Electron Theory of Metals

4.1 Introduction

The electrons in the outermost orbitals of the atoms, which constitute the solid, determine its electrical properties. The electron theory of solids aims to explain the structures and properties of solids through their electronic structure. The electron theory is applicable to all solids both metals and non-metals. It explains the electrical, thermal and magnetic properties of solids etc. The theory has been developed in three main stages.

(i) **The Classical Free Electron Theory:**

Drude and Lorentz developed this theory in 1900. According to this theory, the metals containing free electrons obey the laws of classical mechanics.

(ii) **The Quantum free electron theory:**

Sommerfeld developed this theory during 1928. According to this theory, free electrons obey quantum laws.

(iii) **The Zone theory:**

Bloch stated this theory in 1928. According to this theory, the free electrons move in a periodic field provided by the lattice. This theory is also called "***Band theory of solids***".

4.2 The Classical Free Electron Theory of Metals (Drude-Lorentz theory of metals)

The classical free electron theory is based on the following postulates:

(a) In an atom electrons revolue around the nucleus and a metal is composed of such atoms.

(b) The valence electrons of atoms are free to move about the whole volume of the metals like the molecules of a perfect gas in a container. The collection of valence electrons from all the atoms in a given piece of metal forms electron gas. It is free to move throughout the volume of the metal.

(c) These free electrons move in random directions and collide with either positive ions fixed to the lattice or other free electrons. All the collisions are elastic i.e. there is no loss of energy.

(d) The movements of free electrons obey the laws of the classical kinetic theory of gases.

(e) The electron velocities in a metal obey the classical Maxwell - Boltzmann distribution of velocities.

(f) The free electrons move in a completely uniform potential field due to ions fixed in the lattice.

(g) When an electric field is applied to the metal, the free electrons are accelerated in the direction opposite to the direction of applied electric field.

4.2.1 Electrical conductivity

Let us now derive an expression for electrical conductivity in terms of number of free electrons and their mobility.

In metals free electrons roam freely through the crystal lattice. In the absence of applied external field the net current due to the movement of electrons is zero since they move randomly in all directions. In between two collisions the electrons move with uniform velocity. During every collision both the direction and the magnitude of velocity change.

In 1900, P. Drude made use of the electron gas model to explain electrical conduction in metals.

Ohm's law governs the electrical conduction in metals. At constant temperature the current I flowing through a wire is directly proportional to the potential difference V applied across the wire. i.e., $I \propto V$

$$I = \frac{V}{R}$$

where R is the resistance of the wire.

The current is due to the motion of the conduction electrons under the influence of the electric field. The field E exerts a force - eE on the electron. The accelerated electron collides with the rest of the medium and its velocity drops to zero due to such collision. Due to the field it is again accelerated. We can consider that there is a frictional force acting on the electron due to its collision. If v is the velocity of the electron and τ is the time between two consecutive collisions, the frictional force can be written as $-m\frac{v}{\tau}$ where m is the effective mass of the electron. Using Newton's law

$$m\frac{dv}{dt} = -eE - m\frac{v}{\tau} \tag{1}$$

Under steady-state condition

$$\frac{dv}{dt} = 0$$

Hence from Eq. (1)

$$v = \frac{-e\tau}{m}E \tag{2}$$

This is the ***steady-state velocity*** of the electron.

Drift velocity and mean free path

Actually there are two different velocities associated with the electron. ***In the absence of the field the electrons have random motion, just as gas molecules move randomly in a gas container. The randomly moving electrons undergo scattering and change the direction***. This random motion contributes zero current and the corresponding velocity is called the ***random velocity***. ***In the presence of a field, in addition to random velocity, there is an additional net velocity associated with electrons called drift velocity due to the applied electric field***. Due to drift velocity v_d, electrons with negative charge move opposite to the field direction. This is given by Eq. (2).

If n is the number of conduction electrons per unit volume, then the charge per unit volume is $(-ne)$. The amount of charge crossing a unit area per unit time is given by the current density J.

$$\begin{aligned} J &= (-ne)v_d = -ne\left(\frac{-e\tau}{m}E\right) \\ &= \frac{ne^2\tau}{m}E \end{aligned}$$

Since $J = \sigma E$ where σ is the conductivity.

$$\sigma = \frac{ne^2\tau}{m}. \tag{3}$$

We find that with increase of electron concentration n, the conductivity σ increases. (Later we are going to study that the electrons behave to possess varying mass when accelerated by a periodic electric potential. Hence inside periodic potential of lattice the mass of the electron is called effective mass m^*). As m increases, the motion of electron becomes slow and hence the conductivity σ decreases. τ is the ***mean free lifetime*** which is actually the time between two consecutive collisions. ***The average distance travelled by an electron between two successive collisions in the presence of applied field is known as mean free path***.

Relaxation Time

The mean free lifetime τ is also called the ***relaxation time***. To understand the meaning of the τ, let us assume that the applied field is cut off after the drift velocity of the electron has reached its steady value. Drift velocity after this instant is governed by

$$m\frac{dv_d}{dt} = -m\frac{v_d}{\tau}$$

(from Eq. (1), reducing $E = 0$)

$$\text{or} \quad \frac{dv_d}{v_d} = -\frac{dt}{\tau}$$

$$\text{or} \quad v_d(t) = v_d(0)\exp(-t/\tau) \tag{4}$$

where $v_d(0)$ is the steady state drift velocity (i.e. the drift velocity at the instant the field E is cut off; i.e. at $t = 0$). This equation is graphically represented in Fig. 1.

To define τ, let $t = \tau$ in Eq. (4), then

$$v_d(t) = \frac{v_d(0)}{e} \tag{5}$$

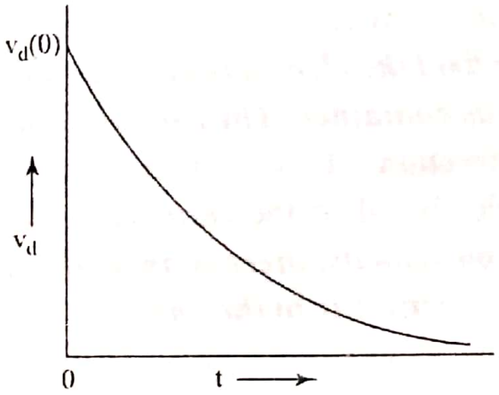


Fig.1 Relaxation of electrons after electric field is cut off.

Hence *relaxation time can be defined as the time taken for the drift velocity to decay to $1/e$ of its initial value.*

Mobility of the electron μ is defined as the steady state drift velocity $\langle v_d \rangle$ per unit electric field.

From Eq. (2),

$$\mu = \frac{\langle v_d \rangle}{E} = \frac{e\tau}{m} \tag{6}$$

Substituting this in Eq. (3)

$$\sigma = \frac{ne^2\tau}{m} = ne \cdot \frac{e\tau}{m}$$

$$\boldsymbol{\sigma = ne\mu} \tag{7}$$

Therefore the resistivity of the material of the conductor is given by

$$\rho = \frac{1}{\sigma} = \frac{1}{ne\mu} = \frac{m}{ne^2\tau} \tag{8}$$

Eq. (7) has great significance. The electrical conductivity σ depends on two factors, the charge density n and their mobility μ. These two quantities depend on temperature. In metals n is constant and μ decreases slightly with temperature and hence with increase of temperature, the conductivity decreases. In semiconductors, the exponential increase of n with temperature is responsible for increase of conductivity with temperature. In insulators n remains constant and above certain temperature μ increases exponentially resulting in dielectric breakdown.

