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E-NOTES

SUBJECT: CONDENSED MATTER PHYSICS

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UNIT : 5

SYLLABUS:

Experimental facts: Occurrence - Effect of magnetic fields - Meissner effect – Critical field – Critical current - Entropy and heat capacity - Isotope effect - Energy gap - Type I and Type II superconductors. Theoretical explanation: Thermodynamics of super conducting transition - London equation - BCS Theory - Coherence length –- Cooper pairs - Single particle Tunneling - Josephson tunneling - DC and AC Josephson effects - High temperature super conductors - SQUIDS.

The electrical resistivity of many metals and alloys drops suddenly to zero when the specimen is cooled to a sufficiently low temperature, often a temperature in the liquid helium range. This phenomenon, called superconductivity, was observed first by Kamerlingh Onnes[1] in Leiden in 1911, three years after he first liquified helium. At a critical temperature T_c the specimen undergoes a phase transition from a state of normal electrical resistivity to a superconducting state, Fig. 1.

Superconductivity is now very well understood. It is a field with many practical and theoretical aspects. The length of this chapter and the relevant appendices reflect the richness and subtleties of the field.

EXPERIMENTAL SURVEY

In the superconducting state the dc electrical resistivity is zero, or so close to zero that persistent electrical currents have been observed to flow without attenuation in superconducting rings for more than a year, until at last the experimentalist wearied of the experiment.

The decay of supercurrents in a solenoid was studied by File and Mills[2] using precision nuclear magnetic resonance methods to measure the magnetic field associated with the supercurrent. They concluded that the decay time of the supercurrent is not less than 100,000 years. We estimate the decay time below.

In some superconducting materials, particularly those used for superconducting magnets, finite decay times are observed because of an irreversible redistribution of magnetic flux in the material.

The magnetic properties exhibited by superconductors are as dramatic as their electrical properties. The magnetic properties cannot be accounted for by the assumption that a superconductor is a normal conductor with zero electrical resistivity.

[1] H. Kamerlingh Onnes, Akad. van Wetenschappen (Amsterdam) 14, 113, 818 (1911): "The value of the mercury resistance used was 172.7 ohms in the liquid condition at 0°C; extrapolation from the melting point to 0°C by means of the temperature coefficient of solid mercury gives a resistance corresponding to this of 39.7 ohms in the solid state. At 4.3 K this had sunk to 0.084 ohms, that is, to 0.0021 times the resistance which the solid mercury would have at 0°C. At 3 K the resistance was found to have fallen below 3×10^{-6} ohms, that is to one ten-millionth of the value which it would have at 0°C. As the temperature sank further to 1.5 K this value remained the upper limit of the resistance." Historical references are given by C. J. Gorter, Rev. Mod. Phys. **36**, 1 (1964).

[2] J. File and R. G. Mills, Phys. Rev. Lett. **10**, 93 (1963).

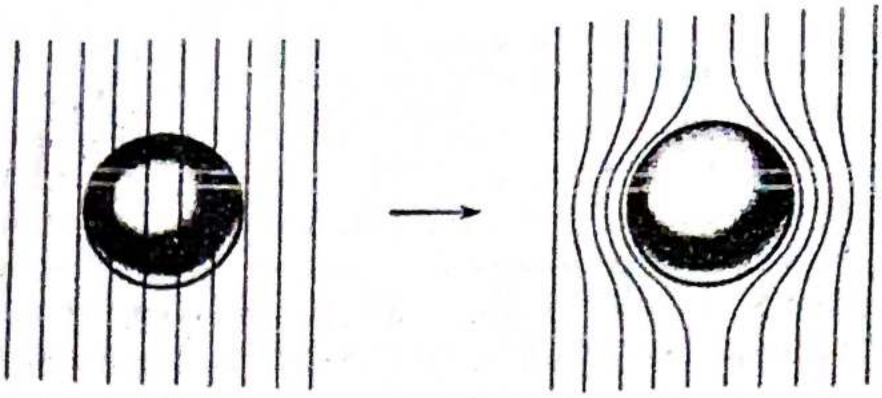

Figure 2 Meissner effect in a superconducting sphere cooled in a constant applied magnetic field; on passing below the transition temperature the lines of induction **B** are ejected from the sphere.

It is an experimental fact that a bulk superconductor in a weak magnetic field will act as a perfect diamagnet, with zero magnetic induction in the interior. When a specimen is placed in a magnetic field and is then cooled through the transition temperature for superconductivity, the magnetic flux originally present is ejected from the specimen. This is called the Meissner effect. The sequence of events is shown in Fig. 2. The unique magnetic properties of superconductors are central to the characterization of the superconducting state.

The superconducting state is an ordered state of the conduction electrons of the metal. The order is in the formation of loosely associated pairs of electrons. The electrons are ordered at temperatures below the transition temperature, and they are disordered above the transition temperature.

The nature and origin of the ordering was explained by Bardeen, Cooper, and Schrieffer.[3] In the present chapter we develop as far as we can in an elementary way the physics of the superconducting state. We shall also discuss the basic physics of the materials used for superconducting magnets, but not their technology. Appendices H and I give deeper treatments of the superconducting state.

Occurrence of Superconductivity

Superconductivity occurs in many metallic elements of the periodic system and also in alloys, intermetallic compounds, and doped semiconductors. The range of transition temperatures best confirmed at present extends from 90.0 K for the compound $YBa_2Cu_3O_{6.9}$ to below 0.001 K for the element Rh. Several *f*-band superconductors, also known as "exotic superconductors," are listed in Chapter 6. Several materials become superconducting only under high pressure; for example, Si has a superconducting form at 165 kbar, with T_c = 8.3 K. The elements known to be superconducting are displayed in Table 1, for zero pressure.

Will every nonmagnetic metallic element become a superconductor at sufficiently low temperatures? We do not know. In experimental searches for superconductors with ultralow transition temperatures it is important to eliminate from the specimen even trace quantities of foreign paramagnetic elements, because they can lower the transition temperature severely. One part of Fe in 10^4 will destroy the superconductivity of Mo, which when pure has $T_c = 0.92$ K; and 1 at. percent of gadolinium lowers the transition temperature of lanthanum from 5.6 K to 0.6 K. Nonmagnetic impurities have no very marked effect on the transition temperature. The transition temperatures of a number of interesting superconducting compounds are listed ~~in Table 2~~. Several organic compounds show superconductivity at fairly low temperatures.

Destruction of Superconductivity by Magnetic Fields

A sufficiently strong magnetic field will destroy superconductivity. The threshold or critical value of the applied magnetic field for the destruction of superconductivity is denoted by $H_c(T)$ and is a function of the temperature. At the critical temperature the critical field is zero: $H_c(T_c) = 0$. The variation of the critical field with temperature for several superconducting elements is shown in Fig. 3.

The threshold curves separate the superconducting state in the lower left of the figure from the normal state in the upper right. Note: We should denote the critical value of the applied magnetic field as B_{ac}, but this is not common practice among workers in superconductivity. In the CGS system we shall always understand that $H_c \equiv B_{ac}$, and in the SI we have $H_c \equiv B_{ac}/\mu_0$. The symbol B_a denotes the applied magnetic field.

Meissner Effect

Meissner and Ochsenfeld (1933) found that if a superconductor is cooled in a magnetic field to below the transition temperature, then at the transition the lines of induction B are pushed out (Fig. 2). The Meissner effect shows that a bulk superconductor behaves as if inside the specimen $B = 0$.

Table 2 Superconductivity of selected compounds

Compound	T_c, in K	Compound	T_c, in K
Nb_3Sn	18.05	V_3Ga	16.5
Nb_3Ge	23.2	V_3Si	17.1
Nb_3Al	17.5	$YBa_2Cu_3O_{6.9}$	90.0
NbN	16.0	Rb_2CsC_{60}	31.3
K_3C_{60}	19.2	La_3In	10.4

in a solenoid of $Nb_{0.75}Zr_{0.25}$ is not less than 10^5 years. Thus existence of persistent current is a proof of the occurrence of superconducting state.

It has been found that the superconducting properties of metals can be changed by varying temperature, magnetic field, magnetic stress, frequency of excitation of applied electric fields, impurities and with atomic structure, size and isotopic mass of the specimen. We shall, in this article, take up some of the effects.

11.2-1 EFFECT OF MAGNETIC FIELD : (THE CRITICAL FIELD)

Superconductivity will disappear if the temperature of the specimen is raised above its T_c or if a sufficiently strong magnetic field is employed. *The critical value of the applied magnetic field necessary to restore the normal resistivity, i.e., to destroy superconductivity is denoted by $H_c(T)$ and is a function of temperature.*

At critical temperature, the critical field is zero, *i.e.*, $H_c(T) = 0$. The variation of critical field as a function of temperature for some elements is shown in fig. 3. We note that curves are nearly parabolic and can reasonably be represented by the relation,

$$H_c = H_0\left(1 - \frac{T^2}{T_c^{\,2}}\right) \qquad ...(1)$$

where H_c is critical field at 0 K. The diagrams look like the phase diagrams. Inside the curve (say any curve, *e.g.*, for Hg) the material (Hg) is in the superconducting phase (resistivity approaches zero) and outside the curve, the material is in the normal phase (normal resistivity is restored). Equation (1) is thus the equation of phase boundary.

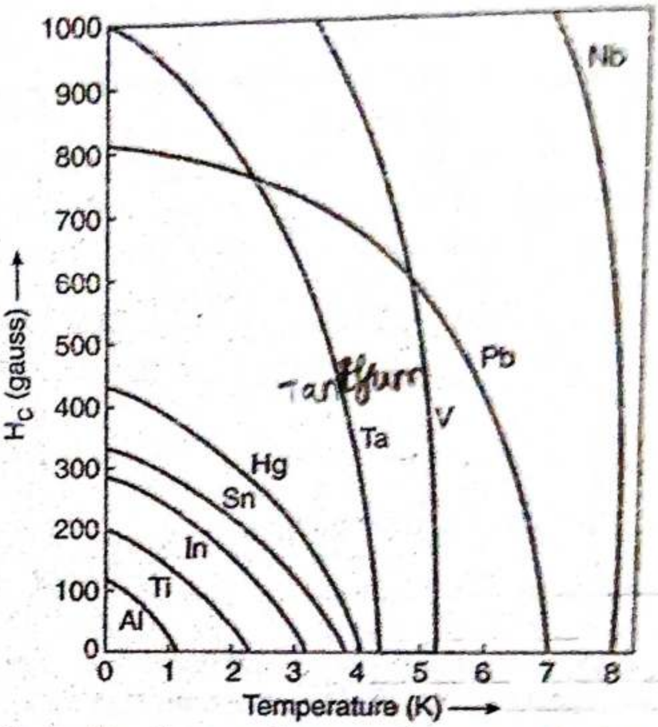

Fig. 3. $H_C - T$ curves for several superconductors. For lead, $T_C = 7{\cdot}19$ K and $H_C = 803$ gauss.

