Thermal Conductivity of metal on the basis of free electron Theory :-

The Co efficient of thermal Conductivity of a material is defined as the quantity of heat energy that flows in a unit time through a unit area of cross section of the material of unit thickness when its opposit faces are maintained at a unit difference of Temperature.

The quantity of heat energy Q that flows in a time t through Two opposit faces each of area A at a distance dx apart maintained at a Temperature difference dT is given by $Q = -KA\frac{dT}{dx}t$.

When $A = 1$ and $t = 1$, $Q = -K\frac{dT}{dx}$ ——→ (1)

or $Q = K\frac{dT}{dx}$ (Ignoring the -ve sign)

Thermal Conductivity of a metal :-

To discuss the Thermal Conductivity of metals on the basis of electronic theory we suppose that there exists an electron gas in the metal and instead of a voltage gradient as in the case of electrical Conductivity there now exists a Temperature gradient $\frac{dT}{dx}$ across a metalic rod. The electron at the higher Tempr end lose energy and electrons on the lower Tempr end gain energy. The amount of heat energy Q passing through a cross section of the rod per unit area, per second according to kinetic theory of gases is given by $Q = \frac{1}{3}nv\lambda\frac{dE}{dx}$ ——— (ii)

where $\frac{dE}{dx}$ is the energy gradient, n the number density of electrons and λ the mean free path, Also on the basis of kinetic theory of gases $E = \frac{3}{2}KT$, where K is the Boltzmann Constant and T the absolute Tempr.

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$$\therefore \frac{dE}{dx} = \frac{3}{2}K\frac{dT}{dx}$$

Substituting in eqn (ii) we have

$$q = \frac{1}{3}\cdot\frac{3}{2}K n v \lambda \frac{dT}{dx} = \frac{1}{2} n v \lambda K \frac{dT}{dx} \quad \text{--- (iii)}$$

Comparing (i) and (iii)

$$K\frac{dT}{dx} = \frac{1}{2} n v \lambda K \frac{dT}{dx}$$

or $K = \frac{1}{2} n v \lambda K$ ——— (iv)

$\therefore$ Thermal conductivity $K = \frac{1}{2} n v \lambda K$.

ELECTRONIC SPECIFIC HEAT :-

~~As~~ The specific heat at constant volume per electron is given by $C_v = \frac{d\bar{E}}{dT}$, where $\bar{E}$ is the average kinetic energy of the electron.

Now $\cancel{\frac{d\bar{E}}{dT}}$ $\bar{E} = E_0\left[1 + \frac{5\pi^2}{12}\left(\frac{KT}{E_{f_0}}\right)^2\right]$

$$\therefore \frac{d\bar{E}}{dT} = E_0 \times \frac{5\pi^2}{12} \times \frac{K^2}{E_{f_0}^2} \times 2T$$

$$\therefore C_v = E_0 \times \frac{5\pi^2}{12} \times \frac{K^2}{E_{f_0}^2} \times 2T$$

~~Here $E_0 = \frac{3}{5}E_{f_0}$ the energy of F-D gas at~~

where $E_0 = \frac{3}{5}E_{f_0}$ = energy per electron

$$\text{or } C_v = \frac{5}{6}\pi^2 \frac{K^2 T}{E_{f_0}^2} \times \frac{3}{5}E_{f_0}$$

E_{f_0} is the Fermi-Energy of the metal.

$$\text{or } C_v = \pi^2\left(\frac{K}{2E_{f_0}}\right) \times KT$$

$$= \pi^2\left[\frac{1}{2}\frac{K}{\frac{E_{f_0}}{K}}\right] \times T. \quad (\because E_{f_0} = E_f)$$

$$\text{or } C_v = \pi^2\left(\frac{K}{2T_F}\right) \times T \longrightarrow (1)$$

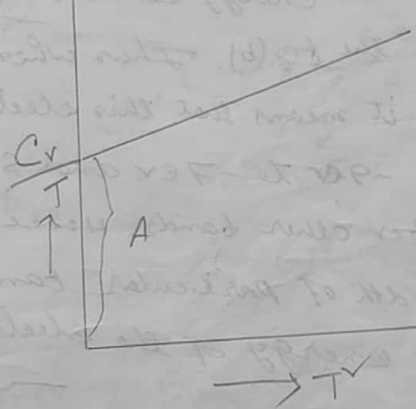
where $T_F = \frac{E_f}{K}$ = Fermi-Temperature.

It is clear from eqn (1) that the electronic specific heat varies linearly with tempr whereas the lattice sp. heat varies as the cube of the absolute tempr at low tempr. The total specific heat at low tempr is given by

$$C_v = AT + BT^3 \quad \text{———} (2)$$

or $$\frac{C_v}{T} = A + BT^2$$

If a graph is plotted between $\frac{C_v}{T}$ and T^2, we get straight line as in the fig. From the slope and intercept constants A and B can be determined.



