

UNIT-III

BAND THEORY OF SOLIDS AND SEMICONDUCTORS

Electron in a periodic potential:

If electron is present in periodic potential, the behaviour of the electron is explained by the following two theories:

→ 1) Bloch-Theory

→ 2) Kronig-penny theory

Kronig-penny-Model:

Kronig penny proposed a one dimensional model for the potential in the form of an array of square wells as shown in figure. It is assumed that the potential energy of e^+ 's is zero near to the nucleus of the +ve ion in the lattice and maximum when it is half way between the two atoms as shown in the following figure

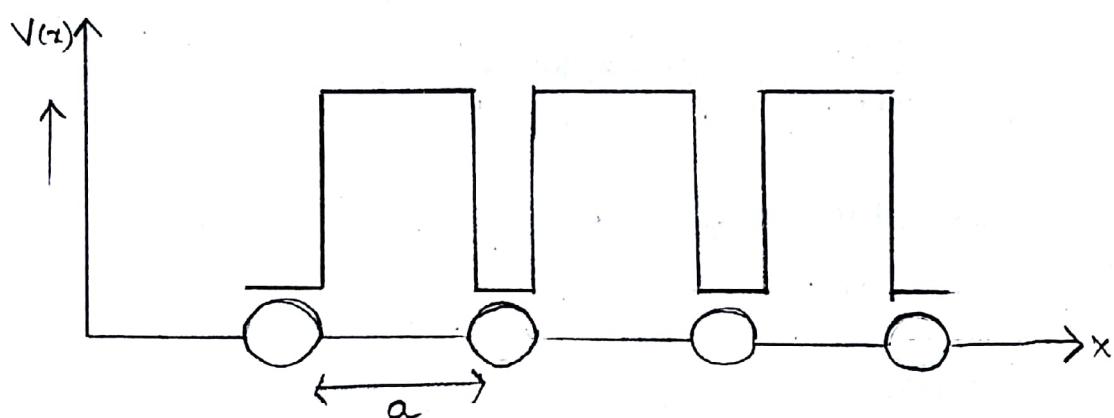


fig:- One dimensional periodic potential

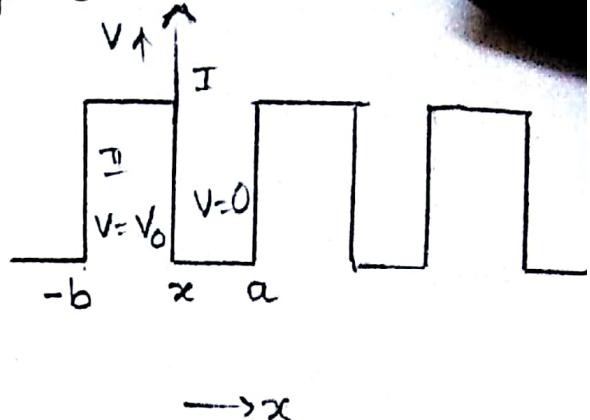
Schrodinger eqn for one-dimensional periodic potential field is denoted by $V(x)$ can be written as

2

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2} (\epsilon - V(x)) \psi = 0$$

(or)

$$\frac{d^2\psi}{dx^2} + \frac{2m}{h^2} (\epsilon - V(x)) \psi = 0$$

Case(i):In region I, $V=0$ above eqⁿ become

$$\frac{d^2\psi}{dx^2} + \frac{2m}{h^2} \epsilon \psi = 0$$

∴ [let $\frac{2m}{h^2} \epsilon = \alpha^2$]

$$\frac{d^2\psi}{dx^2} + \alpha^2 \psi = 0 \quad \text{--- (1)}$$

$$\alpha = \frac{1}{h} \sqrt{2m\epsilon}$$

Case(ii):In region II, $V=V_0$ Schrodinger's wave eqⁿ become

$$\frac{d^2\psi}{dx^2} + \frac{2m}{h^2} (\epsilon - V_0) \psi = 0$$

$$\text{let } \frac{2m}{h^2} (\epsilon - V_0) = -\beta^2$$

$$\frac{d^2\psi}{dx^2} - \beta^2 \psi = 0 \quad \text{--- (2)}$$

According to Bloch theorem,

$$\psi(x) = e^{ikx} U_k(x)$$

the possible solutions for eqn ① & ② are

(3)

$$\cos ka = \frac{P \sin \alpha}{\alpha} + \cos \alpha$$

where

P = Scattering power

$$P = \frac{4\pi^2 m a \sqrt{\nu_0 \omega}}{h^2}$$

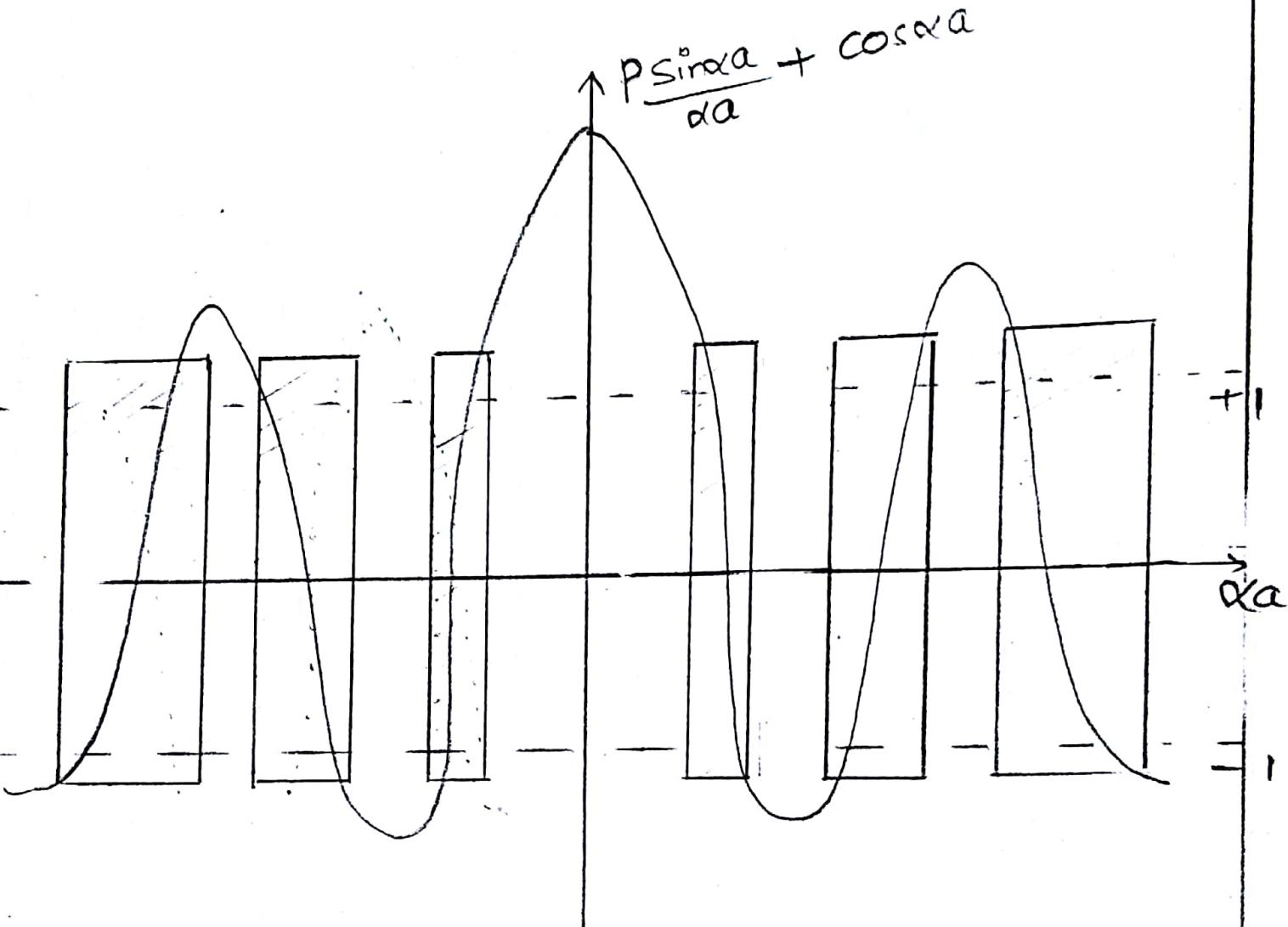
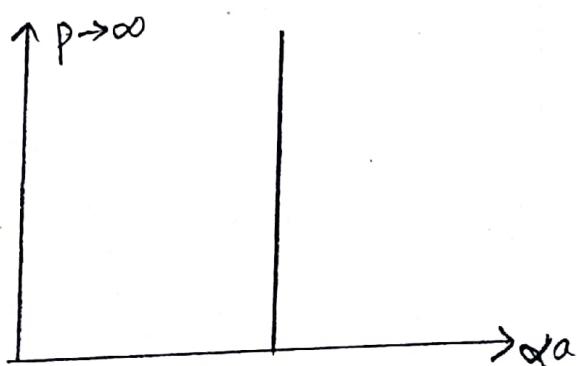