11.2-2 Magnetic Properties of Superconductors : Perfect Diamagnetism or the Meissner Effect

Meissner, in 1935, found that if a superconductor is cooled in a magnetic field down to the transition temperature, then at the transition, the lines of induction B are pushed out (fig. 4). This phenomenon is called Meissner effect. This shows that, in an applied external field, a bulk superconductor behaves as if inside the specimen $B = 0$.

(i) Meissner effect contradicts the Maxwell's equations : Before the Meissner's discovery maxwell's equations were thought to be quite adequate to explain the phenomenon of superconductivity. From Maxwell's equations, we have

$$\vec{\nabla} \times \mathbf{E} = -\frac{d\mathbf{B}}{dt}. \qquad ...(1)$$

From Ohm's law $\mathbf{E} = \rho\, \mathbf{j}$ we see that if the resistivity goes to zero while $\mathbf{j}$ is held finite then $\mathbf{E}$ must be zero. This means $\mathbf{E} = 0$ inside a superconductor. From equation (1), we have then

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

or

$$\mathbf{B} = \text{constant},$$

VI. CRITICAL CURRENTS

The magnetic field which causes a superconductor to become normal from a superconducting state need not necessarily by an external applied field, it may arise as a result of electric current flow in the conductor. The minimum current that can be passed in a sample without destroying its superconductivity is called *critical current* I_c. If a wire of radius r of a Type I superconductor carries a current I, there is a surface magnetic field, $H_I = I/2\pi r$ associated with the current. If H_I exceeds H_c, the material will go normal. If in addition, a transverse magnetic field H is applied to the wire, the condition for the transition to the normal state at the surface is that the sum of the applied field and the field due to the current should be equal to the critical field. Thus we have

$$H_c = H_I + 2H$$

$$H_I = \frac{I_c}{2\pi r} = H_c - 2H$$

$$\boxed{I_c = 2\pi r\,(H_c - 2H)} \qquad (8.2)$$

This is called *Silsbee's rule. The* critical current I_c will decrease linearly with increase of applied field until it reaches zero at $H = H_c/2$. If the applied field is zero, $I_c = 2\pi r H_c$.

VII. FLUX EXCLUSION: THE MEISSNER EFFECT

It was assumed that the effect of a magnetic field on a superconductor would be as that in a metal. However in 1933 Meissner and Ochsenfeld measured the flux distribution outside tin and lead specimens which had been cooled below their transition temperatures while in a magnetic field. They found that at their transition temperatures the specimens spontaneously became perfectly diamagnetic, cancelling all flux inside even though they have been cooled in a magnetic field.

This experiment was the first to demonstrate that superconductors are something more than materials which are perfectly conducting; they have an additional property that a merely resistanceless metal would not possess: A metal in the superconducting state never allows a magnetic flux density to exist in its interior. That is to say, inside a superconducting metal we always have

$$\mathbf{B} = 0$$

whereas inside a merely resistanceless metal there may or may not be a flux density, depending on the circumstances. When a superconductor is cooled in a weak magnetic field, at the transition temperature persistent currents arise on the surface and circulate so as to cancel the flux density inside, in just the way as a magnetic field is applied after the metal has been cooled. This effect, whereby a superconductor never has a flux density even when in applied magnetic field, is called *Meissner effect.*

Suppose a magnetic field of flux density $\mathbf{B}_a$ is applied to a superconductor. In order to neglect demagnetising effects, we consider long superconducting rod with the field applied parallel to its length. An applied magnetic field of flux density $\mathbf{B}_a$ produces in the material flux density equal to $\mu_r\mathbf{B}_a$, where μ_r is the relative permeability of the material. Metals, other than ferromagnetic, have a relative permeability which is very close to unity, *i.e.,* $\mu_r = 1$, so the flux density within them due to the applied magnetic field is equal to $\mathbf{B}_a$. However, as we have seen, the total flux density in a superconducting body is zero. This perfect diamagnetism arises because surface screening currents circulate so as to produce a flux density $\mathbf{B}_s$ which everywhere inside the metal exactly cancels the flux density due to the [illegible] field, $\mathbf{B}_i = -\mathbf{B}_a$. A rod-shaped superconducting specimen [illegible] behaves like a long solenoid [illegible] circulating current that creates a flux density exactly equal in magnitude, but opposite in direction, [illegible] flux density due to the applied magnetic field. To create a flux density of $-\mathbf{B}_a$, the magnitude of [illegible] circulating surface current per unit length must, from the ordinary solenoid formula, be $\mathbf{j} = \dfrac{\mathbf{B}}{\mu_0}$.

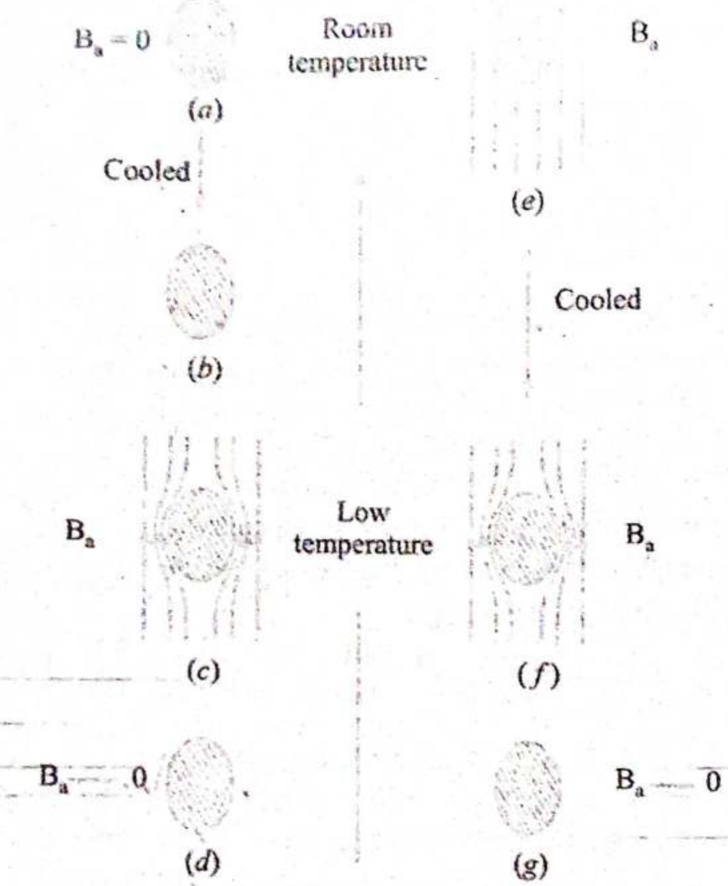

Fig. 8.6 Magnetic behaviour of a superconductor
(a)–(b) Specimen becomes resistanceless in the absence of a magnetic field
(c) Magnetic field applied to a superconducting specimen
(d) Magnetic field removed
(e)–(f) Specimen becomes superconducting in applied magnetic field
(g) Applied magnetic field removed

In other words, $\mathbf{j} = \mathbf{H}_a$, where $\mathbf{H}_a$ is the applied field strength.

We can, however, describe the *perfect diamagnetism* in another way. Because we cannot actually observe the surface screening currents which arise when a magnetic field is applied, we could suppose that the perfect diamagnetism arises from some special bulk magnetic property of the superconducting metal, and we can describe the perfect diamagnetism simply by saying that for a superconducting metal $\mu_r = 0$, so that the flux density inside, $\mathbf{B} = \mu_r\,\mathbf{B}_a$, is zero. Here we do not consider the mechanism by which the diamagnetism arises; the effect of the screening currents is included in the statement $\mu_r = 0$. The strength $\mathbf{H}_a$ of the applied magnetic field is given by

$$\mathbf{H}_a = \mathbf{B}_a/\mu_0$$

and the flux density in a magnetic material is related to the strength of the applied field by

$$\mathbf{B} = \mu_0 (\mathbf{H}_a + \mathbf{M}) \tag{8.3}$$

where **M** is the *magnetisation or intensity of magnetisation* of the material. The magnetisation of a superconductor, in which **B** = 0, must therefore be

$$\mathbf{M} = -\mathbf{H}_a$$

and the magnetic susceptibility

$$\boxed{\chi = \mathbf{M}/\mathbf{H}_a = -1} \tag{8.4}$$

This is the maximum value for the susceptibility of a diamagnet. In this sense a superconductor is a perfect diamagnet. However, it must be noted that superconductivity is not only a strong diamagnetism, but also a new type of diamagnetism.

VIII. THERMAL PROPERTIES

Like the electromagnetic properties, the thermal properties—entropy, electronic specific heat, etc. of a metal also change sharply as the temperature is lowered through the transition temperature of superconductivity. We have shown that the Meissner effect shows that the transition in the presence of magnetic field through the normal-superconducting (N-S) boundary $H_c = H_0 [1 - (T/T_c)^2]$ is reversible, and therefore, that the laws of thermodynamics also apply to (N-S) phase transition.

(i) Entropy

In all superconductors the entropy decreases markedly on cooling below the critical temperature.

We know that, entropy is a measure of the disorder of a system and hence the observed decrease in entropy between the normal state and the superconducting state tells us that the superconducting state is more ordered than the normal state.

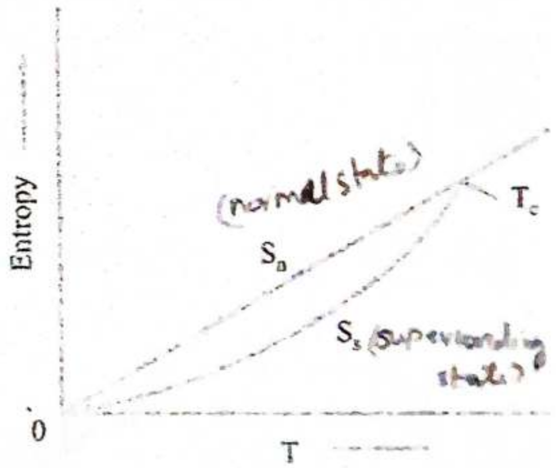

Fig. 8.7 Entropy of aluminium

For aluminium we observe that the change in entropy is small and of the order of $10^{-14}\,k_B$ per atom. The decrease is entropy between the normal state and the superconducting state means that some or all of the electrons thermally excited in the normal state are ordered in the superconducting state. It has been predicted that in simple superconductors (Type I), there is a spatial order which extends over a distance of the order of 10^{-6} metre. This range is called *coherence length*. Entropy of aluminium in the normal and superconducting states as a function of temperature is plotted in Fig. 8.7.