4.2.2 Success of classical free electron theory

1) It verifies Ohm's law.

2) It explains the electrical and thermal conductivities of metals.

3) It derives Wiedemann-Franz law. (i.e. the relation between electrical conductivity and thermal conductivity)

4) It explains optical properties of metals.

4.2.3 Drawbacks of classical free electron theory

Inspite of the success seen above, classical theory has the following drawbacks.

1. The phenomena such as photoelectric effect, Compton effect and the black body radiation couldn't be explained by classical free electron theory.

2. According to the classical free electron theory the value of specific heat of metals is given by 4.5 R_u where R_u is the Universal gas constant whereas the experimental value is nearly equal to $3\,R_u$. Also according to this theory the value of electronic specific heat is equal to $\frac{3}{2}R_u$ while the actual value is about $0.01\,R_u$ only.

3. Electrical conductivity of semiconductor or insulators couldn't be explained using this model.

4. Though $\frac{K}{\sigma T}$ is a constant (Wiedemann-Franz Law) according to the Classical free electron theory, it is not a constant at low temperature.

5. Ferromagnetism couldn't be explained by this theory. The theoretical value of paramagnetic susceptibility is greater than the experimental value.

Solved Problem 1

The density of silver is 10.5×10^3 kg/m^3. The atomic weight of silver is 107.9. Assuming that each silver atom provides one conduction electron (i) calculate the density of electrons. The conductivity of silver at 20°C is 6.8×10^7 ohm^{-1} m^{-1} (ii) calculate the mobility of electrons in silver.

Solution

(i) Molar volume of silver is $\left(\frac{M_A}{\rho_s}\right)$

Thus $\left(\frac{M_A}{\rho_s}\right)$ m^3 contains N_A electrons

1 m^3 will contain $\left[\frac{\rho_s N_A}{M_A}\right]$ electrons

$$\text{i.e.,} \quad n = \frac{\rho_s N_A}{M_A}$$

with $\rho_s = 10.5 \times 10^3$ kg/m^3

$N_A = 6.02 \times 10^{26}$/k mol (Avogadros' number)

$M_A = 107.9$

Thus $n = \dfrac{10.5 \times 10^3 \times 6.02 \times 10^{26}}{107.9} = 5.86 \times 10^{28}$ (Answer)

(ii) with $\sigma = ne\mu$

or $\mu = \sigma/ne$

$\sigma = 6.8 \times 10^7$ ohm^{-1}m^{-1}

$n = 5.86 \times 10^{28}$

$e = 1.6 \times 10^{-19}$ coulomb

$$\mu = \frac{6.8 \times 10^7}{5.86 \times 10^{28} \times 1.6 \times 10^{-19}}$$

$= 0.725 \times 10^{-2}$m^{2}V^{-1}s^{-1} (Answer)

Solved Problem 2

Calculate the mobility of the electrons in copper obeying classical laws. Given

Density $= 8.92 \times 10^3$ kg/m^3

Resistivity of copper $= 1.73 \times 10^{-8}$ ohm-m

Atomic weight $= 63.5$

Avogadro's number $= 6.02 \times 10^{26}$ per k-mol.

(June 2008, Set No:3)

Solution

We know i) $\sigma = ne\mu$

$$\therefore \quad \mu = \frac{\sigma}{ne} = \frac{1}{\rho ne}$$

$$\text{ii)} \ \rho = \frac{m}{ne^2\tau}$$

$$\therefore \quad \tau = \frac{m}{ne^2\rho}$$

i) Number of copper atoms/m^3 $= n = \dfrac{\text{density} \times \text{Avogadro number}}{\text{Atomic weight}}$

$$= \frac{8.92 \times 10^3 \times 6.02 \times 10^{26}}{63.5}$$

$$= 8.456 \times 10^{28}$$

Hence $\mu = \dfrac{1}{\rho ne} = \dfrac{1}{1.73 \times 10^{-8} \times 8.456 \times 10^{28} \times 1.6 \times 10^{-19}}$

$$= 0.427 \times 10^{-2}\,\text{mV}^{-1}\text{s}^{-1} \qquad \text{(Answer)}$$

(ii) $\tau = \dfrac{m}{ne^2\rho}$

$$= \frac{9.1 \times 10^{-31}}{8.456 \times 10^{28} \times (1.6 \times 10^{-19})^2 \times 1.73 \times 10^{-8}}$$

$$= 2.43 \times 10^{-14}\,\text{s} \qquad \text{(Answer)}$$

Solved Problem 3

Find the relaxation time of conduction electrons in a metal of resistivity 1.54×10^{-8} ohm-m, if the metal has 5.8×10^{28} conduction electrons per m^3 (May 2004, Set No. 2; Dec. 2004, Set No. 1, May. 2007, Set No. 2)

Solution

$$\text{Resistivity} \quad \rho = \frac{m}{ne^2\tau}$$

$$\text{Hence} \quad \tau = \frac{m}{ne^2\rho}$$

$$\text{Given} \quad P = 1.54 \times 10^{-8}\ \text{ohm-m}$$

$$n = 5.8 \times 10^{28}\ \text{electron/m}^3$$

$$m = 9.108 \times 10^{-31}\ \text{kg}$$

$$e = 1.602 \times 10^{-19}\ \text{C}$$

$$\text{Hence} \quad \tau = \frac{9.108 \times 10^{-31}}{5.8 \times 10^{28} \times (1.602 \times 10^{-19})^2 \times 1.54 \times 10^{-8}}$$

$$= \frac{9.108 \times 10^{-13}}{22.923} = 0.397 \times 10^{-13}$$

$$= 3.97 \times 10^{-14}\ \text{s} \qquad \text{(Answer)}$$

Solved Problem 4

Calculate the free electron concentration, mobility and drift velocity of electrons in aluminium wire of length of 5 m and resistance 0.06Ω carrying a current of 15 A, assuming that each aluminium atom contributes 3 free electrons for conduction

Given:

Resistivity of aluminium = $2.7 \times 10^{-8}\,\Omega\,\text{m}$
Atomic weight = 26.98
Density = $2.7 \times 10^3\ \text{kg/m}^2$
Avagadro number = 6.025×10^{23}

(June 2005, Set No. 2 and Set No. 3)

Solution

$$\text{Given} \quad R = 0.06\Omega$$

$$l = 5\,\text{m}$$

$$\rho = 2.7 \times 10^{-8}\,\Omega\,\text{m}$$

$$M_A = 26.98$$

$$N_A = 6.025 \times 10^{23}\ \text{mole}^{-1} = 6.025 \times 10^{26}\ \text{k mole}^{-1}$$

$$\text{density} \quad \rho_s = 2.7 \times 10^3\,\text{kg/m}^3$$

Molar volume of aluminium is $\left(\frac{M_A}{\rho_s}\right)$ i.e. $\left(\frac{M_A}{\rho_s}\right)$ m^3 contains N_A atoms. Since each atom contains 3 free electrons 1 m^3 will contain $\left(\frac{\rho_s N_A}{M_A}\right) \times 3$ electrons

$$\begin{aligned} \text{i.e.,} \quad n &= \frac{3\rho_s N_A}{M_A} \\ &= \frac{3 \times 2.7 \times 10^3 \times 6.025 \times 10^{26}}{26.98} \\ &= 1.8088 \times 10^{29}\,\text{electrons/m}^2 \qquad \text{(Answer)} \end{aligned}$$