fig: plot of $\frac{P \sin \alpha}{\alpha} + \cos \alpha$ Vs α

(4)

conclusions:

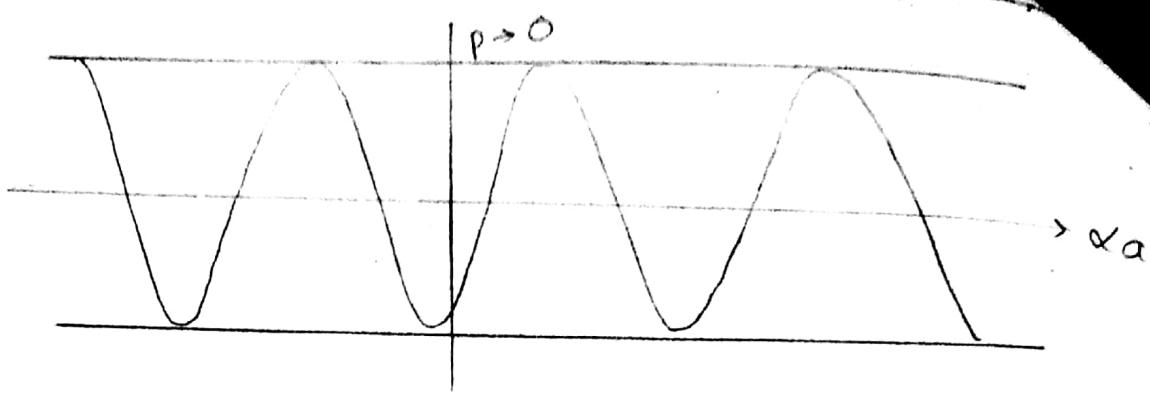
- The notion of electrons in a periodic potential is characterised by the allowed energy bands separated by forbidden energy gaps
- As per ' α' value increases the width of the allowed energy bands also increases and width of the forbidden energy gaps decreases.
- As the p -value increases the width of the allowed energy band decreases and the width of the forbidden energy gap is increases
- If $p \rightarrow \infty$, the allowed energy band reduces to one single line. The electron becomes completely bound.



→ if $p \rightarrow 0$

$$\cos k\alpha = \cos \alpha$$

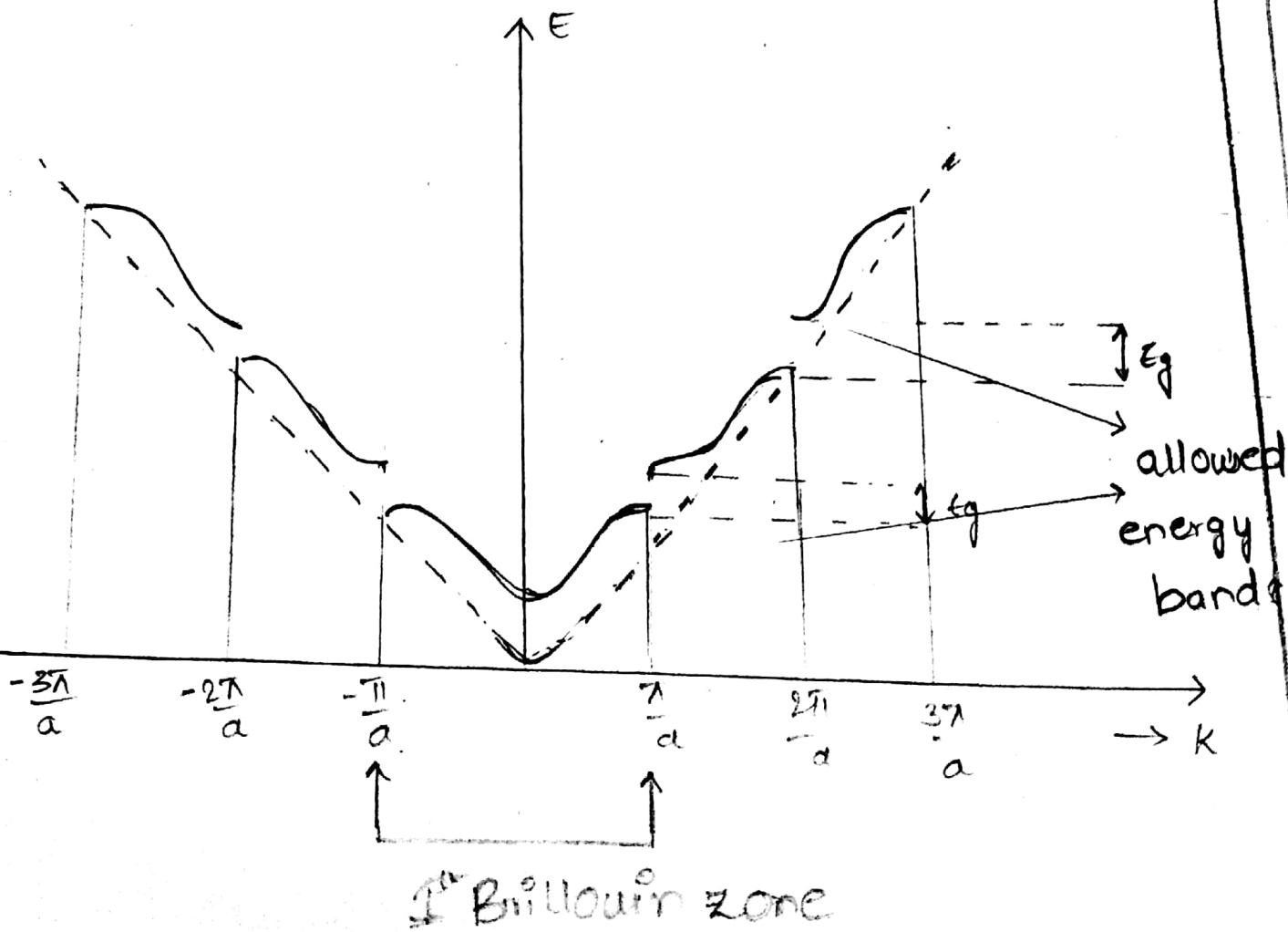
This indicates that the particle is completely free and no forbidden energy gap exist