(ii) specific heat

The specific heat of the normal metal is seen to be of the form.

$$C_e(T) = \gamma T + \beta T^3 \tag{8.5}$$

The first term is equation (8.5) is the specific heat of electrons in the metal and the second term is the contribution of lattice vibrations at low temperatures. The specific heat of the superconductor shows a jump at T_c. Since the superconductivity affects electrons mainly, it is natural to assume that the lattice vibration part remains unaffected, *i.e.*, it has the same value βT^3 in the normal and superconducting states. On subtracting this, we notice that the electronic specific heat C_{es} is not linear with temperature. It rather fits an exponential form

$$\boxed{C_{es}(T) = A \exp(-\Delta/k_B T)} \tag{8.6}$$

This exponential form is an indication of the existence of a finite gap in the energy spectrum of electrons separating the ground state from the lowest state (Fig. 8.9).

The number of electrons thermally excited across the gap varies exponentially with the reciprocal of temperature. The energy gap is believed to be a characteristic feature of the superconducting state which determines the thermal properties as well as high frequency electromagnetic response of all superconductors.

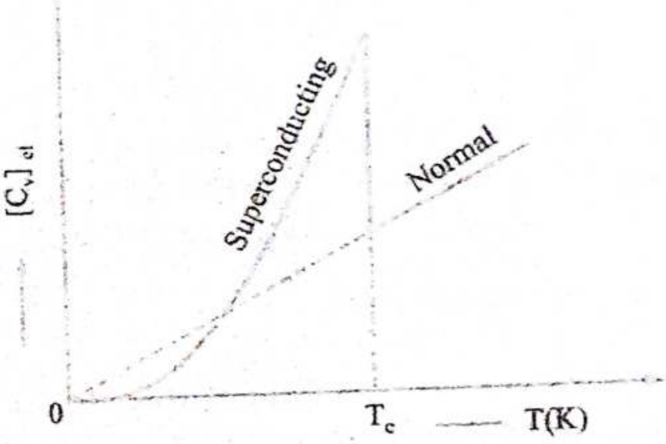

Fig. 8.8 Temperature dependence of the electronic specific heat in the normal and superconducting states

(iii) Thermal Conductivity

Prof. Hulm and others discussed the results of thermal conductivity in superconductors. The thermal conductivity of superconductors undergoes a continuous change between the two phases and is usually lower in the superconducting phase, suggesting that the electronic contribution drops, the superconducting electrons possibly playing no part in heat transfer.

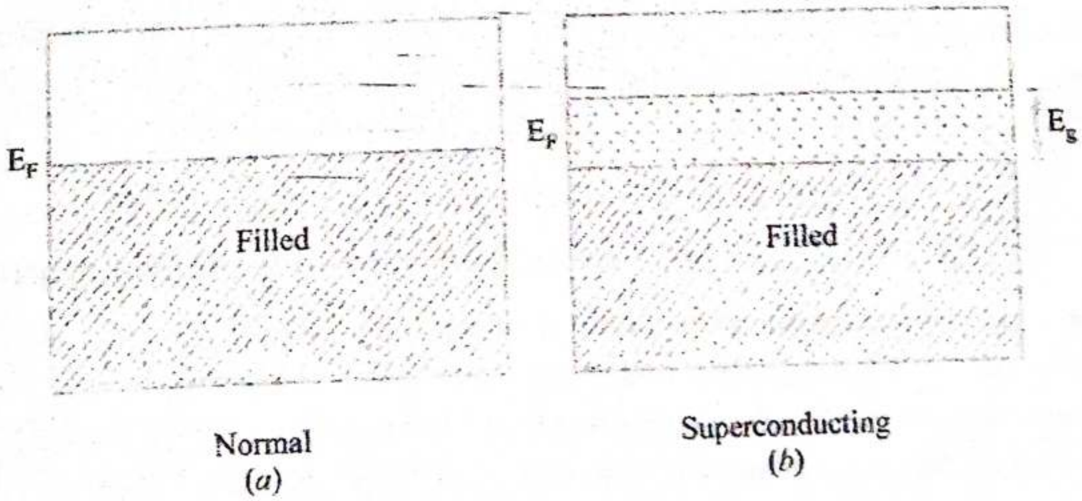

Fig. 8.9 (*a*) Conduction band in the normal state
(*b*) Energy gap at the fermi level in the superconducting state [illegible]

The thermal conductivity of tin at 2 K is 34 W cm^{-1} K^{-1} for the normal phase and 16 W cm^{-1} K^{-1} for the superconducting phase. At 4 K, it is 55 W cm^{-1} K^{-1} (At 4 K there is no superconducting phase for tin as $T_c = 3.73$ K).

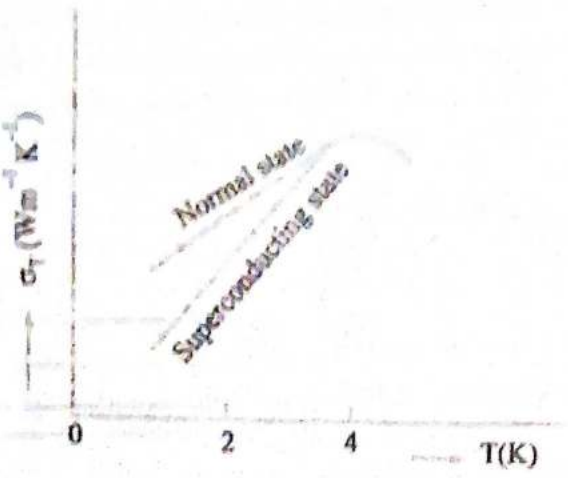

Fig. 8.10 Thermal conductivity of a specimen of tin in the normal and superconducting states

(iv) Acoustic Attenuation

When sound wave propagates through a metal, the microscopic electric fields due to the displacement of the ions can impart energy to electrons near the Fermi level, thereby removing energy from the wave. This is expressed by the *attenuation coefficient*, α, of acoustic waves. The ratio of α for superconducting and normal state is given by

$$\frac{\alpha_s}{\alpha_n} = \frac{2}{1 + \exp(\Delta / k_B T)} \tag{8.7}$$

At low temperature

$$\frac{\alpha_s}{\alpha_n} = 2\,[\exp(-\Delta / k_B T)] \tag{8.8}$$

IX. THE ENERGY GAP

The heat capacity in the superconducting state varies with temperature in an exponential manner; that is, it is of the form $\exp(-\Delta/k_B T)$ with $\Delta = b\, k_B\, T_c$, where b is a constant. This indicates, in accordance with the fact that the exponential form is compatible with the thermal excitation across a gap in energy, that an energy gap may exist in the superconducting electron levels. The jump in the heat capacity at the critical temperature T_c supports this idea of the existence of the energy gap further. See Fig. 8.9. The energy gap in superconductors differs from the gap in semiconductors or insulators in a very fundamental way. The energy gap in superconductors is often an entirely different nature than the energy gap in insulators because in the former, the gap is attached to the Fermi gas whereas in the later the gap is tied to the lattice. In semiconductors, the gap prevents the flow of electrical current. Energy must be added to lift electrons from the valence band into the conduction band before current can flow. In a superconductor, on the other hand, current flows despite the presence of a gap. The energy gap has no effect upon the behaviour of the special electrons that carry current in a superconductor. Superconductors contain normal electrons as well, and it is these electrons that are affected by the gap.

The existence of energy gap in superconductors has been confirmed by a number of experiments: Electron tunnelling observation across the superconducting junctions by Giaever being one of them. Some experiments have been employed for the experimental determination of its value. From theory and from comparison with optical and other methods of determination of gap, it is concluded that

$$E_g = 2\Delta = 2b\,(k_B T_c)$$

or

$$[E_g/k_B T_c] = 2b \qquad (8.9)$$

$2b$ is about 3.5 *i.e.*, the gap decreases from a value of about 3.5 $k_B T_c$ at 0 K to zero at the transition temperature. Values of energy gap of some selected superconductors are given in Table 8.3.

X. ISOTOPE EFFECT

It has been observed that the critical temperature of superconductors varies with isotopic mass. The observation was first made by Maxwell and others, who used mercury isotopes. To give an idea of the λ has been shown to be much greater than atomic distance. It ranges from 300 to 5000 Å depending on material. This varies with temperature and becomes quite large close to the critical temperature T_c. Slight variation with applied field has also been observed.

(iv) Intermediate state : Type I and type II Superconductors : The ideal magnetic behaviour of superconductors falls into two classes : Type I and Type II.

Type I superconductors : They exhibit complete Meissner effect, *i.e.*, they are completely diamagnetic. The magnetisation curve for Type I material is shown in fig. 6. Refer to fig. 4 which illustrate a geometric complication. We note that in the superconducting state flux is concentrated at the sides *XX* of the specimen. The concentration of the flux lines at points *X, X* means that the field is higher there than it is at a great distance from the superconductor. Thus, if the field is increased, it will reach a value H_c, the critical field, at points *X, X* before the field at the top and bottom of specimen has this value. Thus at sides *X, X* transition from superconducting state to normal phase starts and the specimen exists as a mixture of normal and superconducting regions. This state of mixture of two phases is called *intermediate state*. If, instead of spherical shape, we take specimen in the form of long cylinders then no such points as *X, X* would be there and the magnetic field, parallel to the axis of cylinder, will remain uniform over the surfaces of such a specimen. Consequently, field will be either greater than H_c or less than H_c for the whole surface of the specimen which implies that either the specimen will be in superconducting state or in normal state. A long cylinder of Type I material parallel to the field, will exclude the field completely if it is below H_c or be completely penetrated by the magnetic flux if the field is above H_c. The magnetisation of normal state is negligible compared to superconducting state and can be ignored. Values of H_c for Type I materials are always too low (of the order of few tens and hundreds of Oersteds) to have any useful technical application in the coils for superconducting magnets.

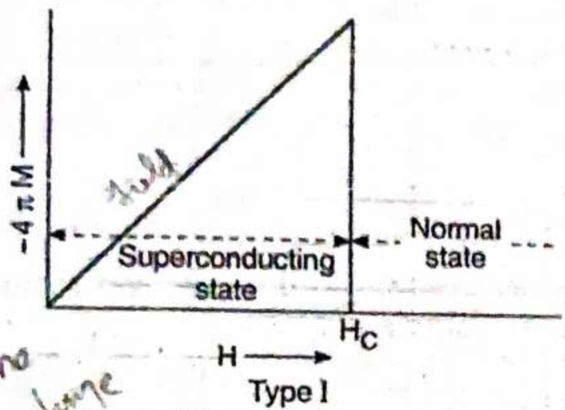

Fig. 6. Magnetic curve for Type I.