We know

$$\frac{1}{\rho} = ne\mu$$

or

$$\mu = \frac{1}{ne\rho} = \frac{1}{1.8088 \times 10^{29} \times 1.602 \times 10^{-19} \times 2.7 \times 10^{-8}}$$

$$= 1.278 \times 10^{-3}\,\text{ms}^{-1}\text{V}^{-1} \qquad \text{(Answer)}$$

We know

$$\mu = \frac{v_d}{E}$$

or drift velocity

$$v_d = \mu E$$

where E is the electric field.

$$E = \frac{V}{D} = \frac{IR}{D}$$

$$\begin{aligned} \text{Given} \quad I &= 15\,\text{A} \\ R &= 0.06\,\Omega \\ D &= 5\,\text{m} \\ \text{Hence} \quad E &= \frac{15 \times 0.06}{5} \\ &= 0.18\,\text{Vm}^{-1} \\ \text{Hence} \quad v_d &= \mu E \\ &= 1.278 \times 10^{-3} \times 0.18 \\ &= 0.230 \times 10^{-3}\,\text{ms}^{-1} \qquad \text{(Answer)} \end{aligned}$$

4.3 Quantum Theory of Free Electrons (Sommerfeld's theory of metals)

We assume that electrons move freely in a solid similar to gas molecules. They may be considered to be subjected to a constant potential V. For convenience if we assume the potential to be zero, the Schrodinger equation becomes

$$-\frac{\hbar^2}{2m}\nabla^2\psi = E\psi$$

where E the total energy is totally kinetic in this case.

We assume a plane wave solution of the type,

$$\psi = \psi_o \exp(ik \cdot r) \tag{9}$$

where the wave-vector $k = 2\pi/\lambda$ and $r^2 = x^2 + y^2 + z^2$

$$\text{Hence} \quad \frac{\partial \psi^2}{\partial x^2} = -k^2 x\psi$$

$$\frac{\partial^2 \psi}{\partial y^2} = -k^2 y\psi$$

$$\frac{\partial^2 \psi}{\partial z^2} = -k^2 z\psi$$

so that

$$\begin{aligned}\nabla^2\psi &= \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \\ &= -(k_x^2 + k_y^2 + k_z^2)\psi \\ &= -k^2\psi\end{aligned} \tag{10}$$

$$\text{Therefore } -\frac{\hbar^2}{2m}(-k^2\psi) = E\psi$$

$$\begin{aligned}\text{or} \quad E &= \frac{\hbar^2 k^2}{2m} = \left(\frac{h}{2\pi}\right)^2 \left(\frac{2\pi}{\lambda}\right)^2 \cdot \frac{1}{2m} \\ &= \frac{h^2}{2m\lambda^2} = \frac{h^2 p^2}{2mh^2} \quad (\text{since} \quad \lambda = h/p) \\ E &= \frac{p^2}{2m}\end{aligned} \tag{11}$$

Equation (6.11) represents the energy of a free particle (i.e., electron). From the Fig. 2 it is seen that the energy is continuous. If L is the length of the solid, applying the boundary conditions,

$$k = \frac{2\pi n}{L} \quad \text{we get}$$

$$E(n) = \frac{\hbar^2 k^2}{2m} = \frac{n^2 h^2}{8mL^2} \qquad (12)$$

If L is large, say 1 cm, the adjacent permitted energy levels differ by about 10^{-19} eV. Since the separation is too small, the energy levels can be considered to form a quasicontinuous band.

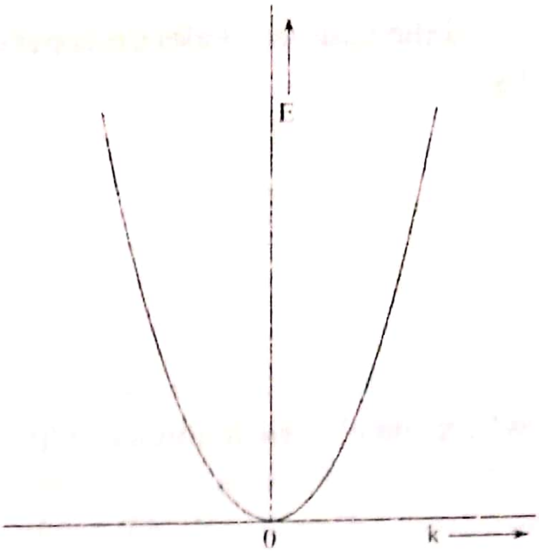


Fig.2 Electron energy (E) as a function of wave number (k) of free electrons.

When an external electric field E is applied, the force exerted on the electron is $-eE$. Since force is also rate of change of momentum,

$$-eE = \frac{dp}{dt}.$$

Since momentum $p = \frac{h}{\lambda} = \frac{h}{2\pi} \times \frac{2\pi}{\lambda} = \hbar k$

$$-eE = \frac{d}{dt}(\hbar k) = \hbar \left(\frac{dk}{dt}\right) \qquad (13)$$

$$\text{or} \quad dk = -\frac{eE}{\hbar} dt. \qquad (14)$$

This means that origin of the k space moves through a distance dk in time dt on application of external field. Because of collisions with imperfections, displacement of k space becomes steady ($= \Delta k$) and dt is then the average collision time τ.

$$\text{Hence} \quad \Delta k = -\frac{eE\tau}{\hbar}.$$

Since $p = mv = \hbar k$, incremental velocity Δv is given by

$$\Delta v = \frac{\hbar}{m}\Delta k = -\left(\frac{\hbar}{m}\right)\left(\frac{eE\tau}{\hbar}\right)$$

$$= -\frac{eE\tau}{m}. \qquad (15)$$

If the number of electrons per unit volume is n, then the current density J is given by

$$\begin{aligned} J &= n(-e)\Delta v \\ &= \frac{ne^2E\tau}{m} \\ &= \sigma E \quad \text{(Ohm's law)} \end{aligned}$$

where the electrical conductivity

$$\sigma = \frac{ne^2\tau}{m} \tag{16}$$

4.4 Fermi Distribution Function

Now let us consider how the electrons in real material distribute among the different possible energy states. The assembly of electrons may be considered as 'electron gas' behaving like a system of Fermi particles obeying ***Fermi - Dirac statistics***. Accordingly, the probability $F(E)$ of an electron occupying an energy level E is given by

$$F(E) = \frac{1}{1 + \exp\left(\frac{E-E_F}{kT}\right)} \tag{17}$$

where E_F is called ***Fermi energy*** and is a constant for a given system. $F(E)$ is called ***Fermi function***. The Fig. 3(b) gives the shape of Fermi function at different temperatures.

$$\begin{aligned} \text{At}\quad T = 0\,\text{K for } E < E_F, &\qquad F(E) = 1 \\ E > E_F, &\qquad F(E) = 0 \end{aligned} \tag{18}$$