Brillouin zones (E-K Curve)

The Brillouin zone is a representation of the allowable values of k of the e^- in one, two or three dimensions.

The energy spectrum of an e^- moving in the periodic potential is divided into allowed zones and forbidden zones as shown in following figure.



The dotted curve shows the free e^\ominus parabola

- The electron has allowed energy values in the region or zone extending from $k = -\frac{\pi}{a}$ to $\frac{\pi}{a}$. This zone is called "first Brillouin Zone".
- After forbidden gap, we get another allowed zone of energy values in the region extending from $k = -\frac{\pi}{a}$ to $-\frac{2\pi}{a}$ and $\frac{\pi}{a}$ to $\frac{2\pi}{a}$. This zone is called as "Second Brillouin Zone".
- Similarly other higher order Brillouin-zones can be defined.

Effective mass of electron:

The mass of the electron in the presence of electric field or magnetic field is called effective mass of electron. The mass of electron is indicated by m^* .

According to Newton's 2nd law

$$F = m^*a \quad \text{--- (1)}$$

The group velocity of free e^\ominus wave packet is

$$V_g = \frac{d\omega}{dk} = 2\pi \frac{dV}{dk} = \frac{2\pi dE}{h dk} \quad \therefore \begin{cases} E = h\omega \\ V = \frac{E}{h} \end{cases}$$

$$V_g = \frac{1}{h} \frac{dE}{dk}$$

$$\therefore \left[\frac{h}{2\pi} = \hbar \right] \quad \frac{2\pi}{h} = \hbar$$

Acceleration

$$a = \frac{dVg}{dt}$$

$$= \frac{d}{dt} \left[\frac{1}{\hbar} \frac{dE}{dk} \right]$$

$$a = \frac{1}{\hbar} \frac{d^2 E}{dk^2} \times \frac{dk}{dt} - \textcircled{2}$$

$$\therefore p = \hbar k$$

$$\frac{dp}{dt} = \hbar \frac{dk}{dt}$$

$$\frac{dk}{dt} = \frac{1}{\hbar} \frac{dp}{dt}$$

$$\therefore \frac{dp}{dt} = f$$

∴ above eqⁿ become

$$\frac{dk}{dt} = \frac{f}{\hbar}$$

Substitute this value in eqⁿ $\textcircled{2}$

$$a = \frac{1}{\hbar} \times \frac{d^2 E}{dk^2} \times \frac{f}{\hbar}$$

$$a = \frac{f}{\hbar^2} \frac{d^2 E}{dk^2} \quad \therefore \text{ (from eqⁿ } \textcircled{1})$$

