Unit - V

SOLID STATE PHYSICS

*** Failures of classical free electron theory ⇒**

→ It could not explain photoelectron effect, crompton effect & black body radiation.

→ Electrical conductivity of semiconductors & insulator could not be explained.

→ Wiedmann Franz's law $\left(\frac{K}{\sigma} = T\right)$ is not applicable at lower temp.

→ Ferromagnetism could not be explained.

→ Acc to classical free e^- theory, the specific heat capacity of metal(V) is given by 4.5R where as experimental value is 3R (where R → Universal constant)

*** Quantum free electron theory ⇒ Introduced in 1994.**

• (Sommerfeld's Model)

*** Assumptions of Sommerfeld's Model →**

→ Valence e^- moves freely in a constant potential within the boundaries of metal and is prevented from escaping the metal at the boundaries.

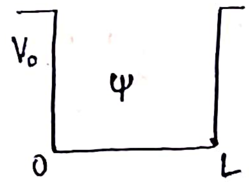
→ The free e^- in a metal can have only discrete energy values.

→ The e_s^- obey Pauli's Exclusion principle & the distribution of energy among e_s^- is acc. to Fermi Dirac's statistics.

→ The force of attraction b/w electron & lattice ion and force of repulsion b/w e_s^- can be neglected.

→ The energy values of e^- are quantised.

⇒ Consider an e^- in a 1D crystal of length (L). At two ends of the crystal the e^- is experiencing high energy potential energy barrier -



$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0$$

$$\psi = A\cos\frac{\sqrt{2mE}}{\hbar}x + B\sin\frac{\sqrt{2mE}}{\hbar}x$$

At $x=0, \psi=0 \Rightarrow A=0$

At $x=L, \psi=0$

$$\Rightarrow \frac{\sqrt{2mE}}{\hbar}L = n\pi$$

$$\left[E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}\right]$$

*** Density of States ⇒**

In case of solids, the energy levels of e^- will spread over a range called energy band. Each energy band consist of no. of states at each energy level. The density of states [g(E)] is defined as the no. of energy states available per unit vol. per unit energy centered at E.

$$\left[g(E)\,dE = \frac{\text{No. of energy states available b/w } E \text{ \& } E+dE}{\text{Vol. of metal}}\right]$$

$\left[N(E)\,dE = \int f(E)\,g(E)\,dE\right]$ where $N(E) \longrightarrow$ No. of e^-

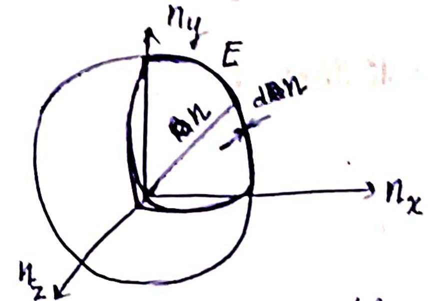
$\Rightarrow$ Electron density $(n) = \frac{N}{V}$

#Note $\Rightarrow$ For 1-D potential well of width (a), the allowed energies for an e^- is given by $E_n = \frac{n^2h^2}{8ma^2}$ where $n = 1, 2, 3, \ldots$ —①

$$\psi(x,y,z) = \sqrt{\frac{2}{L}}\sin\left(\frac{n_x\pi x}{L}\right)\sin\left(\frac{n_y\pi y}{L}\right)\sin\left(\frac{n_z\pi z}{L}\right)$$

For 3D, $E_{n_x,n_y,n_z} = \frac{h^2}{8ma^2}(n_x^2+n_y^2+n_z^2)$

Consider a sphere of radius $n^2 = (n_x^2+n_y^2+n_z^2)$ formed by the points n_x, n_y, n_z with n_x, n_y & n_z as the three mutually $\perp^r$ axes.



Since n_x, n_y, n_z can take only +ve integers, the eq^n represents $\frac{1}{8}$th of the sphere i.e. called the octant.