ENERGY BAND IN SOLIDS:-

Since the atoms in a solid are closely packed, hence the electron in any energy level of a particular atom can have range of energies rather than a single energy. This range of energies is called energy band.

The energy level diagram of an isolated atom is shown in the fig (a). In this atom the electron can have only a single energy for example −12 eV, −8 eV etc and in between the two values no energy is found.

The different energy bands of an electron in a solid is shown in the fig (b).

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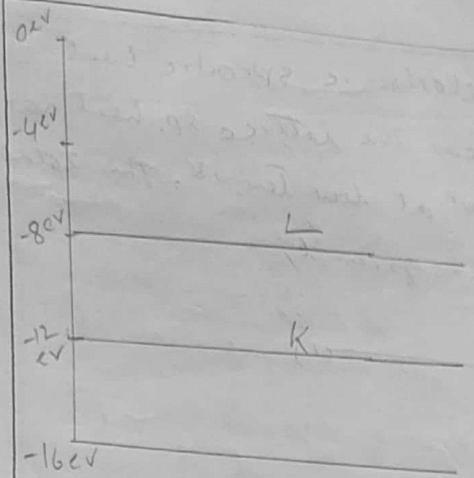
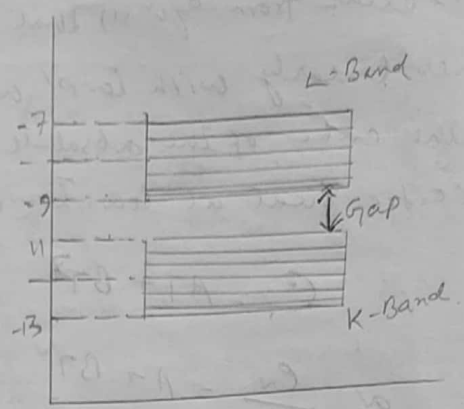


isolated atom

fig (a)



atom in a solid.

fig (b)

The K-band has energy between -13 eV to -11 eV and L-band has energy between -9 eV to -7 eV which is given in the fig (b). Thus when the electron lies in the L-band, it means that this electron can have any energy between -9 eV to -7 eV and similar statement can be given for other bands. Hence the band is continuous. The width of particular band decreases with increasing binding energy of the electron.

BLOCH THEOREM:-

In order to study the electronic structure of molecules and solids, Bloch used one electron equation. From free electron theory, an electron is assumed to move in a constant potential V_0 and hence for one dimensional case, the Schrodinger's wave equation is given by

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V_0)\psi = 0 \longrightarrow (1)$$

$$\text{or} \quad \frac{d^2\psi}{dx^2} + K^2\psi = 0$$

$$\text{Where} \quad K = \frac{\sqrt{2m(E-V_0)}}{\hbar}$$

$$\left(\frac{h}{2\pi} = \hbar\right)$$

$\longrightarrow$

The Solution of (1) is

$$\psi(x) = e^{\pm ikx} \longrightarrow (2)$$

$$\frac{d\psi}{dx} = ike^{\pm ikx}$$

$$\therefore \frac{d_2\psi}{dx^2} = -k^2 e^{\pm ikx}.$$

using these results in (1), we get

$$-k^2 e^{\pm ikx} + \frac{2m}{\hbar^2}(E - V_0)e^{\pm ikx} = 0$$

$$\text{or } -k^2 + \frac{2m}{\hbar^2}(E - V_0) = 0 \text{ as } e^{\pm ikx} \neq 0$$

$$\text{or } k^2 = \frac{2m}{\hbar^2}(E - V_0) \quad \therefore E - V_0 = \frac{\hbar^2 k^2}{2m}$$

$$\therefore \text{Kinetic energy, } E_{k} = E - V_0 = \frac{\hbar^2 k^2}{2m} = \frac{p^2}{2m} \longrightarrow (3)$$

Where $\hbar k = p$ = momentum of an electron.

If an electron is moving in one dimensional periodic potential, the potential energy of an electron can be written as $V(x) = V(x+a) \longrightarrow (4)$

where a is a period, Hence V_n is the periodic potential.

The Schrodinger's wave equation in this Condition Can be written as $\frac{d_2\psi}{dx^2} + \frac{2m}{\hbar^2}[E - V(x)]\psi = 0 \longrightarrow (5)$

For the solution of this equation there is an important theorem ~~Known as~~ which states that there exist solution's of the form

$$\psi(x) = e^{\pm ikx} u_k(x) \longrightarrow (6)$$

$$\text{where } u_k(x) = u_k(x+a) \longrightarrow (7)$$

Thus the solutions are plane waves of type $e^{\pm ikx}$ modulated by the function $u_k(x)$ which has the same periodicity as the lattice constant.

$\longrightarrow \; \times \; \longleftarrow$

Proof:-