$$\cancel{f} = \frac{m^* \cancel{f}}{\hbar^2} \frac{d^2 E}{dk^2}$$

$$m^* = \frac{h^2}{\left[\frac{d^2 E}{dk^2} \right]}$$

This eqⁿ indicates that the effective mass is depends on $d^2 E / dk^2$

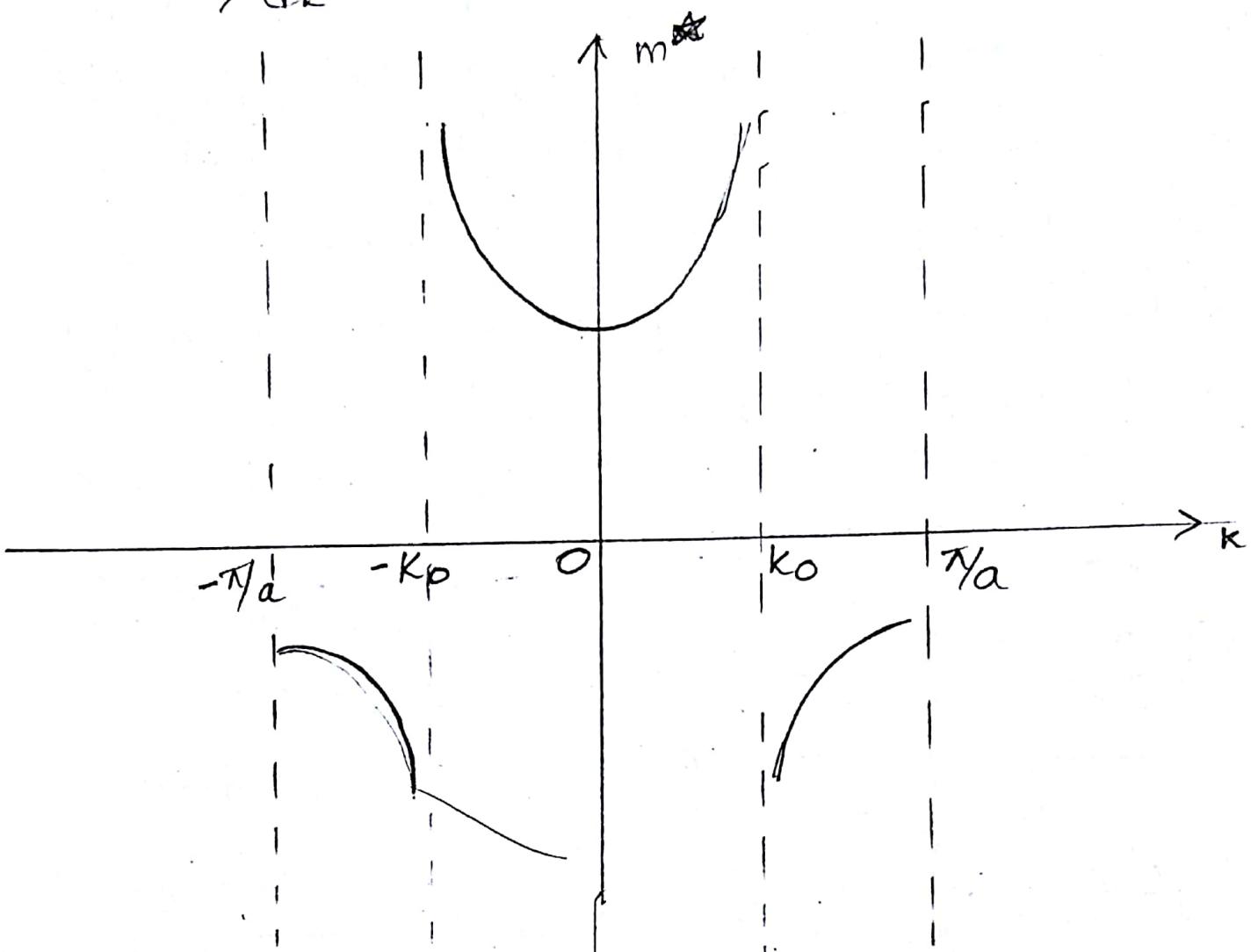
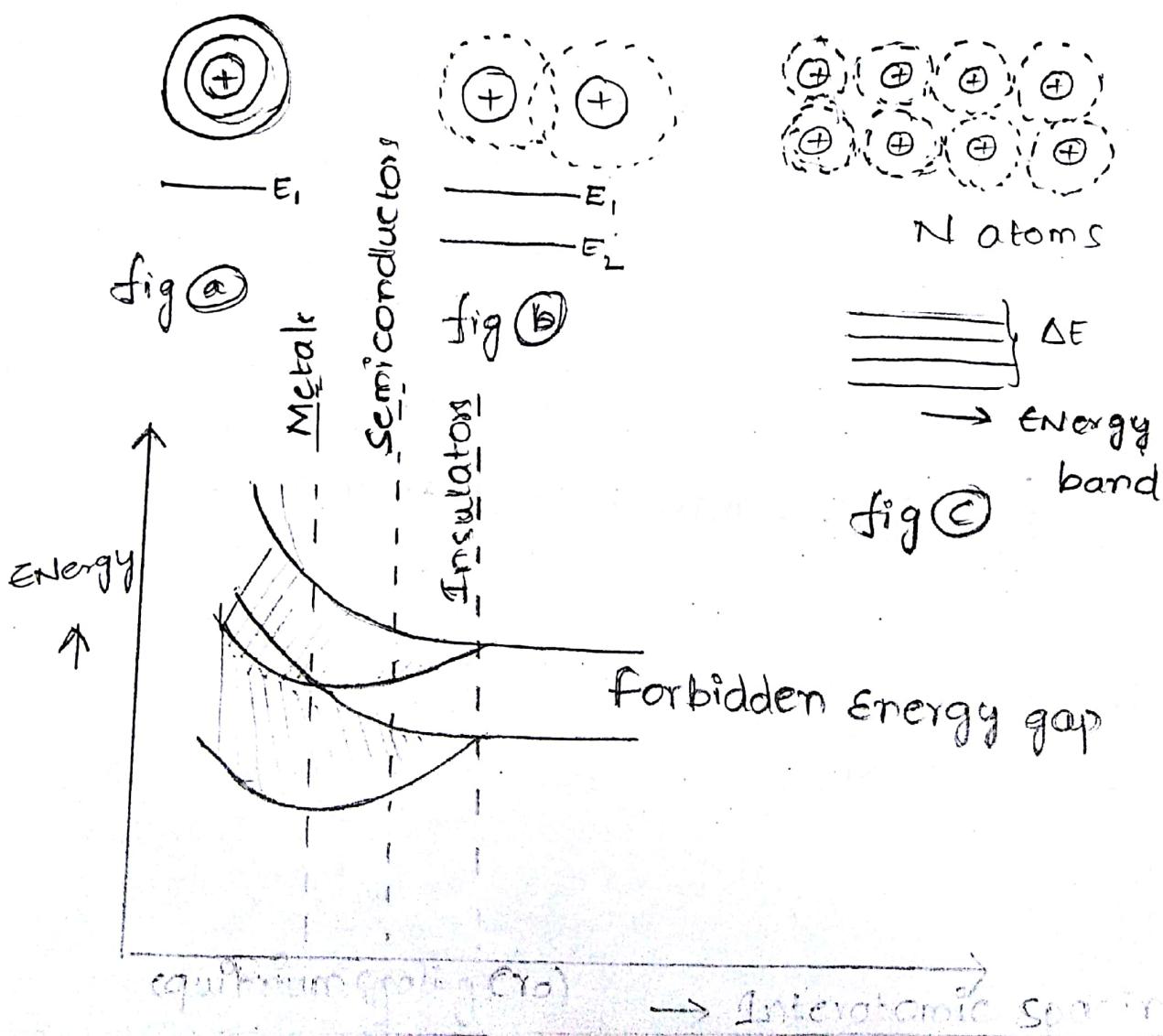


fig: Effective mass as function of 'k'

Energy Band formation in Solids:

In an isolated atom, the e^- s are tightly bound and have discrete, sharp energy levels (fig a). When two identical atoms are brought closer the outermost orbits of these atoms overlap and interact (fig b). If N atoms are present in the solid, each energy level of an atom splits into N levels of energy (fig c). The levels are so close together that they form an almost continuous band. The width of this band depends on the lapping of the bands is shown in figure ②.



- The e^- 's first occupy the lower energy bands. there are tightly bounded to the nucleus .there are not at all responsible for any properties of the solids
- The band corresponding to the outermost orbit (excited state) is called "conduction band"
- the next inner band (adjacent to conduction band) is called "valence band".
- The gap between these two bands is called as "forbidden energy gap".
- Normally valence band is occupied by valence e^- s
conduction band is empty at 0K temperature
- These two bands are very important in determining many properties of solids.

