

→ Free electron theory:

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- in this theory free ele. in metal are treated like gas molecules and maxwell boltzmann statistics is applied.

$$f(E) = \frac{1}{A \cdot e^{E/k_B T}}$$

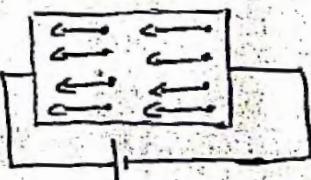
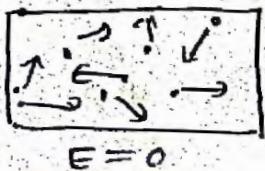
where $f(E)$ - probability that a particle will have energy E

A = normalization const.

e = probability for occupying a given state decreases with time

* Main Assumptions of classical free electron theory:

- ① A solid metal has a nucleus (positive) with revolving electrons (negative). These electrons move freely like molecules in gas.
- ② The free electrons move in uniform potential field due to ions fixed in lattice.
- ③ In absence of ele. field ($E=0$) electrons move in random direction and collide with each other, during the collisions there is NO loss of energy because its elastic collisions.
- ④ When ele field is applied, free electrons are accelerated in a direction opposite to applied field.
- ⑤ Electrons are assumed to be gas, they obey laws of classical theory of gas.
- ⑥ free electrons obey maxwell-Boltzmann statistics



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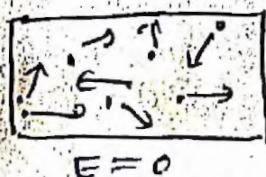
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It will turn parallel to E.E. direction

(ii) drift velocity

The average velocity acquired by electrons due to the applied electric field.

Make a note

(a) mobility (μ_E)

It is the drift velocity acquired by electron per unit electric field

$$\mu_E = \frac{V_d}{E} = m^2/eB^2$$

(b) relaxation time

It is the time taken by an electron to reach equilibrium position from the disturbed position in presence of electric field.

$$\tau = \frac{1}{\mu_E} (5.6)$$

(c) mean collision time (τ_c)

The average time between two successive collision

$$\tau_c = \frac{1}{\sigma v_{th}}$$

(d) mean free path (λ_m)

The average distance travelled by electron before collision.

(e) drift current density

When electric field is applied the electron experiences a force (e.E) which acts along the direction of electric field.

$$F = eE$$

But

$$F = ma$$

or $a = F/m$

$$a = eE/m$$

$$eE/m$$

$\rightarrow (i)$

Suppose that the electron only collide with positive ion core. So electrons are truly random in direction (because collision destroy its tendency to drift). The next collision would change the ele velocity by v_d .

$$\therefore v_d = \sigma T \quad (\tau \text{ mean free path})$$

$$\therefore v_d = \frac{eE}{m} \tau$$

$$\text{current density } J = n \cdot e v_d$$

$$= n \cdot e \left(e \frac{E \cdot \tau}{m} \right)$$

$$= \left(\frac{n e^2 \tau}{m} \right) E$$

$$\text{But } J = \sigma \cdot E$$

$$\therefore \sigma E = \left(\frac{n e^2 \tau}{m} \right) E$$

$$\boxed{\sigma = \frac{n e^2 \tau}{m}}$$

#. Thermal conductivity (k)

It is defined as rate of heat flow across a unit area of conductor per unit temp. gradient

$$k = \frac{Q}{A \left(\frac{dT}{dx} \right)} \quad \text{unit } (W/m \cdot K)$$

$\textcircled{1}$ = rate of heat flow $= \left(\frac{dQ}{dt} \right)$

A = cross sectional area of conductor

$\frac{dT}{dx}$ = temp gradient

$$k = \frac{nn \cdot k_B \gamma}{2} \quad \text{where } n = \text{density of ele.}$$

v = thermal velocity $= \sqrt{\frac{3k_B T}{m}}$

k_B = Boltzmann const

γ = mean free path

Wiedemann - Frond law

This law suggest that the ratio of thermal conductivity to electrical conductivity is directly proportional to absolute temp.

$$\frac{k}{\sigma} \propto T$$

$L = \text{Lorentz number}$.