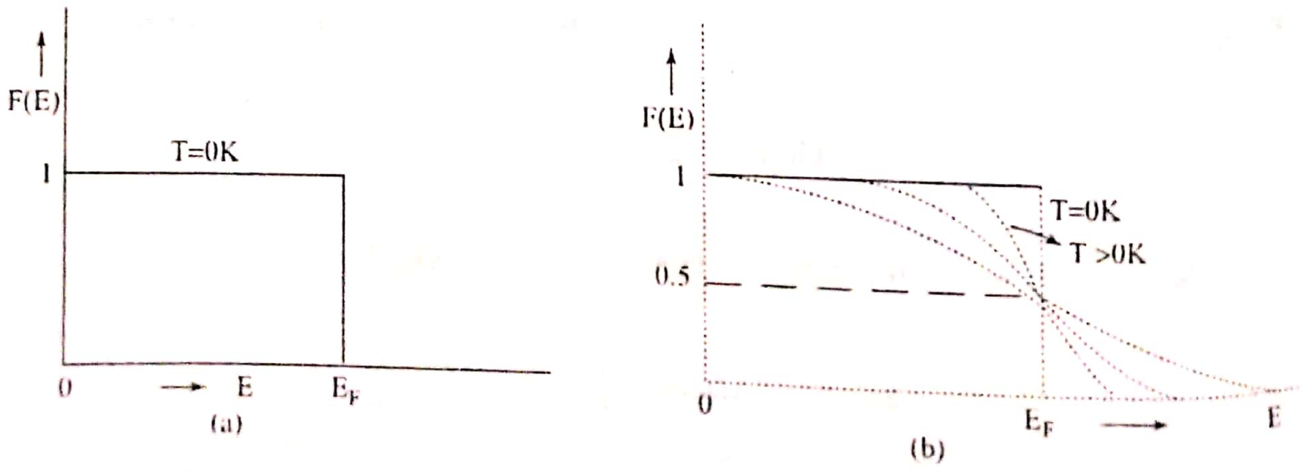


Fig.3 The Fermi distribution function at different temperatures.

This means that at 0 K, all quantum states with energy below E_F are completely occupied and those above E_F are unoccupied as shown in Fig. 3(a). With increase of temperature, the Fermi function plot shows deviation as shown in Fig. 3(b).

At any temperature other than 0K, if $E = E_F$

$$F(E) = 1/2 \tag{19}$$

Hence, the ***Fermi level*** is that state at which the probability of electron occupation is 1/2 at any temperature above 0 K and also it is the level of maximum energy of the filled states at 0 K. ***Fermi energy is the energy of the state at which the probability of electron occupation is 1/2 at any temperature above 0 K. It is also the maximum energy of filled states at 0 K.***

Solved Problem 5

Find the lowest energy of an electron confined in a box of side 0.1 nm each.

✎ **Solution**

The possible energies of a particle in a cubical box of each side L are given by

$$E_{n_1,n_2,n_3} = \frac{h^2}{8mL^2}\left(n_1^2 + n_2^2 + n_3^2\right).$$

For the lowest energy $n_x = n_y = n_z = 1$

Hence $E_1 = \dfrac{3h^2}{8mL^2}$

With $h = 6.62 \times 10^{-34}$ joule sec

$m = 9.1 \times 10^{-31}$ kilogram

$L = 0.1 \times 10^{-9}$ metre

$$E_1 = \frac{3 \times (6.62 \times 10^{-34})^2}{8 \times 9.1 \times 10^{-31} \times (0.1 \times 10^{-9})^2} = 18.06 \times 10^{-18} \text{ joule}$$

$$= \frac{18.06 \times 10^{-18}}{1.6 \times 10^{-19}} \text{ eV} = 112.9\,\text{eV} \qquad \text{(Answer)}$$

Solved Problem 6

Evaluate the Fermi function for an energy kT above the Fermi energy.

Solution

Fermi function

$$F(E) = \frac{1}{1 + \exp\left(\frac{E - E_f}{kT}\right)}$$

Given $E - E_F = kT$

Hence

$$F(E) = \frac{1}{1 + \exp(1)} = \frac{1}{1 + 2.78} = \frac{1}{3.78} = 0.269 \quad \text{(Answer)}$$

Solved Problem 7

At what temperature we can expect a 10% probability that electrons in silver have an energy which is 1% above the Fermi energy? The Fermi energy of silver is 5.5 eV.

Solution

We know that probability function is given by

$$F(E) = \frac{1}{1 + \exp(E - E_F/kT)}$$

Given : $F(E) = 10\% = 0.1$

$$E_F = 5.5\,\text{eV}$$

$$E = E_F + \frac{1}{100} E_F$$

$$E = (5.5 + 0.055) = 5.555\,\text{eV}$$

Hence $E - E_F = 0.055\,\text{eV} = 0.055 \times 1.6 \times 10^{-19}\,\text{J}$.

Substituting in the formula

$$0.1 = \frac{1}{1 + \exp\left(\dfrac{0.055 \times 1.6 \times 10^{-19}}{1.38 \times 10^{-23} \times T}\right)}$$

$$\text{i.e.} \quad 0.1 = \frac{1}{\exp\left(\dfrac{637.7}{T}\right) + 1}$$

$$\exp\left(\frac{637.7}{T}\right) + 1 = 10$$

$$\text{or} \quad \exp\left(\frac{637.7}{T}\right) = 9$$

$$\text{or} \quad \frac{637.7}{T} = \ln 9$$

$$\text{Hence} \quad T = \frac{637.7}{\ln 9} = \frac{637.7}{2.197}$$

$$= 290.2\ \text{K} \qquad \text{(Answer)}$$

4.5 Density of Energy States

Now we have to calculate the carrier concentration i.e., the number of electrons per unit volume in a given energy range of interest. This is given by summing the product of the density of states $Z(E)$ and the occupancy probability $F(E)$; that is

$$n_c = \int_{\text{energy band}} Z(E)\, F(E)\, dE \qquad (20)$$

We know that the number of energy states with a particular value of E depends on how many combinations of quantum numbers result in the same value of n(degeneracy).

The number of energy states having energy values between E and $E + dE$ (i.e. in the energy interval dE) can be shown to be

$$Z(E)\, dE = \frac{\pi}{2} n^2\, dn \qquad (21)$$

From Eq. (12) we know

$$E = \frac{h^2 n^2}{8mL^2}$$

$$\text{i.e.} \quad n^2 = \frac{8mL^2 E}{h^2} \tag{22}$$

$$n = \left[\frac{8mL^2 E}{h^2}\right]^{1/2} \tag{23}$$

Differentiating n^2 in Eq. (22)

$$2n\,dn = \frac{8mL^2}{h^2}\,dE \tag{24}$$

$$\begin{aligned} dn &= \left(\frac{1}{2n}\right)\frac{8mL^2}{h^2}dE \\ &= \left[\frac{8mL^2}{h^2}\right]\left(\frac{1}{2}\right)\left(\frac{h^2}{8mL^2}\right)^{1/2}\frac{dE}{E^{1/2}} \\ &= \left(\frac{1}{2}\right)\left(\frac{8mL^2}{h^2}\right)^{1/2}\frac{dE}{E^{1/2}} \end{aligned} \tag{25}$$

Substituting the values of n^2 and dn from Eqs. (22) and (23) in Eq.(28)

$$\begin{aligned} Z(E)\,dE &= \frac{\pi}{2}\times\left[\frac{8mL^2}{h^2}E\right]\times\frac{1}{2}\times\left(\frac{8mL^2}{h^2}\right)^{1/2}\frac{dE}{E^{1/2}} \\ &= \frac{\pi}{4}\left(\frac{8mL^2}{h^2}\right)^{3/2}E^{1/2}dE. \end{aligned}$$

According to Pauli's exclusion principle two electrons of opposite spin can occupy each state and hence the number of energy states available for electron occupancy is given by

$$\begin{aligned} Z(E)dE &= 2\times\frac{\pi}{4}\left(\frac{8mL^2}{h^2}\right)^{3/2}E^{1/2}dE \\ &= \frac{4\pi}{h^3}(2m)^{3/2}L^3\,E^{1/2}dE \end{aligned} \tag{26}$$

Density of energy states is given by number of energy states per unit volume

$$\text{i.e.,} \quad \textbf{Density of states } Z(E)dE = \frac{4\pi}{h^3}(2m)^{3/2}E^{1/2}\,dE \tag{27}$$

Carrier Concentration:

Substituting the values $F(E)$ and $Z(E)dE$ from Eqs. (17) and (27) in Eq. (20) for calculation of carrier concentration,

$$\begin{aligned} n_c &= \int Z(E)\, F(E)\, dE \\ &= \frac{4\pi}{h^3}(2m)^{3/2} \int_{\text{Energy band}} E^{1/2} \frac{1}{1+\exp\left(\frac{E-E_F}{kT}\right)} dE. \end{aligned} \tag{28}$$

This is the expression for ***density of charge carriers*** at any temperature.