Type II superconductors : They behave differently as shown in fig. 7. For applied field below H_{c1} the material is diamagnetic and hence the field is completely excluded. H_{c1} is termed as *lower critical field*. At H_{c2} the field starts to thread the specimen and this penetration increases until H_{c2} is reached at which the magnetisation vanishes and the specimen becomes normal. H_{c2} is called *upper critical field*. There is gradual fall of magnetisation in the case of Type II superconductor (fig. 7) whereas fall is abrupt in case of Type I (fig. 6). The value of H_c for type II may be 100 times more or even higher than that for

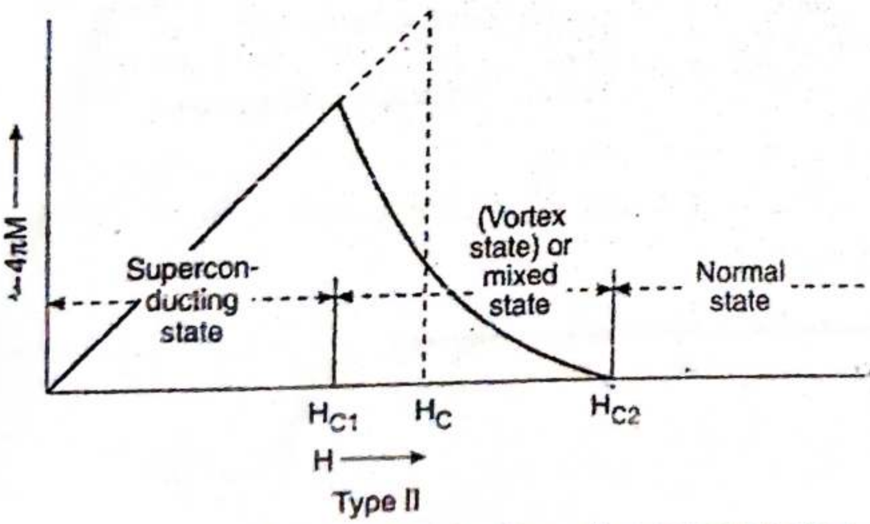

Fig. 7. Magnetization curves for type II superconductors. (Magnetization in normal state has not been shown as it is too small to be seen on this scale). Note that minus $4\pi M$ is plotted on the vertical axis : the negative values of *M* corresponds to diamagnetism.

Type I material. Magnetisation curves for Type I and Type II are both reversible in case of ideal superconductors.

11.2-3 Isotope Effect

It has been observed that the critical temperature of superconductors varies with the isotopic mass. The transition temperature T_c is found to be proportional to the reciprocal of the square root of their respective isotopic masses, *i.e.*,

$$T_c \propto M^{-1/2}$$

or

$$M^{1/2}\, T_c = \text{constant.}$$

In mercury T_c varies from 4·185 K to 4·146 K as the isotopic mass varies from 199·5 to 203·4 a.m.u. Experimental values of α in $M^{1/2}\, T_c =$ constant, for various substances, are listed in table 2.

Table 2. Experimental Values of α

Substance	α
Zn	0·45 ± 0·05
Cd	0·32 ± 0·07
Sn	0·47 ± 0·02
Hg	0·50 ± 0·03
Pb	0·49 ± 0·02
Tl	0·61 ± 0·10
Ru	0·00 ± 0·05
Mo	0·33
Nb_3Sn	0·08 ± 0·02
Zr	0·00 ± 0·05

A heavier isotopic mass lowers the lattice vibrations. It is known that Debye temperature Θ_D of the phonon spectrum is also proportional to $M^{-1/2}$, so that

$$\Theta_D\, M^{1/2} = \text{constant.}$$

Therefore we find that

$$\frac{T_c}{\Theta_D} = \text{constant} \qquad ...(1)$$

Or in general we can write

$$T_c \propto \Theta_D \propto M^{-1/2} \qquad ...(2)$$

Equation (1) or (2) indicates that the lattice vibrations or the electron phonon interactions may be important for the occurrence of superconductivity.

11.2-4 Thermodynamic Effects

There are a number of thermodynamic effects in the normal and superconducting states discussed below :

(i) Entropy : In all superconductors the entropy decreases markedly on cooling below the critical temperature T_c. From the lowered entropy in the superconducting state, it can be concluded that superconducting electrons are more ordered for the entropy is a measure of disorder. It has been predicted that in simple superconductors (Type I) there is a spatial order which extends over a distance of the order of 10^{-6} metre. This range is called *coherence length.* Entropy of aluminium in the normal and superconducting states as a function of temperature is plotted in fig. 8.

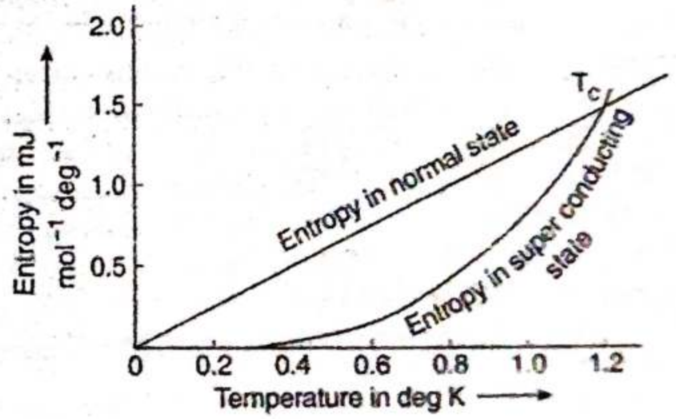

Fig. 8. Entropy of aluminium.

microscopic theory (*BCS* theory) which accounts for the observed properties of superconductors. We shall take up these theories in brief.

11.3-1 Thermodynamics of the Superconducting Transition

We know that thermodynamics can be well applied to all reversible processes. Meissner effect shows that superconducting transition is reversible for we have seen that super-currents are restored when magnetic field is removed [art. 11.2-2 (ii)]. Keesom also demonstrated that transition between superconducting and normal states is thermodynamically reversible exactly like the transition between liquid and vapour phases of a substance under conditions of low evaporation.

In the present discussion we shall consider only Type I superconductor so that $\mathbf{B} = 0$ inside the conductor. Further, we shall study the superconducting transition under constant temperature and pressure conditions when the two phases (normal and superconducting) are in equilibrium. For such a study it is useful to consider the Gibbs function (G) which remains invariant during the isothermal isobaric process. The Gibb's function is given by

$$G = U + pV - TS, \quad \ldots(1)$$

where S is entropy. Basing on the analogy of $\mu_0 H$ to p and M to $-V$, we can write

$$G = U - TS - \mu_0 HM \quad \ldots(2)$$

where M is magnetisation.

Differentiating,

$$dG = dU - T\,dS - S\,dT - \mu_0 H\,dM - \mu_0 M\,dH.$$

Since $\quad dU = T\,dS + \mu_0 H\,dM$

we find that $\quad dG = -S\,dT - \mu_0 M\,dH \quad \ldots(3)$

For a process at constant temperature, we shall have

$$G = -\mu_0 M\,dH. \quad \ldots(4)$$

The normal state of most superconductors is paramagnetic and the magnetisation is small compared with that of the superconducting state. Therefore we can neglect the normal state magnetisation. Consequently from equation (4), $dG = 0$ or we can state that Gibbs function G_N in the normal state is not changed by the application of the magnetic field. Hence

$$G_N(T, H) = G_N(T, 0). \quad \ldots(5)$$

But in superconducting state of the specimen under constant pressure, temperature and magnetic field (same conditions as for normal state), we know that

$$\begin{cases} \mathbf{B} = 0 \\ M = -H, \end{cases} \quad \text{(from Meissner effect)}$$

and

so that from equation (3) with $dT = 0$ at constant temperature,

$$dG = \mu_0 H\,dH, \quad \ldots(6)$$

or on integrating (as a function of magnetic field),

$$G_s(T, H_c) - G_S(T, 0) = \mu_0 \int_0^{H_c} H\,dH$$

$$G_S(T, H_c) = G_s(T, 0) + \frac{1}{2}\mu_0 H_c^2 \quad \ldots(7)$$

or

At the critical field, the free energies of the normal and superconducting states must be equal for equilibrium of two phases, *i.e.*,

$$G_N(T, H_c) = G_s(T, H_c). \quad \ldots(8)$$

Combining equations (7) and (8), we get

$$G_N(T, H_c) = G_S(T, 0) + \frac{1}{2}\mu_0 H_c^2. \qquad ...(9)$$

Combining equations (5) and (9), we get

$$G_N(T, 0) = G_S(T, 0) + \frac{1}{2}\mu_0 H_c^2, \qquad ...(10)$$

which is the basic equation obtained by Gorter.

We know that when $H > H_c$,

$$G_S > G_N,$$

interpreting that for magnetic fields $H > H_c$, the normal state is more stable or in other words material can not be in superconducting state when $H > H_c$ which is expected.

Entropy : Let us now calculate the difference in entropy of two phases. For solids entropy, S, is given by

$$S = -\left(\frac{dG}{dT}\right)_{p,H},$$

so that equation (10), on differentiating with T, gives

$$S_N = S_S - \mu_0 H_c \frac{dH_c}{dT}. \qquad ...(11)$$

At $T = T_c$, $H_c = 0$ so that equation (11) yields

$$S_N = S_S$$

i.e., entropies of the phases are equal at the critical temperature. At any lower temperature.

$$H_c > 0 \text{ and } \frac{dH_c}{dT} \text{ is negative so that } S_N > S_S.$$

This means entropy in superconducting state is lower which implies that superconducting state is a more orderly state.

Specific heat : The specific heat is given by

$$T\frac{dS}{dT},$$

so that on differentiating (11) with respect to T and multiplying by T, we get

$$T\frac{dS_N}{dT} - T\frac{dS_S}{dT} = -T\frac{d}{dT}\left(\mu_0 H_c \frac{dH_c}{dT}\right)$$

or

$$C_N - C_S = -\mu_0 . H_c . T . \frac{d^2 H_c}{dT^2} - \mu_0 T\left(\frac{dH_c}{dT}\right)^2$$

At $T = T_c$, $H_c = 0$ and therefore

$$\Delta C = C_N - C_S = -\mu_0 T_c \left(\frac{dH_c}{dT}\right)^2 \qquad ...(12)$$

which shows that if the metal is cooled or warmed in the absence of magnetic field, there will be a discontinuity in specific heat in passing the transition temperature. We note equation (12) that when $H_c = 0$,

$$C_S > C_N,$$

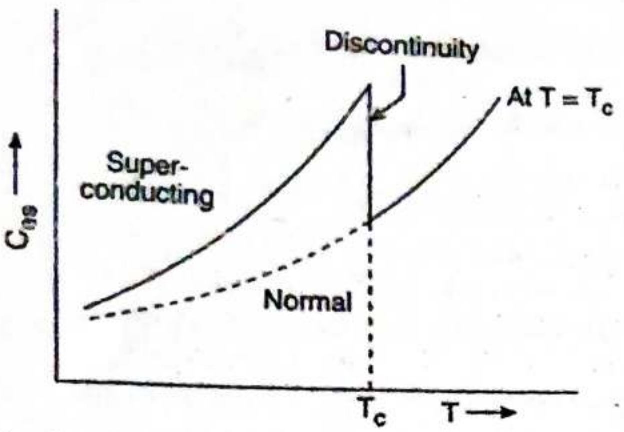

Fig. 15. Specific heat variation with temperature for Bismuth in two phases.

but at lower temperatures when superconductivity is destroyed in a magnetic field, the sign of $C_S - C_N$ must change corresponding to the fact that $S_N - S_S$ passes through maxima. The discontinuity in specific heat at the transition temperature has been experimentally verified. For example, the specific heat of tin with 4% bismuth alloy is found to be discontinuous at $T = T_c$ as shown in fig. 15. It is found that electronic specific heat C_{es}, rises exponentially with temperature unlike that of normal metals for which the electronic specific heat varies linearly with temperature.