$$\therefore \frac{k}{\sigma} = LT$$

$$1.5 \times 10^{-8} \text{ W} \cdot \Omega^{-1} \text{ K}^{-2} = 2.44 \times 10^{-8} \text{ W} \cdot \Omega^{-1} \text{ K}^{-2}$$

we know that

$$\sigma = \frac{\pi e^2 \cdot n v}{3 k_B T}$$

$$\text{and } k = \frac{n v k_B}{2}$$

$$\therefore \frac{k}{\sigma} = \frac{3}{2} \left(\frac{k_B}{e} \right)^2 T \rightarrow (1)$$

$$\frac{k}{\sigma} = LT \quad (\because L = \frac{3}{2} \left(\frac{1.38 \times 10^{-23}}{1.6 \times 10^{-19}} \right)^2)$$

$$L = 1.12 \times 10^{-8} \text{ W} \cdot \Omega^{-1} \text{ K}^{-2}$$

Advantages of free electron theory

① It verify ohm's law

② It explains thermal conductivity of metal

③ It explains electrical conductivity of metal

④ It help to deduce Wiedemann - Frond law.

⑤ It explains optical properties of metals.

→ Disadvantages of free electron theory.

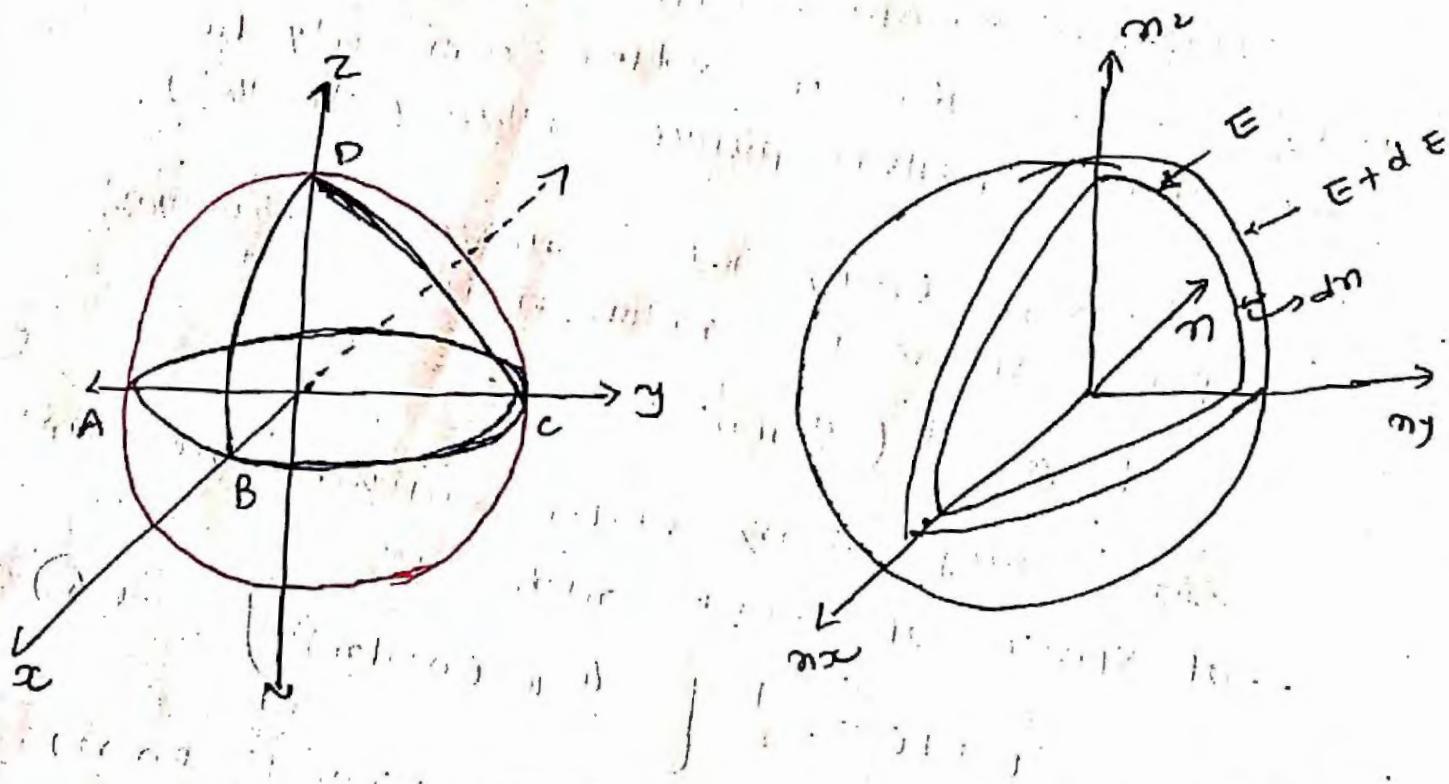
- ① The theoretical values of specific heat of metal and obtained by this theory do not match.
- ② Electrical conductivity of Insulator can't be explain by this theory.
- ③ The theoretical value of paramagnetic Susceptibility is greater than the experimental value.
- ④ Ferromagnetism can't be explained by this theory.
- ⑤ At lower temp K and σ change in different ways. So K/GT is not const. but according to this theory it is const. for all temp.
- ⑥ Photo electric effect, compton effect and black body radiation can't be explained by this theory.