The no. of allowed energy values i.e. $N(E)\,dE$ available within the sphere of radius $n+dn$ is equal to the product of $\frac{1}{8}$th of vol. of sphere b/w the two shells of radius n & $n+dn$.

So, the no. of points per unit vol. is given as :-

$$N(E)\,dE = \frac{1}{8}\left[\frac{4}{3}\pi(n+dn)^3\right] - \frac{1}{8}\left[\frac{4}{3}\pi n^3\right]$$

Solving & neglecting the higher terms,

$$N(E)\,dE = \frac{\pi}{6}(3n^2dn) = \frac{\pi}{2}[n(ndn)]$$

Since each energy values can accomodate only 2e's acc. to Pauli's exclusion principle, the no. of allowed energy states is $2\times\frac{\pi}{2}[n(ndn)]$

$$N(E)\,dE = \pi[n(ndn)] \quad \text{—②}$$

From eq. ①, $n^2 = \frac{8ma^2E}{h^2}$

$$2ndn = \frac{8ma^2}{h^2}dE \quad \text{—③}$$

Substituting the value in eq^n ②

$$\Rightarrow N(E)\,dE = \pi\left[\frac{8ma^2}{h^2}\right]^{1/2}E^{1/2}\times\left[\frac{1}{2}\frac{8ma^2}{h^2}\right]dE$$

$$\therefore N(E)\,dE = \frac{\pi}{2}\left[\frac{8m}{h^2}\right]^{3/2}a^3E^{1/2}dE$$

$$\Rightarrow g(E) = \frac{N(E)\,dE}{V(a^3)} = \frac{\pi}{2}\left[\frac{8m}{h^2}\right]^{3/2}E^{1/2}dE$$

$$\Rightarrow g(E)\,dE = \frac{\pi}{2}\left[\frac{8m}{h^2}\right]^{3/2}E^{1/2}dE$$

Electron density at 0K at fermi-level

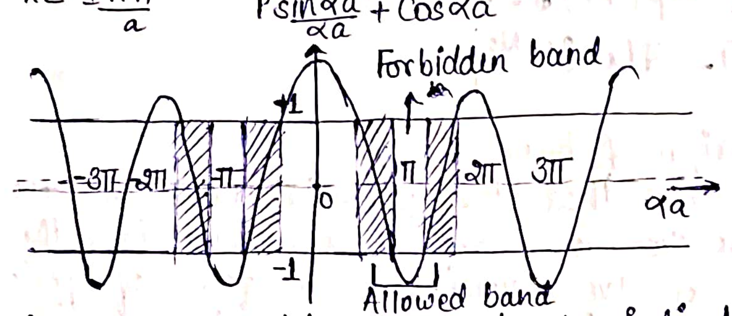
$T = 0K$

$E = E_F$

$f(E) = 1$

Analysis of the eq^n:

$$\cos ka = \pm 1$$
$$ka = \pm n\pi$$
$$k = \frac{\pm n\pi}{a}$$



→ $\cos ka$ can have values b/w +1 and −1 indicated by horizontal lines. Because of this limitation, only certain values of α i.e. E are allowed.

→ The energy spectrum of e⁻ consist of alternate regions of allowed energies (which are shaded) and unallowed known as forbidden energy band. The boundaries of allowed energies of αa which corresponds to the values of $\cos ka$ can have only 1 value with periodicity $\frac{n\pi}{a}$.