Eq. (28) can be used to calculate the carrier concentration in metals and semiconductors.

Solved Problem 8

Find the temperature at which there is 1% probability of a state with an energy 0.5 eV above Fermi energy.

(June 2005, Set No. 1 and Set No. 4; June 2006, Set No. 2, Set No. 3, May 2007, Set No. 1, Set No. 3, Set No. 4)

Solution

$$\text{Formula} \quad F(E) = \frac{1}{\left[1+\exp\dfrac{(E-E_F)}{kT}\right]}$$

Given $E = E_F + 0.5\,\text{eV}$; $F(E) = 1\% = 0.01$

$$\text{Hence} \quad 0.01 = \frac{1}{1+\exp\left(\frac{0.5}{kT}\right)}$$

$$0.01 \exp\left(\frac{0.5}{kT}\right) = (1-0.01) = 0.99$$

$$\exp\left(\frac{0.5}{kT}\right) = 99$$

$$\frac{0.5}{kT} = 2.303 \times \log_{10} 99$$

$$kT = \frac{0.5}{2.303 \times \log_{10} 99}$$

$$= 0.109\,\text{eV}$$

$$T = \frac{1.09 \times 1.6 \times 10^{-19}}{1.38 \times 10^{-23}}$$

$$= 1262\,\text{K} \qquad \text{(Answer)}$$

4.6 Electron Scattering and Resistance

The main factors affecting the electrical resistivity of solids are a) temperature and b) defects, e.g. impurities.

The resistivity change is generally given by the ***Matthiessen's rule***

$$\rho_{\textbf{total}} = \rho_{\textbf{pure}} + \rho_{\textbf{impurity}} \qquad (29)$$

where ρ_{pure} is temperature dependent resistivity due to thermal vibrations of the lattice while ρ_{impurity} is caused by the scattering of electrons by impurity atoms.

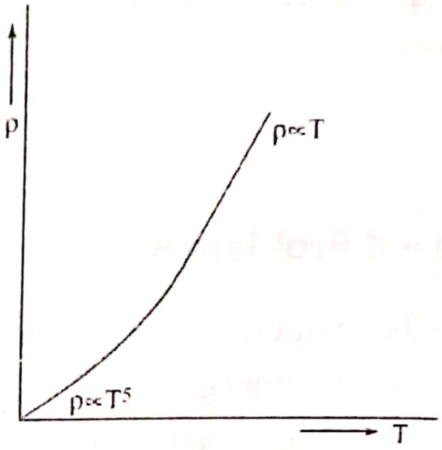


Fig.4 Variation of electrical resistivity with temperature.

4.6.1 The temperature dependence

The temperature dependence of the resistivity arises from the scattering effect of the thermal vibrations of the atoms on the electrons. The mean free path λ is inversely proportional to the mean square of the amplitude of atomic vibrations A_o.

$$\lambda \propto \frac{1}{A_o^2}$$

Since $A_o^2 \propto$ mean potential energy $\propto kT$, $A_0^2 \propto T$ or $\lambda \propto \frac{1}{T}$

$$\text{Hence} \quad \rho \propto \lambda^{-1} \propto T$$

More recent developments of band theory have led to more precise estimates of the relaxation time. One has to take into account the effect of lattice vibrations on electron scattering. This type of scattering leads to a well established T^5 law for ρ at low temperatures.

Over a wide range of temperature, near room temperature $\rho \propto T$ but at low temperature $\rho \propto T^n$ where $n \sim 3$ to 5 and hence $\rho \to 0$ as $T \to 0$.

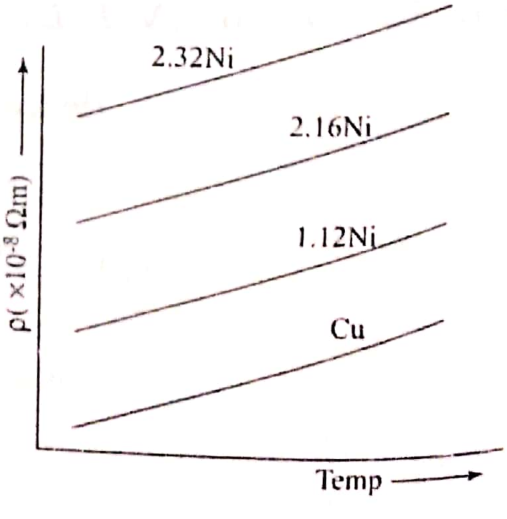


Fig5 The resistivity of copper-nickel alloys.

4.6.2 The defects dependence

The presence of impurity atoms in dilute alloys, introduces additional scattering effects which are not easy to quantify. If the scattering were of the Rutherford nuclear type, then the variation of resistivity is proportional to the square of the excess charge of the impurity atom. Assigning two different relaxation times, the influence of impurities can be separated from normal scattering (due to temperature).

Since

$$\rho = \frac{m}{ne^2\tau}$$

$$= \frac{m}{ne^2}\left(\frac{1}{\tau_o} + \frac{1}{\tau}\right)$$

$$\rho = \rho_o + \rho_{\text{pure}}(T) \quad \text{(Matthiessen's rule)}$$

In this ρ_o is independent of temperature while $\rho_{\text{pure}} \propto T$.

The presence of the two contributions can be seen in the resistivity of copper-nickel alloys as shown in Fig. 5.

The temperature-dependent resistance is added to the residual resistance. It is seen that the residual resistivity increases as the copper lattice is progressively distorted by the addition of impurities. For an alloy consisting of a dilute solution of metal B in metal A, for small concentrations, the resistance follows Nordheim's rule

$$\rho \propto x(1 - x)$$

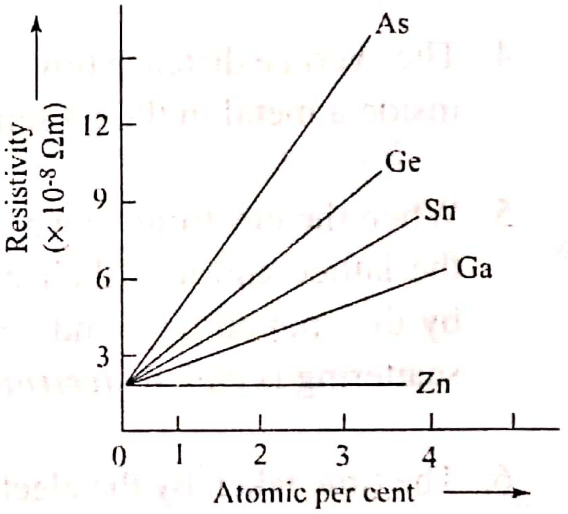


Fig.6 Resistivity of binary alloys of copper as a functions of concentrations of the second component.

where x is the concentration of A atoms $(1 - x)$ is the concentration of B atoms. Fig. 6 illustrates the variation of resistivity of binary alloys of copper as a function of concentrations of the second component. When alloys are no longer dilute, complicated behaviour is exhibited.