Classification of Solids: —

Based on the forbidden energy gap the solids are classified into three types:

- 1) Insulators
- 2) Semiconductors
- 3) Conductors

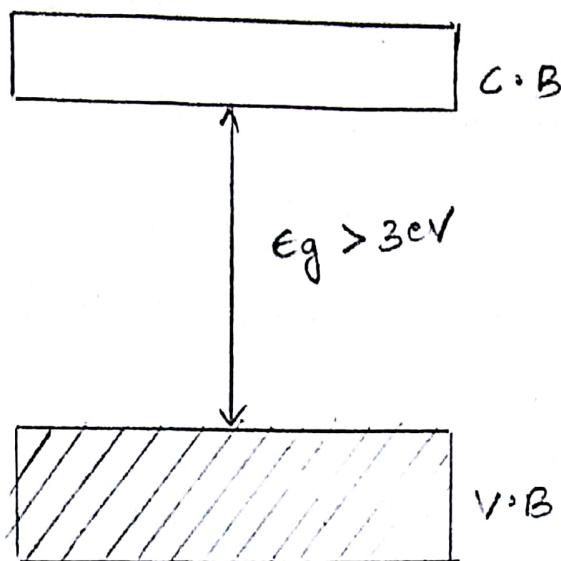
Insulators: —

The substance that does not pass the current is called

"insulators".

^{band}

The energy diagram of insulator is shown in figure:



Characteristics:

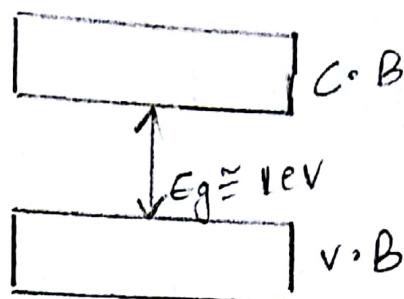
- In case of "insulators" forbidden energy gap is very large i.e. $E_g > 3\text{eV}$
- At room temperature, valence band is completely filled and conduction band is completely empty.
- Hence conductivity is zero
- Insulators have high resistance.
- These are independent of temperature.

Semiconductors: —

A substance with electrical properties intermediate b/w a good conductor and a good insulator is called as "Semiconductor".

- A semiconductor have relatively narrow forbidden

energy gap. $E_g \approx 1\text{eV}$



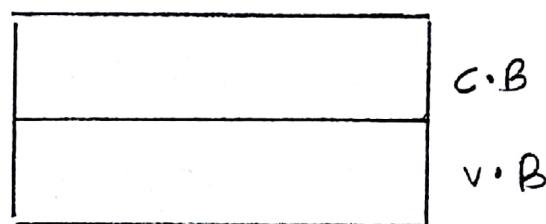
→ At room temperature, Both valency Band and conduction bands are partially filled with e^- 's.

→ Conductivity of semiconductors is directly proportional to temperature.

$$\sigma \propto T$$

→ Semiconductors resistivity values are less when compared to the insulators

Conductors:-



→ In case of conductors, forbidden energy gap does not exist i.e; $E_g = 0$

→ Valency band & Conduction band both are overlapped as shown in figure.

→ At room temperature large no. of free e^- 's are available

in conduction band.

- Hence, conductivity is large.
- Resistivity is low.
- In case of conductors, conductivity is inversely proportional to the temperature.

$$\text{i.e } \sigma \propto \frac{1}{T}$$

- Best example for conductors are Metals.

Density of states: —

The no. of energy states per unit volume is known as density of states.

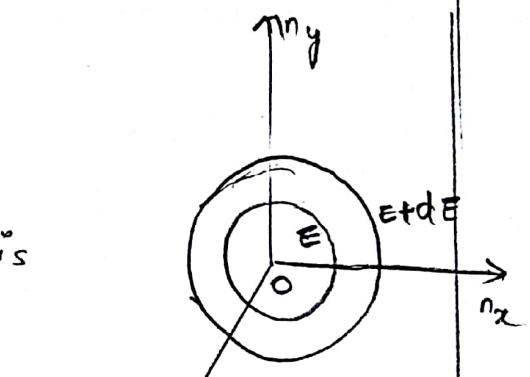
The available energy states within a small energy interval ϵ and $\epsilon + d\epsilon$ is

$$\begin{aligned} Z(\epsilon) d\epsilon &= \frac{1}{8} \times \frac{4}{3} \pi (n+dn)^3 - \frac{1}{8} \times \frac{4}{3} \pi n^3 \\ &= \frac{\pi}{8} [n^3 + 3n^2 dn] - \frac{\pi}{6} n^3 \end{aligned}$$

$$Z(\epsilon) d\epsilon = \frac{\pi}{2} n^2 dn \quad \text{--- (1)}$$

We know that,

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



$$\begin{aligned} (a+b)^3 &= a^3 + 3a^2b + 3ab^2 + b^3 \\ (n+dn)^3 &= n^3 + 3n^2dn + \end{aligned}$$

$$\underbrace{3dn^2n + dn^3}_{\text{neglected}}$$

higher order terms

$\therefore dn$ is very small]

$$n^2 = \left(\frac{8\pi L^2}{h^2} \right) E - ②$$

(15)

Differentiate eqⁿ ②

$$\partial n dn = \left(\frac{8\pi L^2}{h^2} \right) dE$$

$$dn = \frac{1}{2n} \left(\frac{8\pi L^2}{h^2} \right) dE$$

$$dn = \frac{1}{2} \times \frac{1}{\left(\frac{8\pi L^2}{h^2} \right)^{1/2} E^{1/2}} \times \left(\frac{8\pi L^2}{h^2} \right) dE \quad \therefore \text{from eq } ② \ n \\ n = \left(\frac{8\pi L^2}{h^2} \right)^{1/2} E^{1/2}$$

$$dn = \frac{1}{2} \left(\frac{8\pi L^2}{h^2} \right)^{1/2} \frac{dE}{E^{1/2}} \quad ③$$

Substitute eqⁿ ② & eqⁿ ③ in eqⁿ ①

$$Z(E) dE = \frac{\pi}{2} \times \left(\frac{8\pi L^2}{h^2} \right)^{1/2} E \times \frac{1}{2} \left(\frac{8\pi L^2}{h^2} \right)^{1/2} \frac{dE}{E^{1/2}}$$

$$Z(E) dE = \frac{\pi}{4} \left(\frac{8\pi L^2}{h^2} \right)^{3/2} E^{1/2} dE$$

According to pauli's exclusion principle, an e⁺'s can occupy in one state

$$Z(E) dE = \alpha \times \frac{\pi}{4} \left(\frac{8\pi L^2}{h^2} \right)^{3/2} E^{1/2} dE$$

$$= \frac{\pi}{2} \times \frac{L^3}{h^3} \cdot (2) \left(\frac{8\pi}{h^2} \right)^{3/2} E^{1/2} dE$$

$$\therefore Z(E) dE = \frac{\pi}{2} \times \frac{L^3}{h^3} \times 2^3 \times \left(\frac{8\pi}{h^2} \right)^{3/2} E^{1/2} dE$$

$$\therefore Z(E) dE = \frac{4\pi}{h^3} L^3 (2m)^{3/2} E^{1/2} dE$$

Density of the states per unit volume.

$$\boxed{\therefore Z(E) dE = \frac{4\pi}{h^3} (2m)^{3/2} E^{1/2} dE}$$

Fermi - Dirac Distribution:

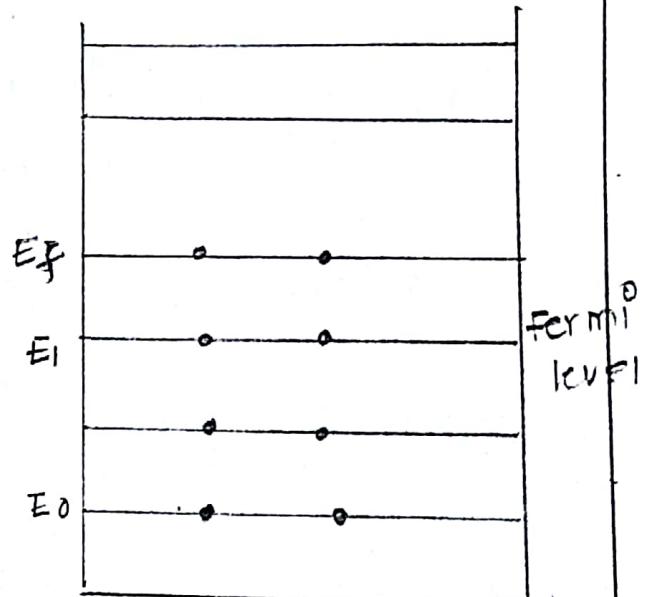
Fermi - Dirac Distribution describes the behaviour of free e^- gas, taking into account the quantum theory and pauli's exclusion principle.

According to quantum theory,

e^- 's have discrete energy

States and according to pauli's exclusion principle only 2 e^- 's

can occupy single state.



At $T=0K$

At absolute zero temperature ($T=0K$), all the lower energy states filled with the e^- 's and higher energy states are empty.

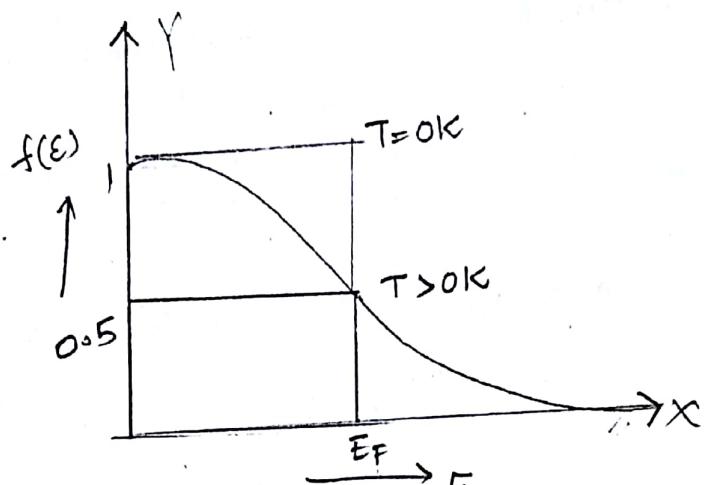
The highest occupied energy level at absolute zero temperature ($T=0K$) is known as Fermi energy level (E_F). It separates the occupied states from

the unoccupied states.

The probability of the occupation of energy level is

$$f(\epsilon) = \frac{1}{1 + \exp\left(\frac{\epsilon - E_F}{kT}\right)}$$

$f(\epsilon)$ = Fermi - Dirac distribution function.



case ①: At $T=0K$

a) if $E < E_F \Rightarrow f(\epsilon) = 1$

b) if $E > E_F \Rightarrow f(\epsilon) = 0$

Hence, at $T=0K$ temperature all the energy states below E_F are filled with e^\ominus s and above E_F are empty.

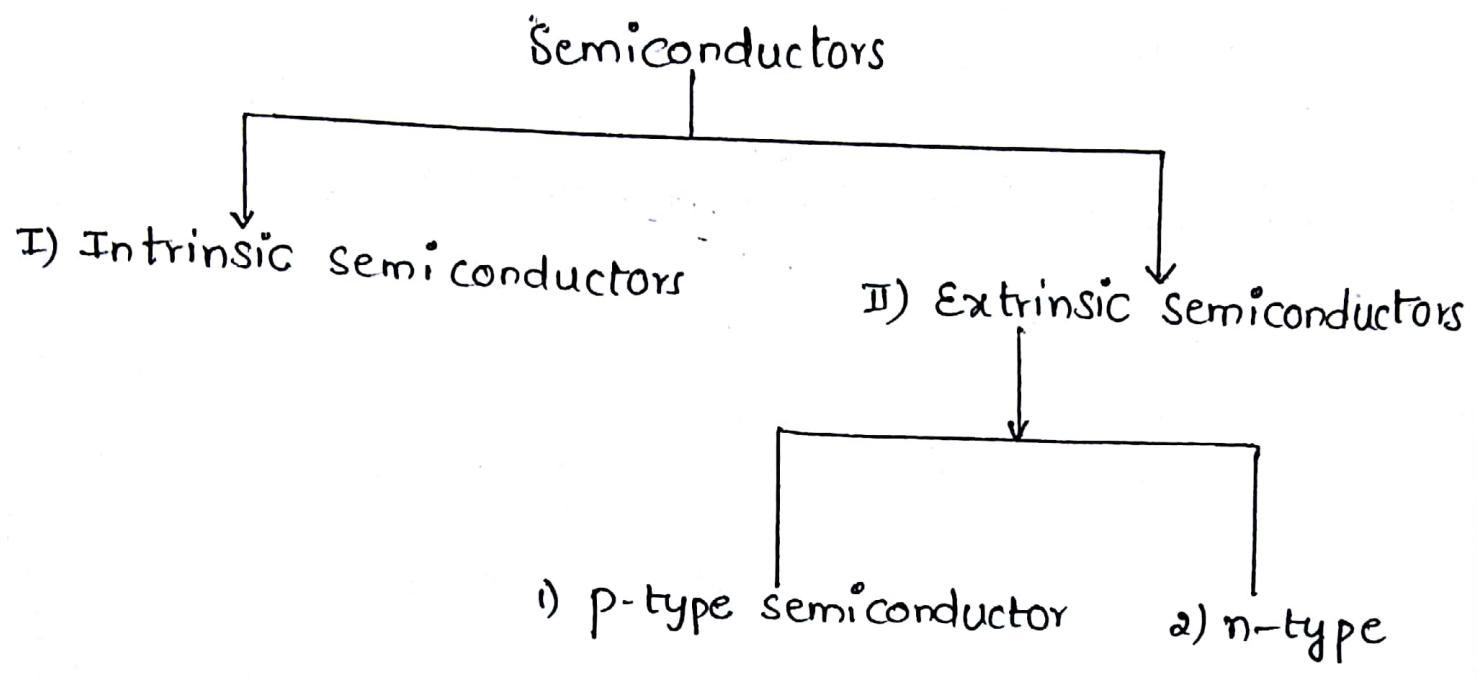
case ②: At $T > 0K$

if $E = E_F \Rightarrow f(\epsilon) = \frac{1}{2}$

At higher temperature, e^\ominus 's will jump from lower energy states to higher energy states

Semiconductors

The semiconductors have narrow forbidden energy gap and in these materials electrons and holes both are responsible for electrical conduction.



