are also called **cuprates** or **copper oxide** or simply **oxide** superconductors because all of them contain copper and oxygen.

Since the pioneering discovery of Bednorz and Muller in 1986, a large number of cuprates with considerably higher transition temperatures have been discovered. In Table 12.2, we have listed systems, their stichiometric formula and T_c of some of the important families of cuprate superconductors.

Tables 12.2: Some of the high T_c superconductors

System	Formula	T_c (K)
LBCO	$(La_{2-x} Ba_x) Cu O_4$	30-40
YBCO	$YBa_2 Cu_3 O_7$	90
Bi 2201	$Bi_2 Sr_2 Cu O_6$	0–20
Bi 2212	$Bi_2 Sr_2 Ca Cu_2 O_8$	85
Bi 2223	$Bi_2 Sr_2 Ca_2 Cu_3 O_{10}$	110
Tl 2201	$Tl_2 Ba_2 Cu O_6$	0–80
Tl 2212	$Tl_2 Ba_2 Ca Cu_2 O_8$	108
Tl 2223	$Tl_2 Ba_2 Ca_2 Cu_3 O_{10}$	125

The crystal structure of conventional superconductors remain unaltered during superconducting transition. *However, in case of some high T_c superconductors, it has been observed that their normal and superconducting phases are characterized by different crystal structures.* Crystal structure of a few representative high T_c systems is shown in Fig.12.15. Detailed analysis of their crystal structures have helped understand the mechanism of superconductivity in these materials. Therefore, we briefly outline the salient crystallographic features of these materials.

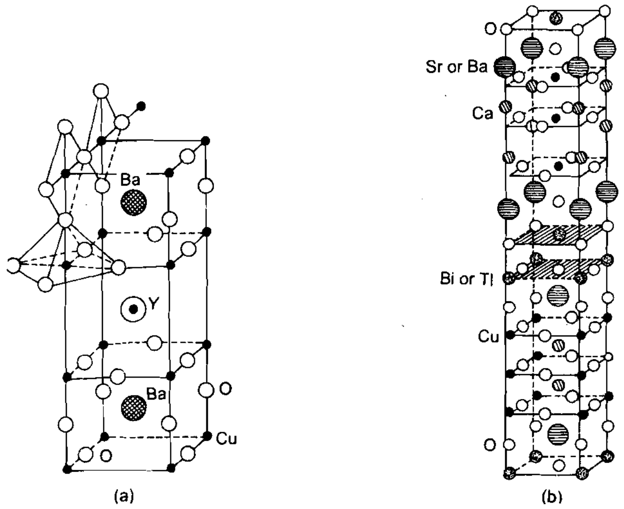

Fig.12.15: Arrangement of atoms in a) YBCO; and b) BSCCO systems of high T_c superconductors

X-ray and neutron diffraction studies have shown that the structure of all these superconductors belong to the same class of perovskite structures with the general formula ABO_3. The crystal structures of these compounds exhibit the following important features:

Perovskite crystal structure is characterised by arrangement of atoms along planes and chains. A typical example of perovskite structure is K_2NiO_4.

a) Copper and oxygen atoms are bound to each other in alternate layers containing planes and chains (refer Fig.12.15).
b) These materials exhibit anisotropic behaviour with respect to many physical properties. For example, electrical resistivity values along the Cu-O planes and along a direction perpendicular to it are very different from each other.
c) In case of YBCO system, superconducting phase has orthorhombic structure whereas normal phase has tetragonal structure; the structure dependent superconductivity is unique to this system of high T_c superconductor.

Refer to Fig.12.15 which shows the arrangement of atoms in crystals of YBCO and BSCCO systems. Unlike LBCO system which contains only Cu-O planes, YBCO system contains Cu-O planes as well as Cu-O chains. Thus, it was thought that Cu-O chains in YBCO was responsible for higher T_c. However, discovery of BSCCO and TBCCO systems indicated that it is Cu-O planes which are important. It is because, in these systems, Cu-O chains were absent and still they had higher T_c than YBCO system. Thus, it is logical to conclude that the (super) conducting properties of these materials are perhaps due to the 'activity' of electrons in Cu-O planes. The importance of Cu-O planes is further emphasised by the fact that in BSCCO (as well as in TBCCO) systems, there are more than one Cu-O planes per unit cell and there are no Cu-O chains. *Thus, presence of Cu-O planes is supposedly the most important structural feature of all the copper oxide superconductors*. Apart from this, there is hardly any physical or chemical property which is common to all high T_c superconductors. Let us now discuss some of the microscopic features of these materials qualitatively.