Superconductivity

9.1 Introduction

One of the most interesting and unusual properties of solids is that ***certain metals and alloys exhibit almost zero resistivity (i.e. infinite conductivity) when they are cooled to sufficiently low temperatures. This phenomenon is called superconductivity***. This phenomenon was first of all observed by H.K. Onnes in 1911 when measuring the electrical conductivity of metals at low temperatures. During the process, he found that when pure mercury was cooled down to below 4K, the resistivity suddenly droped to zero. Similar behaviour observed for Tin is shown in Fig. 1. Since then hundreds of superconductors have been discovered and studied. Ever since the discovery and until quite recently superconductivity was strictly a low temperature phenomenon. Only few years back it was discovered that few new oxides exhibit superconductivity just below 125 K itself. This interesting phenomena has many important applications in many emerging fields such as energy technology, telecommunication, computing, superfast transportation, medicine etc.

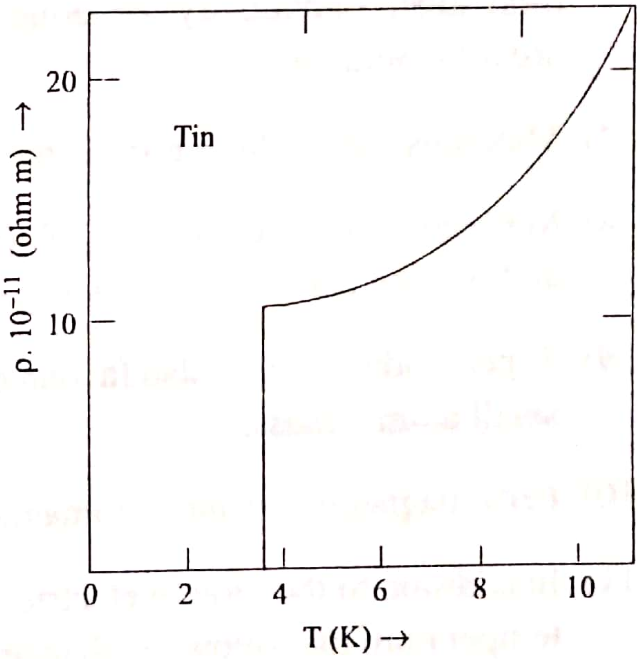


Fig. 1 The electrical resistivity ρ of tin, as a function of temperature near 0 K

9.1.1 General properties

The temperature at which the transition from normal state to superconducting state takes place on cooling in the absence of magnetic field is called the critical temperature (T_c) or the transition temperature.

The following are the general properties/features of superconductors:

1) This transition temperature is different for different substances.

2) For a chemically pure and structurally perfect specimen, the superconducting transition is very sharp. For impure specimens and for those which are structurally imperfect, the transition range is broad (above one tenth of a degree).

3) Superconductivity is found to occur in metallic elements in which the number of valence electron (Z) lies between 2 and 8.

4) Superconducting elements, in general, lie in the inner columns of the periodic table.

5) For elements in a given row in the periodic table, T_c versus Z^2 gives straight line.

6) Transition metals having odd number of valence electrons are favourable to exhibit superconductivity while metals having even number of valence electrons are infavourable.

7) Materials having high normal resistivities exhibit superconductivity.

8) Materials for which $Z\rho > 10^6$ (where Z is the number of valence electrons and ρ is the resistivity) show superconductivity

9) Superconductivity is also favoured by small atomic volume, accompanied by a small atomic mass.

10) Ferromagnetic and antiferromagnetic materials are not superconductors.

11) In addition to the drop in electrical resistivity to zero when cooled to transition temperature the following changes also occur:

    i) the magnetic flux lines are rejected out of the superconductor. This property is known as Meissner effect.

    ii) there is a discontinuous change in specific heat

    iii) there are small changes in thermal conductivity and the volume of the material.

12) The current in a superconducting ring persists for a very long time.

9.2 Effect of Magnetic Field

Superconducting state of a metal mainly depends on temperature and strength of the magnetic field in which the metal is placed. Superconductivity disappears if the temperature of the specimen is raised above T_c or a strong enough magnetic field is applied. This is illustrated in Fig. 2. At temperatures below T_c, in the absence of any magnetic field, the material is in superconducting state. When the strength of the magnetic field applied reaches a critical value H_c the superconductivity disappears.

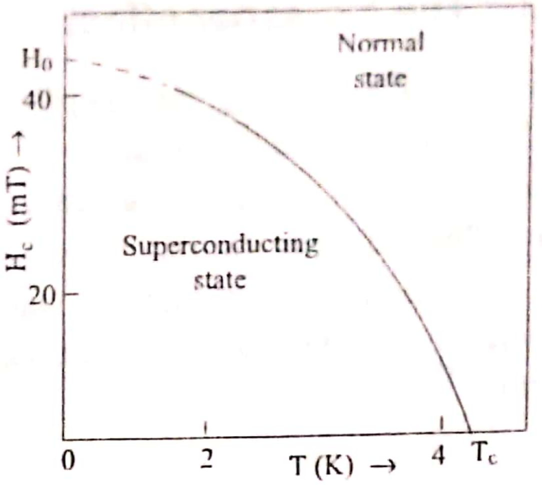


Fig. 2 The critical magnetic field H_c as a function of temperature. For the superconducting-to-normal transition, $H_c = 0$ at T_c

At $T = T_c$, $H_c = 0$. At temperatures below T_c, H_c increases. The dependance of the critical field upon the temperture is given by

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

where $H_c(0)$ is the critical field at 0K. $H_c(0)$ and T_c are constants and characteristic of the material.

Solved Problem 1

A superconducting tin has a critical temperature of 3.7 K at zero magnetic field and a critical field of 0.0306 Tesla at 0K. Find the critical field at 2 K.

(May 2007, Set No. 2)

Solution

Formula $H_c = H_0\left[1 - \left(\frac{T}{T_c}\right)^2\right]$

$$\text{Given} \quad T_c = 3.7\,\text{K}$$
$$H_c(0) = 0.0306\,\text{T}$$
$$T = 2\,\text{K}$$

$$\text{Hence} \quad H_c(2) = 0.0306\left[1 - \left(\frac{2}{3.7}\right)^2\right]$$

$$= 0.02166\,\text{Tesla} \qquad \text{(Answer)}$$

9.2.1 The Meissner effect

When a weak magnetic field is applied to a superconducting specimen at a temperature below transition temperature T_c, the magnetic flux lines are expelled as shown in Fig. 3. ***The specimen acts as an ideal diamagnet. This effect is called Meissner effect.*** This effect is reversible, i.e. when the temperature is raised from below T_c, at $T = T_c$ the flux lines suddenly start penetrating and the specimen returns back to the normal state. Under this condition, the magnetic induction inside the specimen is given by

$$B = \mu_o(H + M) \qquad (2)$$

where H is the external applied magnetic field and M is the magnetisation produced inside the specimen.