11.3-2 Electrodynamics of Superconductors : London Equations

As stated earlier, the magnetic properties of a superconductor can be explained in general terms by considering the superconductor to be a perfect diamagnetic. Refer to art. 11.2-2 (iii), in which it has been pointed out that although, according to Meissner effect, a superconductor will completely eject out the magnetic flux yet we should account for the penetration of magnetic field into the surface of conductor. It has really been found that the penetration depths are much larger than the atomic distances. In order to explain this penetration, it is desirable to modify a constitutive equation of electrodynamics, say Ohm's law, rather than to modify the Maxwell's equations. We already know that Maxwell's equations are inadequate to explain the electrodynamics of superconductors *i.e.*, to account for the conditions $\mathbf{E} = 0$ and $\mathbf{B} = 0$ together. London, in 1935, derived two field equations to explain the superconducting state of matter by modifying Ohm's law.

The way in which the entropy varies with temperature suggests that the number of normal conduction electrons decreases below transition temperature, while superconducting electrons increase. Therefore London, basing on the assumption that there are two types of conduction electrons in a superconductor, namely the super-electrons and normal electrons, put forward the idea that *at any temperature the sum of super electrons and normal electrons is equal to the conduction electron density in the material in the normal state.* Further the super electrons are not subjected to any lattice scattering and are merely accelerated in an electric field.

As pointed out above, at 0 K superconductor consists only super electrons but as the temperature increases the proportion of normal electrons compared to super electrons increases until at transition temperature all electrons are normal.

(i) First London equation : Let n_s be the super electron density at a temperature less than the transition temperature. Then super current density will be

$$\mathbf{J}_S = -e\, n_s\, \mathbf{v}_S, \qquad \ldots(1)$$

where $\mathbf{v}_s$ is the drift velocity of super electrons. Since super electrons are not subjected to any lattice scattering, they are continuously accelerated by the electric field. With force on super electron being $e\,\mathbf{E}$, we can write the equation of motion as

$$m \frac{d\mathbf{v}_S}{dt} = -e\,\mathbf{E} \qquad \ldots(2)$$

Differentiating (1),

$$\frac{d\mathbf{J}_S}{dt} = -e\, n_S \frac{d\mathbf{v}_S}{dt}$$

which with equation (2) gives

$$\frac{d\mathbf{J}_S}{dt} = \frac{n_s e^2}{m}\mathbf{E}. \qquad ...(3)$$

This is the first London equation which describes the absence of resistance. The equation shows that it is possible to have steady currents in the absence of electric field (for $\mathbf{E} = 0$, $\mathbf{J}_s$ is finite and steady) which is the phenomenon of superconductivity. The corresponding expression for normal current density is

$$\mathbf{J}_N = \sigma \mathbf{E}$$

which shows that no current is possible in the absence of an electric field which is in line with the behaviour of the material in the normal state.

(ii) Second London Equations : From Maxwell's equation, we write

$$\text{curl } \mathbf{E} = -\frac{d\mathbf{B}}{dt}$$

or

$$\nabla \times \mathbf{E} = -\mu_0 \frac{d\mathbf{H}}{dt} \qquad ...(4)$$

Taking curl of equation (3), we write

$$\vec{\nabla} \times \frac{d\mathbf{J}_S}{dt} = \frac{n_S e^2}{m}(\vec{\nabla} \times \mathbf{E})$$

$$= -\frac{\mu_0 n_S e^2}{m}\frac{d\mathbf{H}}{dt}, \qquad ...(5)$$

on applying equation (4).

On integrating equation (5), we arrive at

$$\text{curl } \mathbf{J}_S = -\frac{\mu_0 n_S e^2}{m}(\mathbf{H} - \mathbf{H}_0), \qquad ...(6)$$

where H_0 is a constant of integration. Since Meissner effect prohibits magnetic fields inside the superconductor, H_0 must be zero. Therefore

$$\text{curl } \mathbf{J}_S = -\frac{\mu_0 n_S e^2}{m}\mathbf{H}. \qquad ...(7)$$

which is second London equation and explains Meissner effect.

(iii) Calculation of penetration depth : Equation (7) explains Meissner effect. We shall now see whether equation predicts the penetration of supercurrent and magnetic flux in a superconductor or not.

Taking curl of equation (7), we get

$$\text{curl curl } \mathbf{J}_S = -\frac{\mu_0 n_S e^2}{m}\text{curl } \mathbf{H}$$

$$(\text{grad div } \mathbf{J}_S - \nabla^2 \mathbf{J}_S) = -\frac{\mu_0 n_s e^2}{m}\text{curl } \mathbf{H}$$

Since div $\mathbf{J}_S$ is zero, we find that

$$\nabla^2 \mathbf{J}_S = \frac{\mu_0 n_S e^2}{m} \text{ curl } \mathbf{H}. \quad \ldots(8)$$

From Maxwell's equations, we have

$$\text{curl } \mathbf{H} = \mathbf{J}_N + \mathbf{J}_S + \frac{d\mathbf{D}}{dt},$$

where **D** is the electric displacement vector. For direct current case, under consideration, we can neglect $\mathbf{J}_N$ and $\frac{d\mathbf{D}}{dt}$ (displacement current) so that

$$\text{curl } \mathbf{H} = \mathbf{J}_S \quad \ldots(9)$$

From eqs. (8) and (9), we find

$$\nabla^2 \mathbf{J}_S = \frac{\mu_0 n_S e^2}{m} \mathbf{J}_S$$

or

$$\nabla^2 \mathbf{J}_S = \frac{\mathbf{J}_S}{\lambda^2}, \quad \ldots(10)$$

where

$$\lambda^2 = \frac{m}{\mu_0 e^2 n_S} \quad \ldots(11)$$

The parameter λ has the dimensions of length and is called *penetration depth.* Since λ contains λ_S, the density of superconducting electrons, it varies with temperature. In one dimension, equation (10) can be expressed as

$$\frac{d^2\mathbf{J}_S}{dx^2} = \frac{\mathbf{J}_S}{\lambda^2}$$

the solution of which can be written as

$$\mathbf{J}_S = A\, e^{x/\lambda} + B\, e^{-x/\lambda}, \quad \ldots(12)$$

where A and B are the two constants. x represents the distance into the metal from the surface. The first factor $A\, e^{x/\lambda}$ of above equation predicts that $\mathbf{J}_S$ increases with x which is contrary to the fact. Therefore only second factor of eq. (12) would lead to the appropriate solution. Thus

$$\mathbf{J}_S = B\, e^{-x/\lambda}$$

Let $\mathbf{J}_S = \mathbf{J}_0$ at $x = 0$; so that

$$\mathbf{J}_S = \mathbf{J}_0\, e^{-x/\lambda} \quad \ldots(13)$$

When

$$x = \lambda, \ \frac{\mathbf{J}_S}{\mathbf{J}_0} = \frac{1}{e},$$

which defines the penetration depth as the distance into the superconductor at which the current value falls to $1/e$ of its value at the surface ($\mathbf{J}_0$).

Drawback of the theory : Though the London's theory explains the two conditions $\mathbf{E} = 0$ and $\mathbf{B} = 0$, characterising the superconducting state but it does not give any insight into the underlying electronic processes in superconductors. BCS theory gives the better understanding of the phenomenon of superconductivity.

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The terms :

$\frac{H}{\lambda^2}$ — represents the field penetration due to supercurrent.*

$-\omega^2 \mu_0 \varepsilon H$ — represents the field penetration due to the displacement current, and

$\omega \mu_0 \sigma_N H$ — represents the field penetration due to the eddy currents.

We note that :

(i) For d.c. fields the last two terms reduce to zero and we get

$$\nabla^2 \mathbf{H} = \frac{\mathbf{H}}{\lambda^2},$$

which is the same as predicted by London theory.

(ii) At microwave frequencies, frequency ω will be sufficiently high and wavelength λ_0 will be small. As

$$\omega^2 \mu_0 \varepsilon = \omega^2/c^2 = \frac{4\pi^2 n^2}{c^2} = \frac{4\pi^2}{\lambda_0^2}$$

Therefore equation (8) becomes

$$^{\dagger}\nabla^2 \mathbf{H} = \left(\frac{1}{\lambda^2} - \frac{4\pi^2}{\lambda_0^2} + j\,\omega\,\mu_0\,\sigma_N\right)\mathbf{H} \qquad \ldots(9)$$

Obviously as penetration depth λ varies from 300 Å to 5000 Å, the term due to eddy current will predominate. In other words, it is σ_N which determines the properties of superconductors in this range of frequencies, which, in its turn, *i.e.*, σ_N, depends on the number of normal conduction electrons that is quite large at high frequencies.

Penetration depth λ and skin depth δ : We note from equations (4) and (6) that

$$\frac{\mathbf{J}_N}{\mathbf{J}_S} = \mu_0\,\omega\,\sigma_N\,\lambda^2$$

The penetration depth λ and a.c. skin depth δ are related by

$$\frac{\lambda^2}{\delta^2} = \frac{\lambda^2 \mu_0\,\omega\,\sigma_N}{2} = \frac{1}{2}\frac{\mathbf{J}_N}{\mathbf{J}_S} \quad \text{or} \quad \delta^2 = \frac{2}{\mu_0\,\omega\,\sigma_N}$$

which predicts that when frequency is sufficiently high, δ is small; and penetration depth λ becomes larger compared to skin depth δ. With $\lambda > \delta$, we infer that $\mathbf{J}_N > \mathbf{J}_S$ or normal current predominates. *This implies that at high frequencies, superconductors behave like normal conductors.*

11.3-4 BCS Theory of Superconductivity

It is interesting to note that in the experimental survey of superconducting state, a sufficient quantitative information has been given without any reference in particular to any superconducting element, *e.g.*, we have discussed magnetic properties, thermodynamic effects for all the superconducting elements without specifying any particular element. This means any theory that aims to explain the phenomenon of superconductivity must ignore the complicated feature which characterise any individual element and must be presented in the form of idealised model of metal.