Firstly, in these layered materials, superconductivity is supposedly confined to Cu-O planes. In case of YBCO system, the Cu-O planes are separated by yttrium atoms (Fig.12.15a). (Other layers in the structure contains remaining barium, copper and oxygen atoms). For this reason Cu-O planes are called *charge conducting layers* and planes containing Ba, Cu and O are called *charge reservoir layers*. The electrical and structural properties of a particular system or of a particular stichiometry within a system depends on the relative size and electron affinities of the conducting layer and reservoir layer atoms. In addition, high T_c superconductors exhibit following features:

a) As in case of conventional BCS type superconductors, charge carriers in high T_c superconductors are bound in pairs. However, the separation between these charge carriers is much smaller than in a pair in conventional superconductor.

b) High T_c materials do not exhibit isotope effect. Recall that isotope effect is an important experimental evidence in support of BCS theory. This suggests that the role of lattice vibrations (phonons) is not significant in these materials.
c) Existence of energy gap has also been confirmed experimentally.
d) They are type-II superconductors characterized by two critical magnetic fields. Also, the upper critical magnetic field of high T_c superconductor is very high — an important result from the applications point of view.
e) The critical current density has been found to be very low compared to that of conventional superconductors.

Till now, you have studied about characteristic features of high T_c superconductors. It is important to mention here that superconductivity is one of those rare areas in science in which substantial progress has been made in the applications side much in advance to the theoretical understanding of the phenomenon itself. One of the major applications of superconductors is in fabrication of electromagnets. It is because the strength of magnetic field produced by an electromagnet is a function of current passing through the coil. However, due to resistive (Joule) heating, there is a limiting maximum value of current we can pass through the coil of an electromagnet made of copper or any other metallic wires. This puts a limitation on the maximum field one can obtain by electromagnet made of non-superconducting materials. However, with superconducting wires, the limiting value of current in an electromagnet increases manifold. You will learn about superconducting magnets and other applications of superconductors in Unit 13 of this course.

Now let us summarise what you have learnt in this unit.

12.6 SUMMARY

- Superconductivity is a phenomenon in which electric current pass through a material without any resistance. Superconducting state of material is observed only below a temperature called **transition or critical temperature**. A large number of metallic elements and alloys have been found to exhibit superconductivity with varying transition temperatures.

- Perfect conductivity of superconductor implies that magnetic flux threading superconducting specimen is constant. This inference does not confirm to experimental observations: superconductors are perfect diamagnet and expel magnetic flux. The perfect diamagnetism of superconducting state is known as **Meissner effect**.

- The Meissner effect and reversibility of superconducting transition imply that the principles of reversible thermodynamics can be applied to understand the phenomenon of superconductivity.

- **Critical magnetic field** of a superconductor is given by

$$B_{ac}(T) = B_{ac}(0)\,[1 - (T/T_c)^2]$$

where T_c is the transition temperature.

- Sudden increase in the value of heat capacity of a superconductor at T_c shows that there exists an energy gap in the energy spectrum of electrons. The gap energy is given as

$$g_s(T, B_{ac}) - g_s(T, 0) = \frac{B_{ac}^2}{2\mu_0}$$

- According to the **two-fluid model**, conduction electrons in a superconductor below its transition temperature consists of super-electrons and normal electrons. The number of super-electrons is given as

  $$n_s = n\,[1 - (T/T_c)^4]$$

  where n is the total number of conduction electrons.

- According to the **BCS theory**, superconducting state has lower energy than the normal state and it is achieved due to phonon mediated attractive interaction between conduction electrons. Two electrons attracted towards each other form a bond system and are called **Cooper pairs**. Cooper pairs can travel through a superconducting specimen without any resistance.

- BCS theory predicts the following expression for gap energy

  $$E_g = 3.5\, k_B\, T_c$$

- Discovery of **high T_c superconductivity** in oxides is significant for two reasons:

  i) increase in transition temperature from 23K to 30K, and
  ii) it raised the possibility of discovering newer materials with higher values of T_c.

- Analysis of crystal structure of high T_c materials show that it consists of **Cu-O chains** and **Cu-O planes**. The role of Cu-O planes has been found crucial in respect to superconductivity in these materials.

- Like BCS type superconductors, high T_c superconductors also consists of Cooper pairs but they do not show isotope effect.

- Some of the promising applications of superconductivity are in electric power transmission, high field magnets, maglevs and micro-electronics.

12.7 TERMINAL QUESTIONS

1. Suppose that below the transition temperature, a superconductor behaves like a perfect conductor and satisfy the condition $(dB/dt) = 0$. Show that the state of magnetisation of the superconductor is not uniquely determined by external conditions.

2. Explain how a superconductor can be used for magnetic shielding.

12.8 SOLUTIONS AND ANSWERS

Spend 20 min.

Self-Assessment Questions (SAQs)

1. a) True; b) False; c) True; d) False

2. Critical magnetic field is the value of the applied magnetic field which destroys superconductivity and is a function of temperature. Critical current density is the maximum value of the current which a superconducting wire can carry; if current density is increased further, the wire no longer remains superconducting.