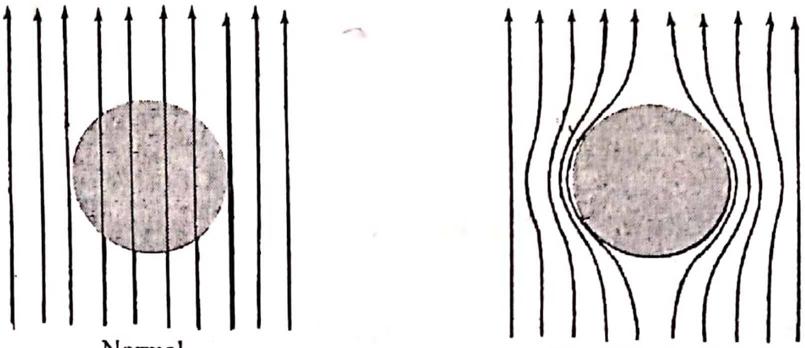
When the specimen is superconducting, according to Meissner effect, inside the bulk superconductor $B = 0$. Hence

$$\mu_o(H + M) = 0$$

$$\text{or} \quad M = -H \qquad (3)$$

Thus the material is perfectly diamagnetic. Magnetic susceptibility can be expressed as

$$\chi = \frac{M}{H} = -1 \qquad (4)$$



Normal
$T > T_c$ or $H > H_c$
(a)

Superconducting
$T < T_c$ or $H < H_c$
(b)

Fig.3 In the superconducting state, the flux lines of a magnetic field are ejected out of the superconductor (b) while in normal state it does not happen (a)

Let us consider a superconducting material under normal state. Let J be the current passing through the material of resistivity ρ. From Ohm's law we know that the electric field $E = J\rho$. On cooling the material to its transition temperature ρ tends to 0. If J is held finite E must be zero. From Maxwell's equation, we know

$$\nabla \times E = -\frac{dB}{dt} \qquad (5)$$

Under superconducting condition since E is zero $\frac{dB}{dt} = 0$; or $B =$ constant. This means that the magnetic flux passing through the specimen should not change on cooling to the transition temperature. The Meissner effect contradicts this result. According to Meissner effect perfect diamagnetism is an essential property of defining the superconducting state. Thus

from zero resistivity $\quad E = 0$
from Meissner effect $\quad B = 0$

9.3 Effect of Current

The critical magnetic field required to destroy superconductivity need not necessarily be applied externally. An electric current flowing through the superconducting material itself may give rise to necessary magnetic field. For example, when a current flows through a superconducting ring, it gives rise to its own magnetic field. As the current is increased to a critical value I_c, the associated magnetic field becomes H_c and the superconductivity disappears. The critical current I_c flowing through a superconducting ring of radius r is given by

$$I_c = 2\pi r H_c \tag{6}$$

This limits the maximum possible current that flows through superconductor. Hence this is the main huddle in producing high field superconducting magnets.

Solved Problem 2

Calculate the critical current for a wire of lead having a diameter of 1 mm at 4.2 K. The critical temperature for lead is 7.18 K and $H_o = 6.5 \times 10^4$ A/m

✎ **Solution**

Formula $H_c = H_0 \left[1 - \left(\frac{T}{T_c}\right)^2\right]$ and $i_c = 2\pi r H_c$

$$\text{Given} \quad T = 4.2\,\text{K}$$

$$T_c = 7.18\,\text{K}$$

$$H_o = 6.5 \times 10^4\ \text{A/m}$$

$$\text{Hence} \quad H_c = 6.5 \times 10^4 \left[1 - \left(\frac{4.2}{7.18}\right)^2\right]$$

$$= 4.276 \times 10^4\ \text{A/m}$$

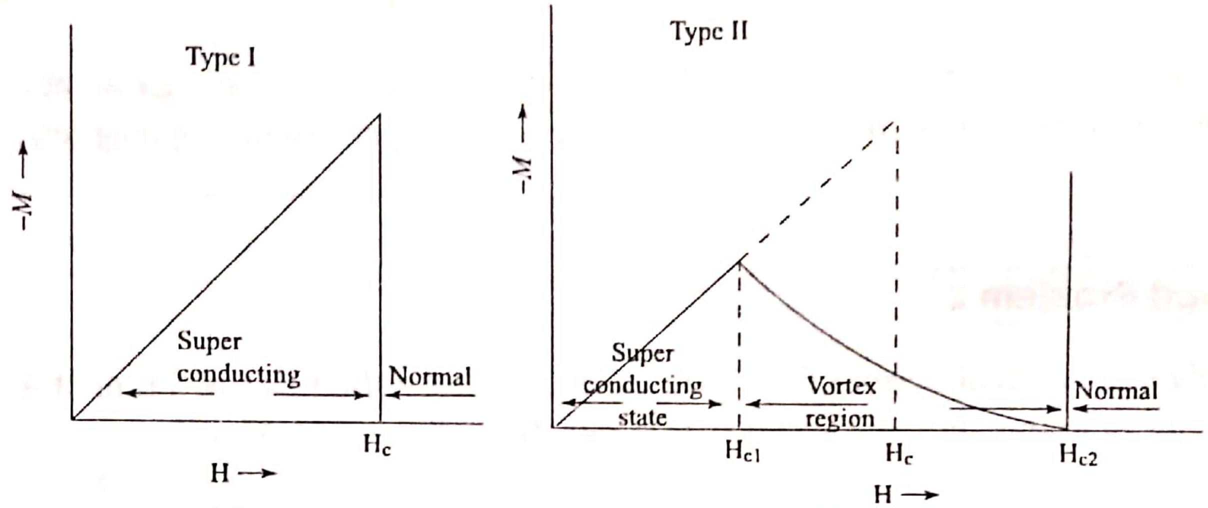
substituting in the formula for the critical current

$$i_c = \pi \times 10^{-3} \times 4.28 \times 10^4$$

$$= 134.51\ \text{A} \qquad \text{(Answer)}$$

9.4 Type I and Type II Superconductors

Based on diamagnetic response superconductors can be classified as type I and type II. Superconductors exhibiting a complete Meissner effect (perfect diamagnetism) are called ***type I superconductors*** (also known as ***soft superconductors***). When the magnetic field strength is gradually increased from its initial value $H < H_c$, at H_c the diamagnetism abruptly disappear and the transition from superconducting state to normal state is sharp as shown in Fig. 4(a). Pure specimens of Al, Zn, Hg and Sn are some examples of type I superconductors.



(a)

(b)

Fig. 4 The magnetization M versus the critical magnetic field H_c for (a) type I and (b) type II superconductors

In ***type II superconductors*** as shown in Fig. 4(b), up to field H_{c_1} the specimen is in a pure superconducting state. The magnetic flux lines are rejected. When the field is increased beyond H_{c_1} (the lower critical field), the magnetic flux lines start penetrating. The specimen is in a mixed state between H_{c_1} and H_{c_2} (the upper critical field). Above H_{c_2}, the specimen is in a normal state. This means that the Meissner effect is incomplete in the region between H_{c_1} and H_{c_2}. This region is known as ***Vortex-region***. Type II superconductors are known as ***hard superconductors***. Zr and Nb are some examples of this type. Type II superconductors are of great practical interest because of the high current densities that they can carry.

9.5 Thermal Properties

In a superconducting state the thermal properties such as entropy and electronic specific heat etc. also change abruptly.