The theory discussed earlier do not relate the phenomenon of superconductivity with electronic and atomic structures. The microscopic theory put forward by Bardeen, Cooper and Schrieffer (BCS), in 1957, provides the better quantum explanation of superconductivity and accounts very well for all the properties exhibited by the superconductors. This theory involves the electron interactions through phonons as mediators. In this article only qualitative description of the theory will be given in following steps :

(i) Electron-Lattice-Electron Interaction : The basis of the formulation of BCS theory are the two experimental conclusions namely the isotope effect and the variation of specific heat of superconductors. From isotope effect $T_c M^{1/2}$ = constant, one can infer that the transition resulting in superconducting state must involve the dynamics of ion motions, lattice vibrations or phonons. Further we note that T_c, attains a value zero when M appoaches infinity. This all suggests that *non zero transition temperature is a consequence of the finite mass of the ions which can contribute phonons by their vibrations.* Frohlich and Bardeen, in 1950, pointed out that an electron moving through a crystal lattice has a self energy accompanied by 'virtual' phonons. This means that an electron moving through the lattice distorts the lattice and lattice, in turn, acts on the electron by virtue of electrostatic forces between them. The oscillatory distortion of the lattice is quantised in terms of phonons and so one can interpret the interaction between the lattice and electron as the constant emissiion and re-absorption (creation and annihilation) of phonons by the latter.

BCS showed that the basic interaction responsible for superconductivity appears to be that of a pair of electrons by means of an interchange of virtual phonons. This is explained as follows :

Suppose an electron approaches a positive ion core. It suffers attractive coulomb interaction. Due to this attraction, ion core is set in motion and consequently distorts the lattice. Smaller the mass of positive ion core, greater will be the distortion. Suppose towards that side another electron comes and sees this distorted lattice. Then the interaction between the two–the electron and the distorted lattice, occurrs which in its effect lowers the energy of the second electron. Thus we interpret that the two electrons interact *via* the lattice distortion or the phonon field resulting in the lowering of energy for the electrons. The lowering of electron energy implies that the force between the two electrons is attractive. This type of interaction is called electron-lattice-electron interaction. This interaction is strongest when the two electrons have equal and opposite momenta and spins.

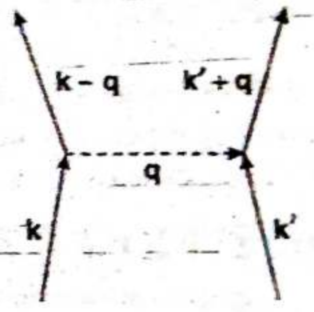


Fig. 16. Electron-phonon interaction.

Since the oscillatory distortion of lattice, as pointed out earlier, is quantised in terms of phonons and therefore above interaction can also be interpreted as the electron-electron interaction through phonons the mediator. Suppose, as shown in fig. 16, an electron of wave vector K emits a virtual phonon q which is absorbed by an electron K'. K is thus scattered as $K - q$ and K' as $K' - q$. The process being a virtual one, energy need not be conserved (the phonons involved are called virtual phonons because, as a consequence of uncertainty principle, their very short life time renders it unnecessary to conserve the energy in the process). Infact the nature of the resulting electron-electron interaction depends on the relative magnitudes of the electronic energy change and the phonon energy $\hbar\omega_q (= h\nu_q)$. If this phonon energy exceeds electronic energy, the interaction is attractive.

(ii) Cooper Pair : The fundamental postulate of BCS theory is that the superconductivity occurrs when such an attractive interaction, mentioned above, between two electrons, by means of a phonon exchange, dominate the usual repulsive coulomb interaction. Two such electrons which interact attractively in the phonon field are called a *Cooper pair*. These Cooper pairs have certain aspects of single particles. The energy of the pair of electrons in the bound state is less than the energy of the pair in free state (electron separated). The difference of the energy of the two states is the binding energy of the Cooper pair and should, therefore, be supplied if the pair is broken. At temperatures less than critical temperature, electron-lattice-electron interaction is stronger than electron-electron coulomb interaction, and so the valence electrons tend to pair up. Pairing is complete at $T = 0$ K and is completely broken at critical temperature.

(iii) Existence of energy gap : The energy difference between the free state of the electron (*i.e.*, energy of individual electron—a case of normal state) and the paired state (the energy of paired electron—a case of superconducting state) appears as the energy gap at the Fermi surface. The normal electron states are above the energy gap and superconducting electron states are below the energy gap at the Fermi surface. Energy gap is a function of temperature unlike to case of constant energy gap in semiconductors and insulators. Since pairing is complete at 0 K, the difference in energy of free and paired electron states (*i.e.*, normal and superconducting electron states) is maximum or in other words energy gap is maximum at absolute zero. At $T = T_c$ pairing is dissolved and energy gap reduces to zero.

Across the energy gap there are many excited states for the superconducting Cooper pairs. BCS theory thus predicts many electron ground states as well as excited states for the superconductor in the range 0 to T_c and in these states Cooper pairs are supposed to be in condensed state with a definite phase coherence. At critical temperature, this coherence disappears and the pairs are broken resulting in the transition of superconducting state to normal state.

(iv) Coherence length : The paired electrons (Cooper pairs) are not scattered because of their peculiar property of smoothly riding over the lattice imperfections without ever exchanging energy with them. Consequently, they can maintain their coupled motion upto a certain distance called coherence length. The latter is found to be of the order of 10^{-4} cm.

11.3-5 The Theory of the Superconducting Energy Gap

A qualitative description of BCS theory is given in the previous article. While describing the Cooper pairs it has been pointed out that the energy of the pair of electrons in the bound state (the so-called superconducting state) is less than the energy of the pair in free state (the so-called normal state). The energy of this state lies below that of the ground state of the Fermi sea and the wave function of the pair is localised. This thus evidently indicates the possibility of a new kind of ground state. In order to minimise the energy of the new (superconducting) ground state, the electron states from which the Cooper pairs are to be formed must be chosen so as to maximise the binding energy of each pair and to obtain the greatest possible number of such pairs. As we know that in the scattering processes, due to electron interactions, the total momentum (or the total K-vector) is in general conserved and therefore, the maximum number of pairs that can be scattered coherently is obtained by pairing states such that *their total momentum is a constant. In particular for the ground state, which carries no net current, the best possible pairing is between states of equal and opposite momentum* *i.e.*, the state K and $-K$ are always occupied simultaneously. In the stabilization energy. To estimate H_{c1} in terms of H_c, we consider the stability of the vortex state at absolute zero in the impure limit $\xi < \lambda$; here $\kappa > 1$ and the coherence length is short in comparison with the penetration depth.

We estimate in the vortex state the stabilization energy of a fluxoid core viewed as a normal metal cylinder which carries an average magnetic field B_a. The radius is of the order of the coherence length, the thickness of the boundary between N and S phases. The energy of the normal core referred to the energy of a pure superconductor is given by the product of the stabilization energy times the area of the core:

(CGS) $$f_{core} \approx \frac{1}{8\pi} H_c^2 \times \pi\xi^2 , \qquad (32)$$

per unit length. But there is also a decrease in magnetic energy because of the penetration of the applied field B_a into the superconducting material around the core:

(CGS) $$f_{mag} \approx -\frac{1}{8\pi} B_a^2 \times \pi\lambda^2 . \qquad (33)$$

For a single fluxoid we add these two contributions to obtain

(CGS) $$f = f_{core} + f_{mag} \approx \tfrac{1}{8}(H_c^2\xi^2 - B_a^2\lambda^2) . \qquad (34)$$

The core is stable if $f < 0$. The threshold field for a stable fluxoid is at $f = 0$, or, with H_{c1} written for B_a,

$$H_{c1}/H_c \approx \xi/\lambda . \qquad (35)$$

The threshold field divides the region of positive surface energy from the region of negative surface energy.

We can combine (30) and (35) to obtain a relation for H_c:

$$\pi\xi\lambda H_c \approx \Phi_0 . \qquad (36)$$

We can combine (30), (31), and (35) to obtain

$$(H_{c1}H_{c2})^{1/2} \approx H_c , \qquad (37a)$$

and

$$H_{c2} \approx (\lambda/\xi)H_c = \kappa H_c . \qquad (37b)$$

Single Particle Tunneling

Consider two metals separated by an insulator, as in Fig. 20. The insulator normally acts as a barrier to the flow of conduction electrons from one metal to the other. If the barrier is sufficiently thin (less than 10 or 20 Å) there is a significant probability that an electron which impinges on the barrier will pass from one metal to the other: this is called **tunneling**. In many experiments the

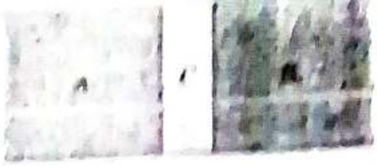


Figure 20 Two metals, A and B, separated by a thin layer of an insulator C.

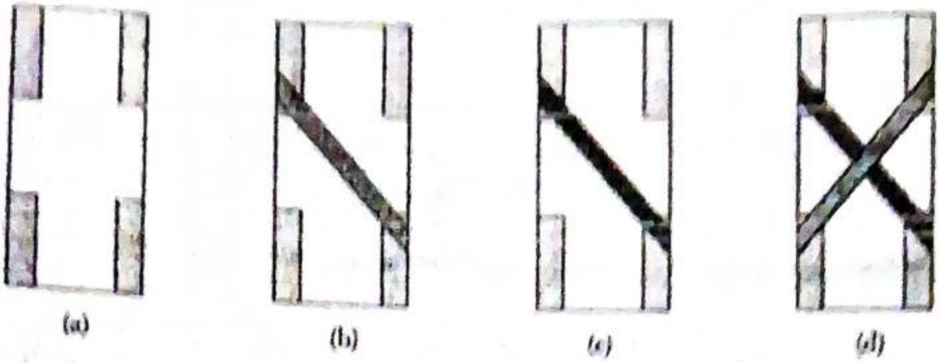


Figure 21 Preparation of an $Al/Al_2O_3/Sn$ sandwich. (a) Glass slide with indium contacts. (b) An aluminum strip 1 mm wide and 1000 to 3000 Å thick has been deposited across the contacts. (c) The aluminum strip has been oxidized to form an Al_2O_3 layer 10 to 20 Å in thickness. (d) A tin film has been deposited across the aluminum film, forming an $Al/Al_2O_3/Sn$ sandwich. The external leads are connected to the indium contacts; two contacts are used for the current measurement and two for the voltage measurement. (After Giaever and Megerle.)