→ Density of states

it is given by number of available electron states per unit volume per unit energy range at a certain energy level E

Density of states $Z(E)dE$

number of energy states $N(E)dE$



Density of states

$$Z(E)dE = \frac{\text{No. of energy state } N(E)dE}{\text{unit volume of the sample}} \quad (1)$$

→ assume that here sphere is divided into number of shells.

each shell is known, as (m_x^2, m_y^2, m_z^2)
and will have their energy

→ E is the energy of the point which is same for all point represented on sphere.

The radius of sphere is with energy E is

$$m^2 = m_x^2 + m_y^2 + m_z^2 \rightarrow (2)$$

Num

energy states within a sphere

of r

$n = \text{volume of the sphere}$

$$= \frac{4}{3} \pi n^3$$

→ eqn ② gives full volume of the sphere.

quantum numbers can only have positive

integer values. The n -values can only be defined in ~~positive~~ positive octant (like th).

number of energy state within one octant of the sphere in radius n is

$$E_n = \frac{1}{8} \left(\frac{4}{3} \pi n^3 \right) \quad \rightarrow ③$$

Same way energy states within one octant of sphere of radius $n+dn$ is

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

The number of energy states having energy values between E and $(E+dE)$ is given by

$$N(E) dE = (E+dE) - (E)$$

$$N(E) dE = (E+dE)^3 - E^3$$

from eqn ③, ④

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

$$= \frac{1}{8} \left(\frac{4\pi}{3} \right) ((n+dn)^3 - n^3)$$

Expanding $(n+dn)^3$ by $(a+b)^3 = a^3 + b^3 + 3ab^2 + 3a^2b$
we get $(n+dn)^3 = n^3 + dn^3 + 3n^2dn + 3ndn^2$

$$\therefore N(E) dE = \frac{\pi}{6} (n^2 + dn^3 + 3n^2dn + 3ndn^2 - n^3) \rightarrow ⑤$$

$$= \frac{\pi}{6} (dn^3 + 3n^2dn + 3ndn^2)$$

Neglecting here higher powers of dn like d^2n , d^3n , etc.

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

$$N(E) dE = \frac{\pi}{2} n^2 dn \rightarrow (6)$$

$$\therefore N(E) dE = \frac{\pi}{2} n \cdot (ndn) \rightarrow (7)$$

Suppose a cubic metal with cube edge

$$E = \frac{n_x^2 h^2}{8 m a^2}$$

$$\therefore E = \frac{h^2}{8 m L^2} (n_x^2 + n_y^2 + n_z^2)$$

$$\text{therefore, } E = \frac{h^2 n^2}{8 m L^2}$$

Now from above eqn

$$n^2 = \frac{8 m a^2}{h^2} \cdot \frac{dE}{dE} \rightarrow (8)$$

$$n = \left(\frac{8 m a^2 E}{h^2} \right)^{1/2} \rightarrow (9)$$

taking differentiation \uparrow

$$2ndn = \frac{8 m a^2}{h^2} dE \rightarrow (10)$$

$$ndn = \frac{8 m a^2}{2 h^2} \cdot dE \rightarrow (11)$$

Putting the values of n and ndn from the eqn (9) (11) into eqn (7)