3. From Eq. (12.13),

   $$E_g = 2\Delta_0 = 3.5\, k_B\, T_c.$$

Thus, for Al,

$$E_g = 3.5 \times (1.38 \times 10^{-23}\ \mathrm{JK^{-1}}) \times (1.8\ \mathrm{K})$$

$$= 0.34 \times 10^{-3}\ \mathrm{eV}$$

For Hg,

$$E_g = 3.5 \times (1.38 \times 10^{-23}\ \mathrm{JK^{-1}}) \times (4.153\ \mathrm{K})$$

$$= 1.65 \times 10^{-3}\ \mathrm{eV}$$

For Pb,

$$E_g = 3.5 \times (1.38 \times 10^{-23}\ \mathrm{JK^{-1}}) \times (7.193\ \mathrm{K})$$

$$= 2.73 \times 10^{-3}\ \mathrm{eV}$$

Terminal Questions (TQs)

1 Refer to Fig. (12.16). Let us assume that a superconductor makes transition to superconducting state in the absence of applied magnetic field. Once in superconducting state, a magnetic field B_a is applied on the specimen. Since the state of magnetisation of the specimen in superconducting state can not change, the magnetic flux is expelled from the body of the specimen, Figs. (12.16a) to (12.16c). When the applied magnetic field is now reduced to zero, the specimen in superconducting state remains in demagnetised state (Fig.12.16d).

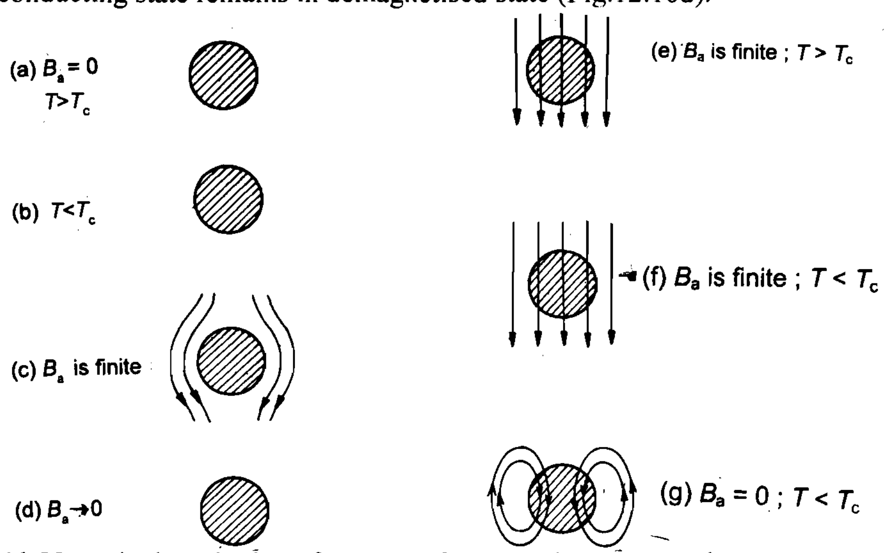

Fig.12.16: Magnetisation behaviour of a superconductor considered as a perfect conductor

Now, consider another sequence in which superconducting transition takes places in the presence of magnetic field B_a (Fig.12.16e). Therefore, when the specimen is in superconducting state, it is magnetised (Fig.12.16f). Now, let the applied magnetic field is reduced to zero. Since the flux density cannot change in superconducting state, surface currents are induced in the specimen due to changing magnetic field to keep $dB/dt = 0$. *Thus, the specimen remains magnetised even when the value of applied field is reduced to zero.* Thus, the condition $dB/dt = 0$ leads to different states of magnetisation depending upon initial conditions; that is, magnetisation of the specimen is not uniquely determined.

2 Since superconducting state is a state of perfect diamagnetism, magnetic lines of induction are expelled out from its interior. Therefore, materials kept in a superconducting container is shielded from magnetic field.

FUNDAMENTAL PHYSICAL CONSTANTS

Quantity	Symbol	Value
speed of light in vacuum	c	2.998×10^{8} ms^{-1}
permeability of vacuum	μ_0	1.257×10^{-6} NA^{-2}
permittivity of vacuum	ε_0	8.854×10^{-12} $C^2N^{-1}m^{-2}$ 8.988×10^{9} Nm^2 C^{-2}
universal gravitational constant	G	6.673×10^{-11} $m^3kg^{-1}s^{-2}$
Planck's constant	h	6.626×10^{-34} Js
$h/2\pi$	$\hbar$	1.055×10^{-34} Js
charge of the electron	$-e$	-1.602×10^{-19} C
charge of the proton	e	1.602×10^{-19} C
electron rest mass	m_e	9.109×10^{-31} kg
proton rest mass	m_p	1.673×10^{-27} kg
proton-electron mass ratio	m_p/m_e	1836
Rydberg constant	R_∞	1.097×10^{-7} m^{-1}
Avogadro constant	N_A	6.022×10^{23} mol^{-1}
molar gas constant	R	8.315 J mol^{-1}
Boltzmann constant (R/N_A)	k_B	1.381×10^{-23} JK^{-1}

Non-SI units used with SI

electron volt	$1eV = 1.602 \times 10^{-19}$ J
(unified) atomic mass unit	$1u = 1.661 \times 10^{-27}$ kg