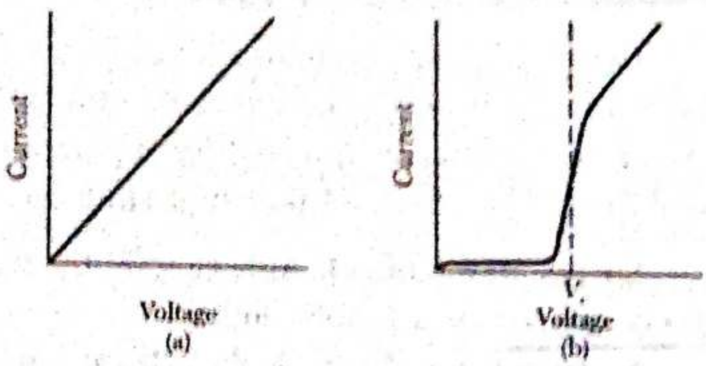


Figure 22 (a) Linear current-voltage relation for junction of normal metals separated by oxide layer; (b) current-voltage relation with one metal normal and the other metal superconducting.

insulating layer is simply a thin oxide layer formed on one of two evaporated metal films, as in Fig. 21.

When both metals are normal conductors, the current-voltage relation of the sandwich or tunneling junction is ohmic at low voltages, with the current directly proportional to the applied voltage. Giaever (1960) discovered that if one of the metals becomes superconducting the current-voltage characteristic changes from the straight line of Fig. 22a to the curve shown in Fig. 22b.

Figure 23a contrasts the electron density of orbitals in the superconductor with that in the normal metal. In the superconductor there is an energy gap centered at the Fermi level. At absolute zero no current can flow until the applied voltage is $V = E_g/2e = \Delta/e$.

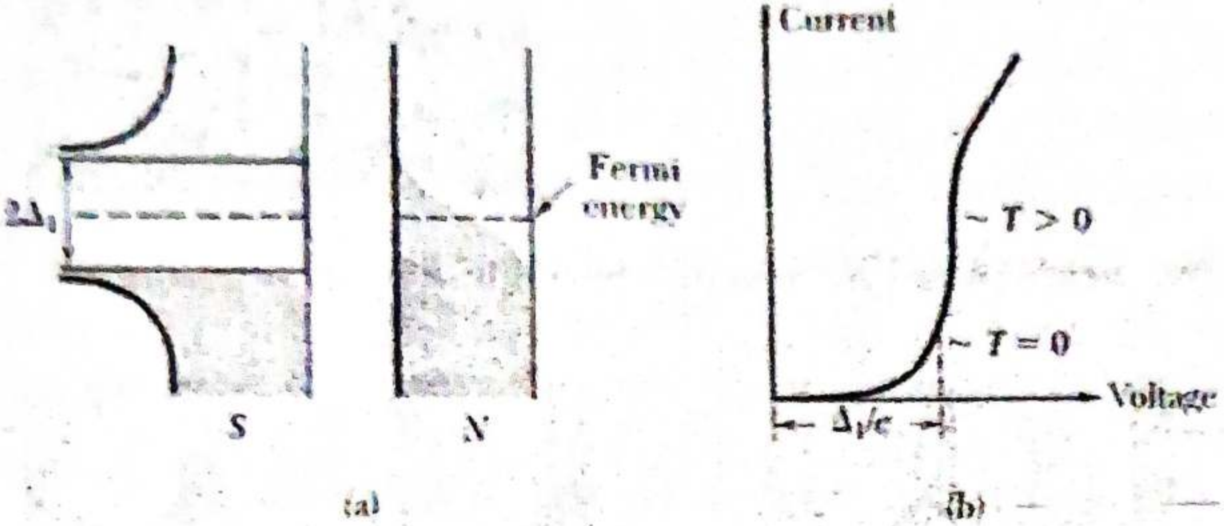


Figure 23 The density of orbitals and the current-voltage characteristic for a tunneling junction. In (a) the energy is plotted on the vertical scale and the density of orbitals on the horizontal scale. One metal is in the normal state and one in the superconducting state. (b) I versus V; the dashes indicate the expected break at $T = 0$. (After Giaever and Megerle.)

The gap E_g corresponds to the break-up of a pair of electrons in the superconducting state, with the formation of two electrons, or an electron and a hole, in the normal state. The current starts when $eV = \Delta$. At finite temperatures there is a small current flow even at low voltages, because of electrons in the superconductor that are thermally excited across the energy gap.

on the right side. There is no current in the circuit until a certain critical voltage V_c is attained and the current begins to increase afterwards somewhat as shown in Fig. 8.23. This is explained on the basis of quantum tunnelling as follows: Quantum mechanically an electron on one side of a barrier has a finite probability of tunnelling through it, if there is an allowed state of equal energy available on the other side of the barrier. Figure 8.22 shows the density of states function in the energy space for a sandwich consisting of a superconductor, an insulator and a normal metal, all at absolute zero. In the normal conductor the electrons fill up to the Fermi level.

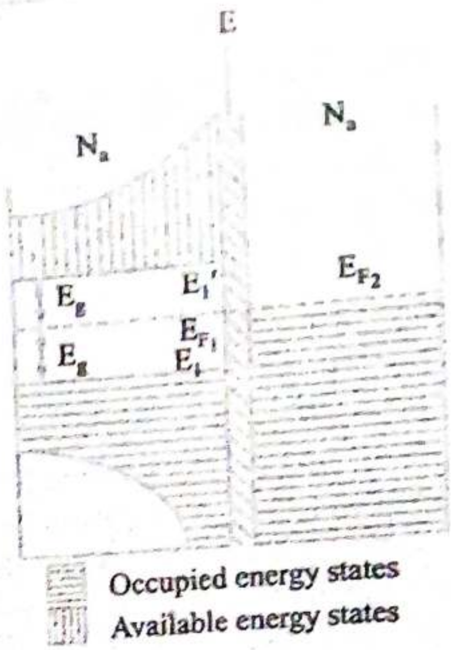


Fig. 8.22 Superconductor-oxide-normal junction at 0 K

In the superconductor the Fermi level is in the middle of the band gap. When the sandwich is formed the Fermi levels are aligned as shown in Fig. 8.22. Suppose a voltage is applied across the barrier so as to raise the Fermi level on the right side of the junction. Until the Fermi level E_{F_2} on the right side raised up to the level E_1' electrons cannot go from right to the left since there are no available energy levels on the left side; since in that portion we have the band gap. Once the Fermi level E_{F_2} rises above the level of E_1' the electrons can tunnel through the barrier from the right to the left since there are energy states available for the electrons on the left-hand side. So the current increases. Obviously there will be no current until the voltage becomes equal to the band gap $(E_1' - E_{F_2})$. Experimental measurements confirm the theoretical prediction.

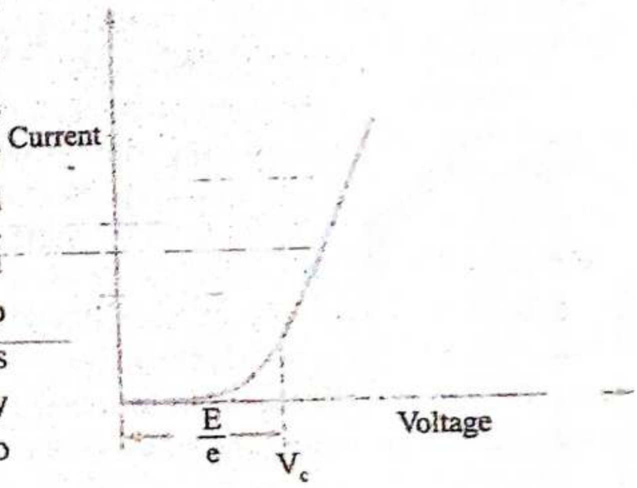
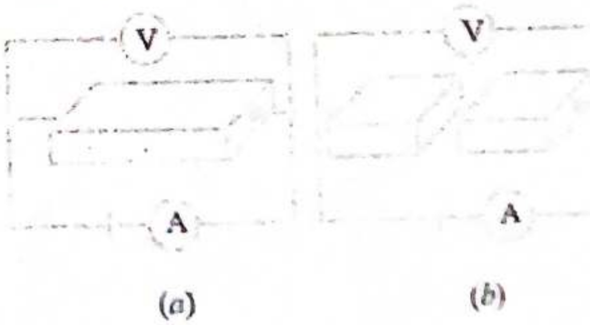


Fig. 8.23 I-V characteristic curve of Giaever tunnelling

X. JOSEPHSON'S TUNNELLING

In Giaever tunnelling current is carried through the insulating barrier as single electrons, and quasi particle excitations are left on the two sides of the junction. In 1962, B.D. Josephson predicted that a *supercurrent* consisting of correlated pairs of electrons can be made to flow across an insulating gap between two superconductors provided the gap is small enough.

The nature of Josephson's effects can be understood like this. A current is made to flow in a bar of superconductor. A voltmeter is connected across the ends of the bar as shown in Fig. 8.24 (*a*).



The voltmeter indicates a drop in voltage as zero across the superconductor according to our expectation.

Suppose the bar is cut into two pieces and the two pieces are separated by say 1 cm as shown in Fig. 8.24 (*b*). No current will flow and the voltmeter will indicate a voltage equal to the open circuit voltage of the current source. If the distance between the pieces is reduced to 1 nm, the voltmeter suddenly shows zero voltage showing thereby that a current flows across the gap in a superconducting way. This is known as the d.c. *Josephson's effect*. Another effect which is observed if that the voltmeter indicates a voltage, but at the same time a very high frequency electromagnetic radiation emanates from the gap, indicating the presence of a very high frequency alternating current in the gap.

This phenomenon is known as a.c. Josephson's effect. All these experimental observations show that the BCS theory is gaining more grounds. The accomplishments of Josephson's effects are:

(*i*) A d.c. current flows across the junction in the absence of any magnetic or electric field.

(*ii*) When a d.c. voltage is applied across the junction, it causes r.f. current oscillations across the junction. This effect has been utilised for the precise determination of the value of $\hbar/e$. Further, an r.f. voltage applied with d.c. voltage can then cause a flow of d.c. current across the junction.

(*iii*) Whan a d.c. magnetic field applied through a superconducting circuit containing two junctions, it causes the maximum supercurrent to show interference effects as a function of magnetic field intensity. This effect can be utilised in sensitive magnetometers.

XXI. THEORY OF D.C. JOSEPHSON'S EFFECT

Let Ψ_1 be the probability amplitude of electron pairs on one side of a junction and Ψ_2 be the amplitude on the other side. For simplicity, let us suppose that both superconductors be identical. Let us also suppose that they are both at zero potential. The time dependent Schrödinger equation is

$$i\hbar\left(\frac{\partial\Psi}{\partial t}\right) = T\Psi \quad \text{[Refer equation (6.39)]}$$

and applied to the amplitudes Ψ_1 and Ψ_2 gives

$$i\hbar\left(\frac{\partial\Psi_1}{\partial t}\right) = \hbar T\Psi_2$$

and

$$i\hbar\left(\frac{\partial\Psi_2}{\partial t}\right) = \hbar T\Psi_1 \qquad (8.59)$$

where $\hbar T$ represents the effect of the electron-pair coupling or transfer interaction across the insulator. In fact, T is a measure of the leakage of Ψ_1 into the region 2 and of Ψ_2 into the region 1 (see Fig. 8.22). If the insulator between the two superconductors is very thick, there is no pair tunnelling and T is zero.