- Intrinsic Semiconductors are pure semiconductors
ex: Si and Ge
- Extrinsic Semiconductors are formed due to the addition of impurities (doping) to the pure semiconductors
Ex: GaAs, InP etc
- If a semiconductor is doped with III -group impurities (ex: Al, Ga, In) is known as p-type semiconductors
- If a semiconductor is doped with V -group

impurities (Ex: P, As, Sb) is known as n-type semi-conductors

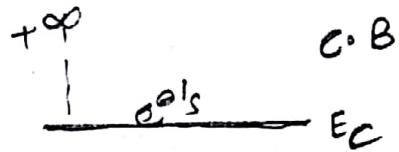
→ If & The conductivity of semiconductors is increased due to the addition of impurities.

Carrier concentration in Intrinsic Semiconductor:

Total number of charge carriers that is number of electrons in conduction band (n) and number of holes in valence band (p) per unit volume of the material is known as carrier concentration in Intrinsic semiconductors.

Case(i): concentration of electrons (n):

Let 'dn' is the number of electrons available between energy interval ϵ and $\epsilon + d\epsilon$ in the conduction band.



$$dn = Z(\epsilon)f(\epsilon)d\epsilon$$

Where

$Z(\epsilon)d\epsilon$ = density of electrons

$f(\epsilon)$ = electron occupancy probability

Total no. of electrons in conduction band is

$$dn = Z(\epsilon)f(\epsilon)d\epsilon$$

$$n = \int_{E_c}^{\infty} dn = \int_{E_c}^{\infty} Z(\epsilon) f(\epsilon) d\epsilon \quad \text{--- ①} \quad (\because \text{Integrating } n \text{ both sides})$$

where:

$$\therefore Z(\epsilon) d\epsilon = \frac{4\pi}{h^3} (2m_e^*)^{3/2} (E - E_c)^{1/2} d\epsilon \quad \text{--- ②}$$

$$f(\epsilon) = \frac{1}{1 + \exp\left(\frac{E - E_F}{kT}\right)} \quad [\because 1 \text{ is neglected}]$$

$$f(\epsilon) \cong \frac{1}{\exp\left(\frac{E - E_F}{kT}\right)} \cong \exp\left(-\frac{E - E_F}{kT}\right)$$

$$f(\epsilon) = \exp\left(\frac{E_F - E}{kT}\right) \quad \text{--- ③}$$

Substitute eqⁿ ② and ③ in eqⁿ ①

$$\therefore n = \int_{E_c}^{\infty} \frac{4\pi}{h^3} (2m_e^*)^{3/2} (E - E_c)^{1/2} \times \exp\left(\frac{E_F - E}{kT}\right) d\epsilon$$

$$n = \frac{4\pi}{h^3} (2m_e^*)^{3/2} \exp\left(\frac{E_F}{kT}\right) \int_{E_c}^{\infty} (E - E_c)^{1/2} \exp\left(-\frac{E}{kT}\right) d\epsilon \quad \text{--- ④}$$

$$\text{Let } E - E_c = x \Rightarrow E = x + E_c$$

$$dE = dx$$

$$\therefore \int_{E_c}^{\infty} (E - E_c)^{1/2} \exp\left(-\frac{E}{kT}\right) dE = \int_0^{\infty} x^{1/2} \exp\left(-\frac{(x + E_c)}{kT}\right) dx$$

$$\begin{aligned}
 &= \exp \frac{-E_C}{kT} \int_0^{\infty} x^{1/2} \exp \frac{-x}{kT} dx \\
 &= \exp \frac{-E_C}{kT} \times (kT)^{3/2} \frac{\pi^{1/2}}{2}
 \end{aligned}$$

Substitute this value in eqⁿ ④

$$n = \frac{2}{h^3} \frac{4\pi}{3} (2m_e^*)^{3/2} \exp \frac{E_F}{kT} \times \exp \frac{-E_C}{kT} \times (kT)^{3/2} \frac{\pi^{1/2}}{2}$$

$$n = 2 \left(\frac{2m_e^* \pi k T}{h^2} \right)^{3/2} \exp \left(\frac{E_F - E_C}{kT} \right)$$

This equation represents the no. of electrons per unit volume of the material.

Case (2) :- Concentration of holes (P) :-

Let 'dp' is the number of holes in the energy interval E and $dE+E$ in the valence band

$$\therefore dp = z(\epsilon) (1 - f(\epsilon)) dE$$

∴ Total no. of holes in the valence band is

$$dp = z(\epsilon) (1 - f(\epsilon)) dE$$

$$\int dp = \int z(\epsilon) (1 - f(\epsilon)) dE$$

$$\therefore P = \int_{-\infty}^{E_V} z(\epsilon) (1 - f(\epsilon)) dE \quad ①$$

where :

$$Z(E) dE = \frac{4\pi}{h^3} (2m_b^*)^{3/2} (E_V - E)^{1/2} dE \quad \text{--- } \textcircled{2}$$

$$\begin{aligned} 1 - f(E) &= 1 - \frac{1}{1 + \exp\left(\frac{E - E_F}{kT}\right)} \\ &= 1 - \left[1 + \exp\left(\frac{E - E_F}{kT}\right) \right]^{-1} \\ &= \frac{1}{1 + \exp\left(\frac{E - E_F}{kT}\right)} \end{aligned}$$

$$1 - f(E) = \exp\left(\frac{E - E_F}{kT}\right) \quad \text{--- } \textcircled{3}$$

Substitute eq $\textcircled{2}$ & $\textcircled{3}$ in eq $\textcircled{1}$

$$P = \int_{-\infty}^{E_V} \frac{4\pi}{h^3} (2m_b^*)^{3/2} (E_V - E)^{1/2} \times \exp\left(\frac{E - E_F}{kT}\right) dE$$

$$P = \frac{4\pi}{h^3} (2m_b^*)^{3/2} \exp\left(-\frac{E_F}{kT}\right) \int_{-\infty}^{E_V} (E_V - E)^{1/2} \exp\left(\frac{E}{kT}\right) dE \quad \text{--- } \textcircled{4}$$

$$\text{let } E_V - E = x \Rightarrow E = E_V - x$$

$$dE = -dx$$

$$\begin{aligned} \therefore \int_{-\infty}^{E_V} (E_V - E)^{1/2} \exp\left(\frac{E}{kT}\right) dE &= \int_0^\infty x^{1/2} \exp\left(\frac{(E_V - x)}{kT}\right) (-dx) \\ &= \int_0^\infty x^{1/2} \exp\left(\frac{(E_V - x)}{kT}\right) dx \\ &= \exp\left(\frac{E_V}{kT}\right) \int_0^\infty x^{1/2} \exp\left(\frac{(-x)}{kT}\right) dx \end{aligned}$$

$$= \exp \frac{E_V}{kT} \times (kT)^{3/2} \frac{\pi^{1/2}}{2}$$

\therefore Eqⁿ ④ becomes

$$p = \frac{2}{h^3} \frac{4\pi}{(2m_b^*)^{3/2}} \exp \frac{-E_F}{kT} \times \exp \frac{E_V}{kT} \times (kT)^{3/2} \frac{\pi^{1/2}}{2}$$

$$p = 2 \left(\frac{2m_b^* \pi kT}{h^2} \right)^{3/2} \exp \left(\frac{E_V - E_F}{kT} \right)$$

\therefore This equation represents the concentration of holes per unit volume.