→ As the value of αa increases, width of forbidden band decreases and width of energy bands (allowed) increases.

$$P\frac{\sin\alpha a}{\alpha a} + \cos\alpha a = \cos ka \quad \text{—— (4)}$$

<u>Case I:- $P \to \infty$</u>

Dividing the whole eq^n by P

$$\Rightarrow \frac{\sin\alpha a}{\alpha a} + \cancel{\frac{\cos\alpha a}{P}}^{0} = \cancel{\frac{\cos ka}{P}}^{0}$$

$$\Rightarrow \sin\alpha a = 0$$
$$\Rightarrow \alpha a = n\pi$$
$$\alpha^2 = \frac{n^2\pi^2}{a^2}$$

$\because \alpha^2 = \frac{2mE}{\hbar^2}$ $\quad\quad \therefore \frac{2mE}{\hbar^2} = \frac{n^2\pi^2}{a^2}$

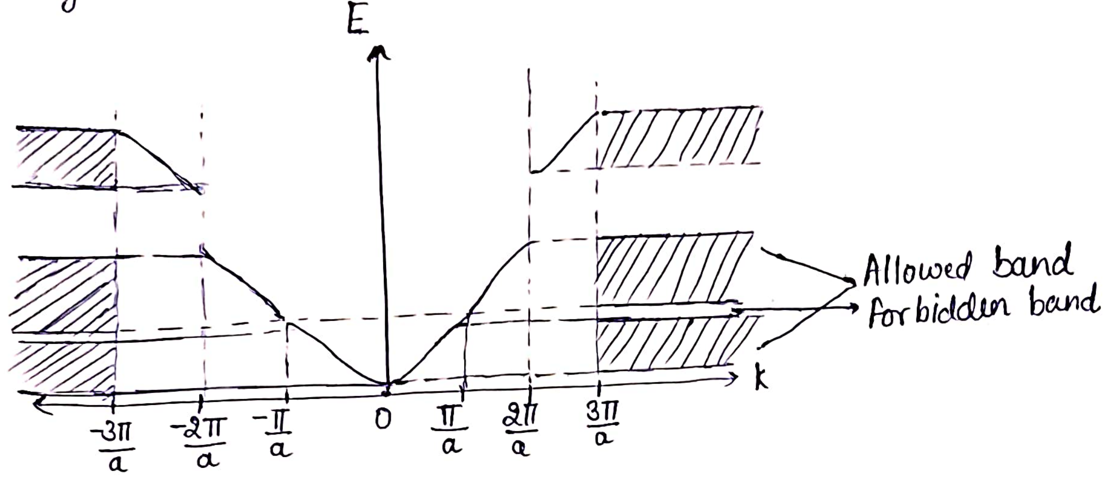
$$\Rightarrow \left[E = \frac{n^2\pi^2\hbar^2}{2ma^2}\right]$$

{The energy levels are discrete and e⁻ is completely bound. It will be within potential and moves only in one cell unless external force is applied.}

<u>Case II:- $P \to 0$</u>

$$\Rightarrow \cos\alpha a = \cos ka$$
$$\Rightarrow \alpha \cancel{a} = k\cancel{a}$$
$$\Rightarrow \alpha = k \quad\quad \text{where } \frac{2\pi}{\lambda} = k$$
$$\therefore \alpha^2 = k^2$$
$$\frac{2mE}{\hbar^2} = k^2 \quad \Rightarrow \left[E = \frac{\hbar^2k^2}{2m}\right] \text{ (Energy of free e⁻)}$$

This ~~energy~~ is equivalent to the case of free particle hence no energy level exist, all energies are allowed to the e^-.



Here discontinuity occurs at $k = \frac{n\pi}{a}$ where $n = 1, 2, 3 ----$.
The k values defines boundaries of brillouin zone

E–K Graph ⇒

1) The e^-'s moving in a periodic potential have energy values b/w allowed energy bands.
2) The allowed energy bands are separated by forbidden energy bands.
3) With eq^n ④ it is possible to plot total energy of e^- Vs propagation vector (k). This lead to following conclusions:-
   a) The discontinuities occur at $k = \frac{n\pi}{a}$ in the Ek graph.
   b) The k values define boundaries of 1, 2 --- brillouin zone.
   For $k = \pi/a$ to $-\pi/a$ (I^{st} brillouin zone)
   The II^{nd} zone consist of two parts :- The first part (π/a to $2\pi/a$)
   The second part ($-\pi/a$ to $-2\pi/a$).
   c) Each portion of the curve may be called a band.