$$N(E) dE = \frac{\pi}{2} n \cdot (ndn)$$

$$N(E) dE = \frac{\pi}{4} \left(\frac{8 m a^2 \cdot E}{h^2} \right)^{1/2} \cdot \left(\frac{8 m a^2}{2 h^2} \right) dE$$

$$(3) \quad N(E) dE = \frac{\pi}{4} \left(\frac{8 m a^2}{h^2} \right)^{3/2} \cdot E^{1/2} \cdot dE$$

a^3 = volume of metal per atom

from pauli's exclusion law

max. 2 ele. with opposite spin can stay in each state

$$\text{So, } N(E) dE = 2 \times \frac{\pi}{2} \left(\frac{8m}{h^2} \right)^{3/2} E^{1/2} dE$$

(if $a^3 = 1$) (12)

eqn (12) is effective number of energy levels in volume a^3 . with energy between E and $E + dE$:

(the number of available energy states per unit volume $a^3 = 1$)

density of states

$$Z(E) dE = \frac{N(E) dE}{V}$$

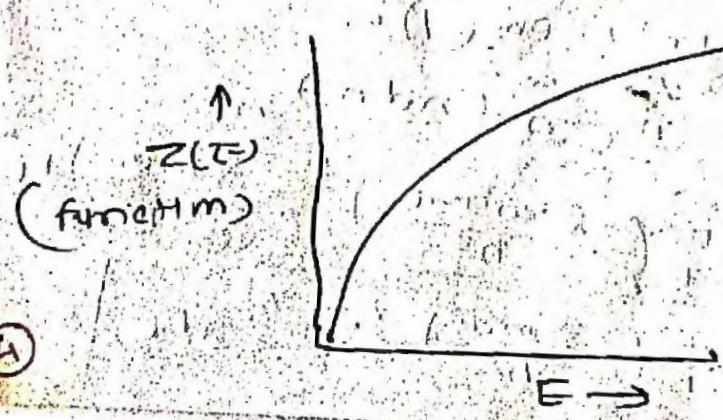
putting value of $N(E) dE$ and $V = a^3 = 1$

$$Z(E) dE = \frac{\pi}{2} \left(\frac{8m}{h^2} \right)^{3/2} E^{1/2} dE \rightarrow (13)$$

to eqn for density of energy states

from above eqn

$$Z(E) \propto E^{1/2}$$



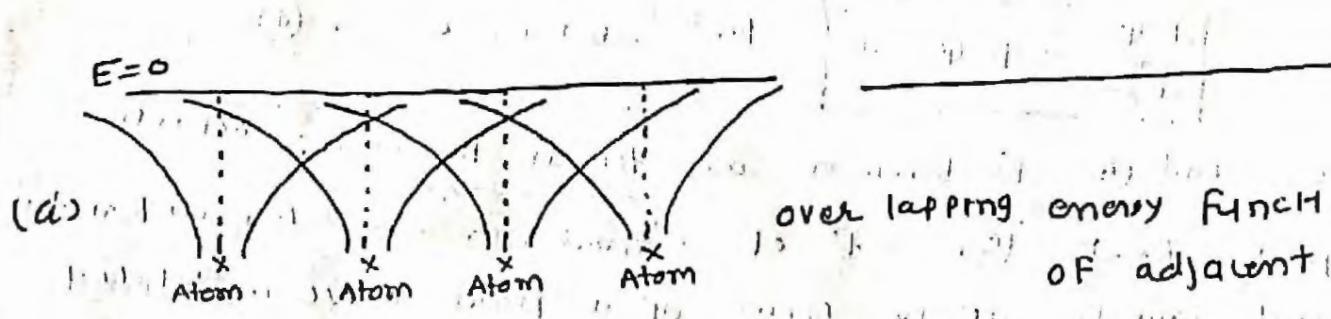
Kroning - Penny Model

In order to find the allowed energy of ele in solid we have to apply Schrodinger eqn. in lattice.