→ In case of intrinsic semiconductors concentration of holes and electrons are equal.

$$n = p;$$

\therefore Carrier concentration in case of intrinsic semiconductors :-

$$n_i^2 = np = 2 \left(\frac{2m_e^* \pi kT}{h^2} \right)^{3/2} \exp \left(\frac{E_F - E_C}{kT} \right) \cdot 2 \left(\frac{2m_b^* \pi kT}{h^2} \right)^{3/2} \exp \left(\frac{E_V - E_F}{kT} \right)$$

$$= 4 \left(\frac{2\pi kT}{h^2} \right)^3 (m_e^* m_b^*)^{3/2} \exp \left(\frac{E_V - E_C}{kT} \right)$$

$\therefore E_C - E_V = E_g$ = forbidden energy gap

$$\therefore n_i^2 = 4 \left(\frac{2\pi kT}{h^2} \right)^3 (m_e^* m_b^*)^{3/2} \exp \left(\frac{-E_g}{kT} \right)$$

$$\therefore n_i = \alpha \left(\frac{2\pi kT}{h^2} \right)^{3/2} (m_e^* m_b^*)^{3/4} \exp \left(-\frac{E_F}{2kT} \right)$$

\therefore This equation represents the carrier concentration in case of intrinsic semiconductors.

Fermi level in intrinsic semiconductors :-

In case of intrinsic semiconductors

$$\therefore n = p$$

$$\cancel{\alpha} \left(\frac{2m_e^* \pi kT}{h^2} \right)^{3/2} \exp \left(\frac{E_F - E_C}{kT} \right) = \cancel{\alpha} \left(\frac{2m_b^* \pi kT}{h^2} \right)^{3/2} \exp \left(\frac{E_V - E_F}{kT} \right)$$

If $m_e^* = m_b^*$, above eqn becomes

$$\exp \left(\frac{E_F - E_C}{kT} \right) = \exp \left(\frac{E_V - E_F}{kT} \right)$$

$$\exp \left(\frac{E_F + E_C}{kT} \right) = \exp \left(\frac{E_V + E_F}{kT} \right)$$

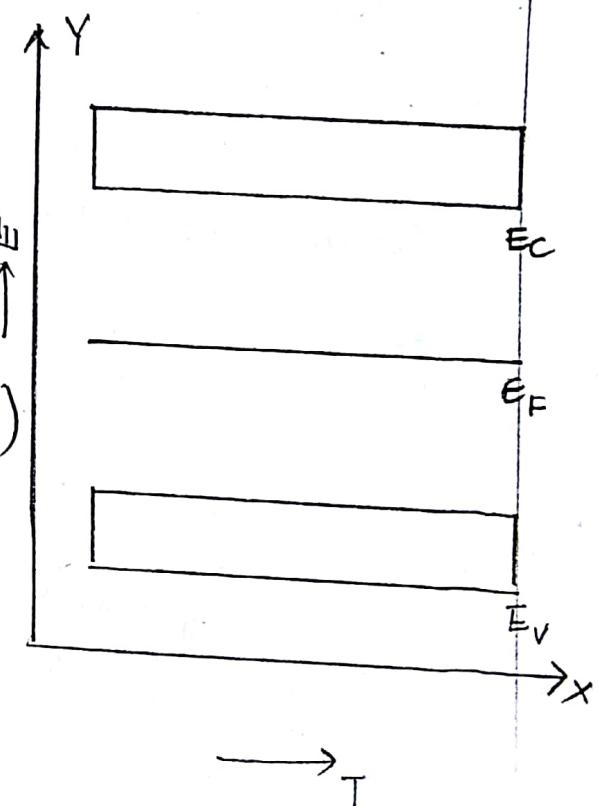
Apply log on both sides

$$\log \exp \left(\frac{E_F - E_C}{kT} \right) = -\log \exp \left(\frac{E_V - E_F}{kT} \right)$$

$$\frac{E_F - E_C}{kT} = \frac{E_V - E_F}{kT}$$

$$2E_F = E_V + E_C$$

$$E_F = \frac{E_V + E_C}{2}$$



\therefore The Fermi energy level for intrinsic semiconductor lies at the middle of the energy gap.

Electrical conductivity of semiconductors. In case of semiconductors, the electrical conductivity (σ) is

$$\sigma = (n_e \mu_e + p_h \mu_h)$$

In case of intrinsic semiconductors,

$$n = p = n_i$$

$$\therefore \sigma = n_i e \mu_e + n_i e \mu_h$$

$$\sigma = n_i e (\mu_e + \mu_h)$$

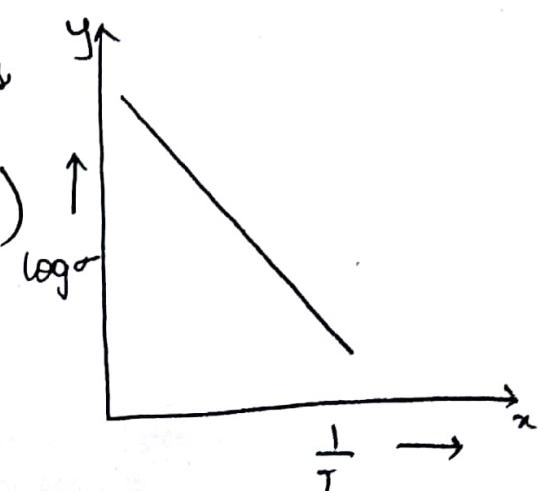
$$\sigma = e(\mu_e + \mu_h) \times 2 \left[\frac{2\pi kT}{h^2} \right]^{3/2} (m_e^* m_h^*)^{3/4} \exp\left(-\frac{E_g}{2kT}\right)$$

$$\boxed{\sigma = A \cdot \exp\left(-\frac{E_g}{2kT}\right)}$$

apply log on both sides

$$\log \sigma = \log (A \cdot \exp\left(-\frac{E_g}{2kT}\right))$$

$$\log \sigma = \log A - \frac{E_g}{2kT}$$



In case of semiconductors the conductivity (σ) is directly proportional to the temperature (T)