Let $\Psi_1 = n_1^{1/2}\exp(i\theta_1)$ and $\Psi_2 = n_2^{1/2}\exp(i\theta_2)$, then

$$\frac{\partial\Psi_1}{\partial t} = \left(\frac{1}{2}\right)n_1^{-1/2}\exp(i\theta_1)\left(\frac{\partial n_1}{\partial t}\right) + in_1^{1/2}\exp(i\theta_1)\left(\frac{\partial\theta_1}{\partial t}\right) = -iT\Psi_2$$

i.e.,

$$\frac{\partial\Psi_1}{\partial t} = \left(\frac{1}{2}\right)n_1^{-1/2}\exp(i\theta_1)\left(\frac{\partial n_1}{\partial t}\right) + in_1^{1/2}\exp(i\theta_1)\left(\frac{\partial\theta_1}{\partial t}\right)$$

$$= -iTn_2^{1/2}\exp(i\theta_2) \qquad (8.60)$$

Similarly,
$$\frac{\partial \Psi_2}{\partial t} = \left(\frac{1}{2}\right) n_2^{-1/2} \exp(i\theta_2)\left(\frac{\partial n_2}{\partial t}\right) + i n_2^{1/2} \exp(i\theta_2)\left(\frac{\partial \theta_2}{\partial t}\right)$$
$$= -iTn_1^{1/2} \exp(i\theta_1) \tag{8.61}$$

Multiplying equation (8.60) by $n_1^{1/2} \exp(-i\theta_1)$ and using $\delta = (\theta_2 - \theta_1)$, one gets

$$\left(\frac{1}{2}\right)\left(\frac{\partial n_1}{\partial t}\right) + i n_1\left(\frac{\partial \theta_1}{\partial t}\right) = -iT(n_1 n_2)^{1/2} \exp[i(\theta_2 - \theta_1)]$$

i.e.,
$$\left(\frac{1}{2}\right)\left(\frac{\partial n_1}{\partial t}\right) + i n_1\left(\frac{\partial \theta_1}{\partial t}\right) = -iT(n_1 n_2)^{1/2} \exp(i\delta) \tag{8.62}$$

Similarly multiplying equation (4.61) by $n_2^{1/2} \exp(-i\theta_2)$ and simplifying, one gets

$$\left(\frac{1}{2}\right)\left(\frac{\partial n_2}{\partial t}\right) + i n_2\left(\frac{\partial \theta_2}{\partial t}\right) = -iT(n_1 n_2)^{1/2} \exp(-i\delta) \tag{8.63}$$

Equating real and imaginary parts of equations (8.62) and (8.63), we get

$$\left|\begin{aligned} \frac{\partial n_1}{\partial t} &= 2T(n_1 n_2)^{1/2} \sin\delta \\ \frac{\partial n_2}{\partial t} &= -2T(n_1 n_2)^{1/2} \sin\delta \end{aligned}\right| \tag{8.64}$$

$$\left|\begin{aligned} \frac{\partial \theta_1}{\partial t} &= -T(n_2/n_1)^{1/2} \cos\delta \\ \frac{\partial \theta_2}{\partial t} &= -T(n_1/n_2)^{1/2} \cos\delta \end{aligned}\right| \tag{8.65}$$

Taking $n_1 \approx n_2$ for identical superconductors, we have from equation (8.65)

$$\frac{\partial \theta_1}{\partial t} = \frac{\partial \theta_2}{\partial t} = \frac{\partial}{\partial t}(\theta_2 - \theta_1) = 0 \tag{8.66}$$

From equation (8.64),

$$\frac{\partial n_2}{\partial t} = -\frac{\partial n_1}{\partial t} \tag{8.67}$$

The current flow through the junction *i.e.*, from 1 to 2 is proportional to $(\partial n_2/\partial t)$ or $(-\partial n_1/\partial t)$. Therefore, we can conclude that the supercurrent J of superconducting pairs across the junction depends on the phase difference δ.

i.e.,
$$\boxed{J = J_0 \sin\delta = J_0 \sin(\theta_2 - \theta_1)} \tag{8.68}$$

Here J_0 is proportional to T and represents the maximum zero voltage current that can be passed by the junction. With zero applied voltage a d.c. current will flow across the junction with a value between J_0 and $-J_0$ depending on the value of the phase difference $(\theta_2 - \theta_1)$. This effect is known as d.c. Josephson's effect.

Let a voltage V be applied across the Josephson's junction. This is possible because the junction is an insulator. An electron pair experiences a potential energy difference qV on passing across the junction, where $q = (-2e)$. One can say that a pair on one side is at a potential energy $-eV$ and the pair on the other side at eV. The equation of motion of a pair are:

$$i\hbar\left(\frac{\partial\Psi_1}{\partial t}\right) = \hbar T\Psi_2 - eV\Psi_1$$

$$i\hbar\left(\frac{\partial\Psi_2}{\partial t}\right) = \hbar T\Psi_1 - eV\Psi_2 \qquad (8.69)$$

Let $\Psi_1 = n_1^{1/2}\exp(i\theta_1)$ and $\Psi_2 = n_2^{1/2}\exp(i\theta_2)$

Now $$\frac{\partial\Psi_1}{\partial t} = \left(\frac{1}{2}\right)n_1^{-1/2}\exp(i\theta_1)\left(\frac{\partial n_1}{\partial t}\right) + n_1^{1/2}i\exp(i\theta_1)\left(\frac{\partial\theta_1}{\partial t}\right)$$

Equation (8.69) becomes

$$i\hbar\exp(i\theta_1)\left[\frac{n_1^{-1/2}}{2}\left(\frac{\partial n_1}{\partial t}\right) + (n_1^{1/2}i)\frac{\partial\theta_1}{\partial t}\right]$$
$$= \hbar T n_2^{1/2}\exp(i\theta_2) - eVn_1^{1/2}e^{i\theta_1}$$

Dividing throughout by $i\hbar\exp(i\theta_1)\,n_1^{-1/2}$, we get

$$\left(\frac{1}{2}\right)\frac{\partial n_1}{\partial t} + in_1\frac{\partial\theta_1}{\partial t} = ien_1V(\hbar)^{-1} - iT(n_1n_2)^{1/2}\exp(i\delta) \qquad (8.70)$$

i.e., $$\frac{1}{2}\left(\frac{\partial n_1}{\partial t}\right) + in_1\left(\frac{\partial\theta_1}{\partial t}\right) = ien_1V(\hbar)^{-1} - iT[\cos\delta + i\sin\delta](n_1n_2)^{1/2}$$

Breaking this into real and imaginary parts, we obtain

$$\frac{1}{2}\left(\frac{\partial n_1}{\partial t}\right) = T(n_1n_2)^{1/2}\sin\delta$$

or $$\frac{\partial n_1}{\partial t} = 2T(n_1n_2)^{1/2}\sin\delta \qquad (8.70a)$$

and $$\frac{\partial\theta_1}{\partial t} = \frac{eV}{\hbar} - T(n_2/n_1)^{1/2}\cos\delta \qquad (8.71)$$

This differs from equation (8.65) by the term $\frac{eV}{\hbar}$. Further, by extension of equation (8.61), we obtain

$$\frac{1}{2}\left(\frac{\partial n_2}{\partial t}\right) + in_2\left(\frac{\partial\theta_2}{\partial t}\right) = -ieVn_2\hbar^{-1} - iT(n_1n_2)^{1/2}e^{-i\delta}$$

CHAPTER 8

where, $$\frac{\partial n_2}{\partial t} = -2T(n_1 n_2)^{1/2} \sin\delta \tag{8.72}$$

and $$\frac{\partial \theta_2}{\partial t} = -(eV/\hbar) - T(n_1/n_2)^{1/2} \cos\delta \tag{8.73}$$

Taking $n_1 \approx n_2$, we obtain from equations (8.71) and (8.73),

$$\frac{\partial(\theta_2 - \theta_1)}{\partial t} = \frac{\partial \delta}{\partial t} = -\frac{2eV}{\hbar} \tag{8.74}$$

Integrating equation (8.74), we see that with a d.c. voltage across the junction, the relative phase of probability amplitudes vary as

$$\delta(t) = \delta(0) - \frac{2eVt}{\hbar} \tag{8.75}$$

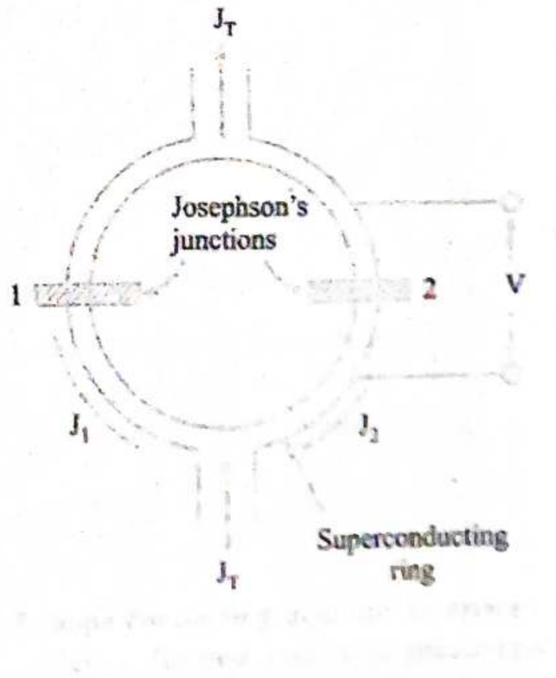
The supercurrent is now given by

$$\boxed{J = J_0 \sin\left[\delta(0) - \frac{2eVt}{\hbar}\right]} \tag{8.76}$$

This shows that the current oscillates with a frequency

$$\boxed{\omega = \frac{2eV}{\hbar}} \tag{8.77}$$

This is called the a.c. Josephson's effect. It permits a determination of $\frac{e}{\hbar}$ from the relationship between voltage and the frequency of the photon emitted when an electrons pair crosses the barrier. A d.c. voltage of 1 μV produces a frequency of 483.6 MHz.



Macroscopic Quantum Interference

The relation (8.76) provides the basis for one family of Josephson's junction device called SQUID (superconducting quantum interference device). The SQUID (Fig. 8.25) is a double-junction quantum interferometer formed from two Josephson junctions mounted on a superconducting ring. Magnetic field is applied normal to the plane of the ring.

In this device we may write the phase as