9.5.1 Entropy

Entropy is a measure of the disorder of a system. In normal metals with decrease of temperature, entropy decreases linearly as shown in Fig. 5. In superconducting metals like Aluminum, the entropy decreases linearly up to critical temperature, T_c. Cooling below this temperature the entropy decreases markedly. This means that the superconducting state is more ordered than the normal state. The decrease in entropy in superconducting state means that the electrons thermally excited are more ordered in the superconducting state. It has been estimated that in type I superconductors there is a spatial order which extends over a distance of the order of 10^{-6} metre. This range is called ***coherence length.***

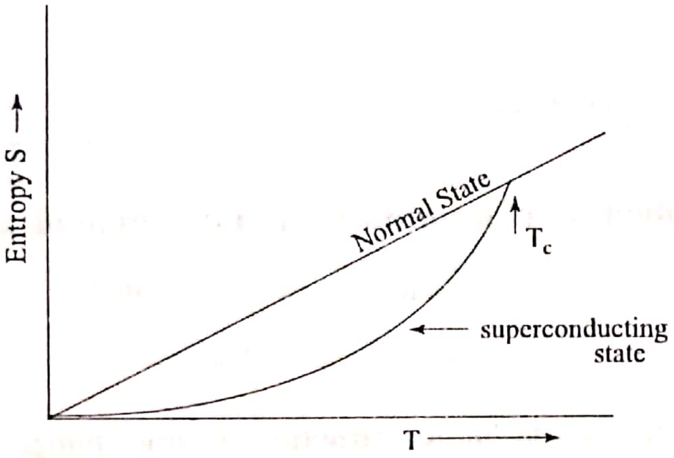


Fig.5 Entropy of aluminium in the normal and superconducting state as a function of temperature

9.5.2 Specific heat

The specific heat of a normal solid is given by the expression

$$C_N = T\frac{dH}{dT}. \tag{7}$$

The specific heat difference between the normal and the superconducting states can be shown as

$$C_N - C_S = -\left[TH_c\frac{d^2H_c}{dT^2} + T\left(\frac{dH_c}{dT}\right)^2\right] \tag{8}$$

at $T = T_c, H_c = 0$

$$C_N - C_S = -T_c\left(\frac{dH_c}{dT}\right)^2 = -ve. \tag{9}$$

This means that near $T_c, C_N < C_S$. But at lower temperatures $C_N > C_S$ as shown in Fig. 6. We find that at the transition temperature there is a discontinuity in the specific heat curve. It must be remembered that both lattice and electrons contribute towards specific heat and hence the total specific heat is

$$C = C_{\text{lattice}} + C_{\text{el}}$$

Hence specific heat in the normal and superconducting states can be written as

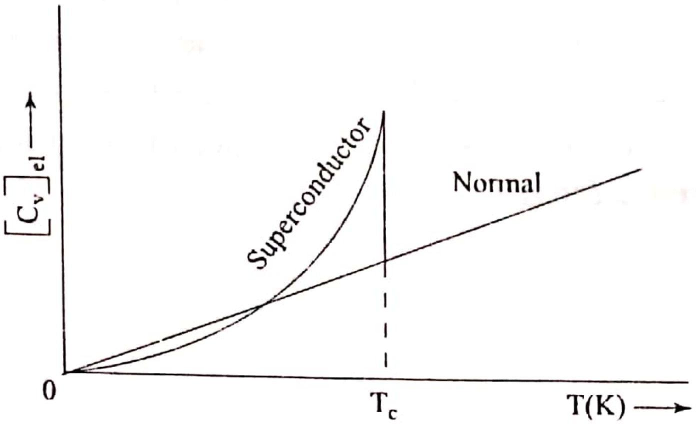


Fig.6 Specific heat of a conductor as a function of temperature

$$C_N = (C_{\text{lattice}})_N + (C_{\text{el}})_N \text{ and}$$
$$C_S = (C_{\text{lattice}})_S + (C_{\text{el}})_S .$$

Since the properties of the lattice structure do not change when a material becomes superconductor,

$$(C_{\text{lattice}})_N = (C_{\text{lattice}})_S$$

$$\text{Hence} \quad C_N - C_S = (C_{\text{el}})_N - (C_{\text{el}})_S .$$

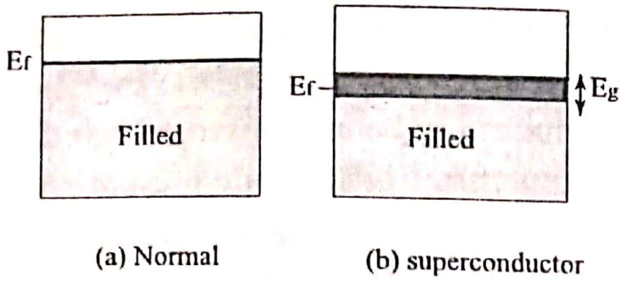
It has been found that below T_c, the electronic specific heat of a metal in the superconducting state varies with temperature in an exponential manner, i.e.,

$$(C_{\text{el}})_S = a\exp\left(-\frac{\Delta}{kT}\right) \tag{10}$$

where a is a constant and Δ is the energy gap.

9.5.3 Energy gap

We have already seen that in at $T = 0\,\text{K}$ in normal metals, all the energy states below E_F are completely filled and all the states above are completely empty. But in superconductors above T_c, superelectrons behave like normal electrons and get excited. Below T_c, these electrons are paired and their total energy is less than $2E_F$. Hence an energy gap is created at the Fermi level in the superconducting state. In an insulator, the gap is associated with the lattice while in the superconductors the gap is associated with superelectrons. In Fig. 7 the presence of an energy gap in the energy spectrum of electron is shown while in Fig. 8 gap in the distribution of density of states can be seen.



(a) Normal (b) superconductor

Fig. 7 (a) conduction band in the normal state (b) energy gap at the fermi level in the conducting state

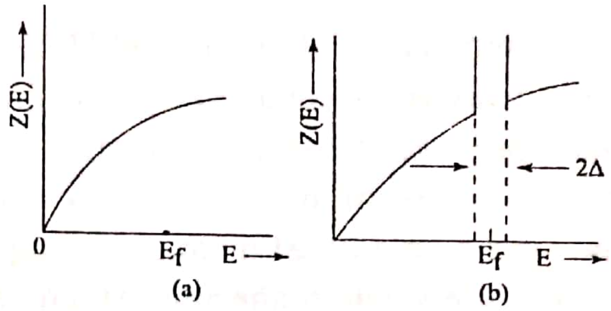


Fig. 8 Density of states as a function of energy (a) normal state b) superconducting state

This energy gap is very small as compared to the gaps in semiconductors and insulators. The variation of energy gap with temperature is shown in Fig. 9

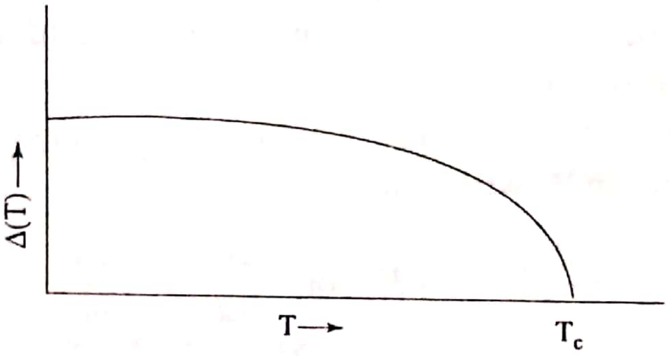


Fig.9 Energy gap as a function of temperature

9.6 Isotope Effect

In superconducting materials the transition temperature varies with the average isotopic mass, M, of their constituents. The variation is found to follow the general form

$$T_c \propto M^{-\alpha} \qquad (11)$$

$$\text{or} \quad M^{\alpha} T_c = \text{constant}$$

where α is called the isotope effect coefficient and is defined as

$$\alpha = \frac{\partial \ln T_c}{\partial \ln M}.$$

The value of α is approximately equal to 0.5. For example, the average isotopic mass of mercury varies from 199.5 to 203.4 atomic mass units and accordingly the transition temperature varies from 4.185 K to 4.146 K.