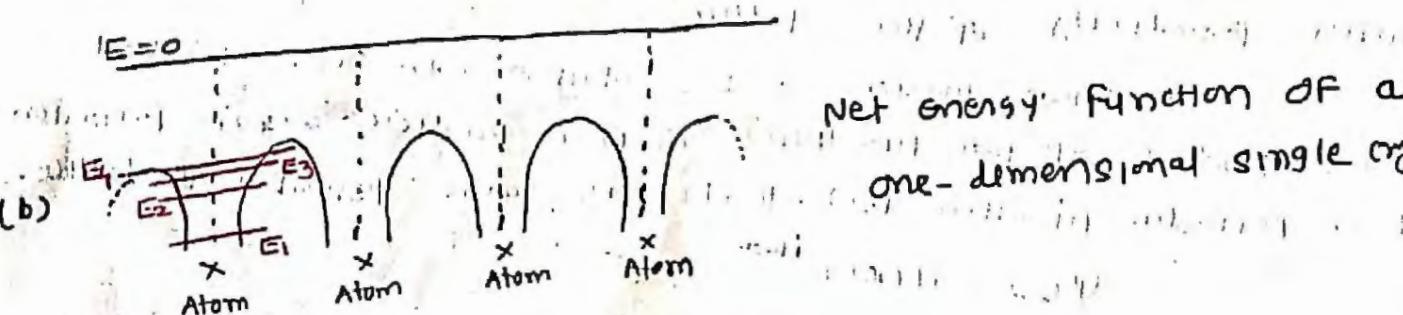
It is assumed that the potential energy of electron is zero near the nucleus of positive ion and maximum when it is halfway between adjacent nuclei.

Kroning and Penny suggested a simplified model consisting of an infinite row of rectangular potential wells separated by barrier of width b as shown in figure.

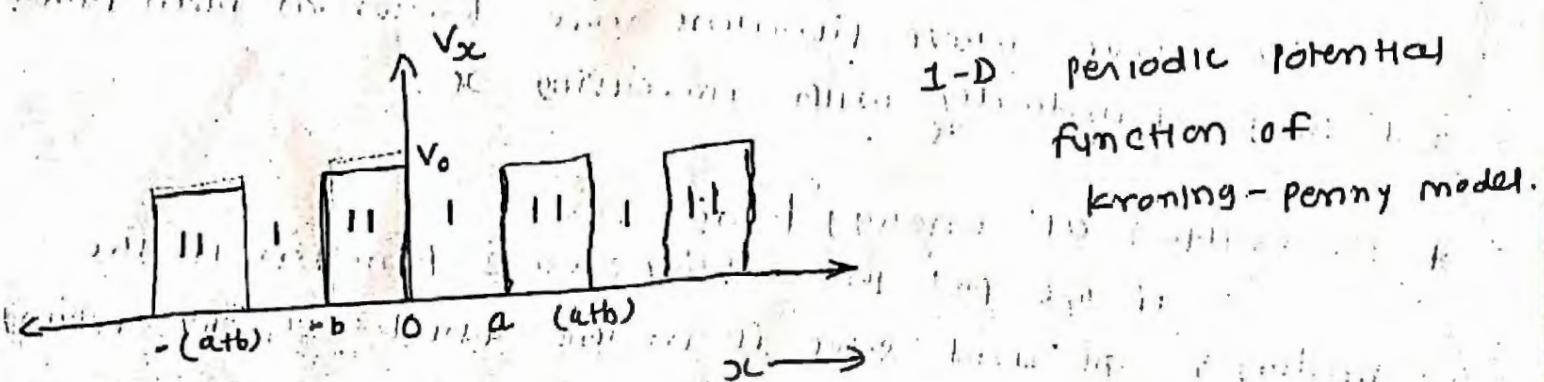
Defⁿ: - The one-dimensional representation of periodic lattice is known as Kroning - Penny model.



overlapping energy functions
of adjacent atoms.



Net energy function of a
one-dimensional single crystal



1-D periodic potential
function of
Kroning - Penny model.

Each well has a width b and depth V_0 . The period of the potential is $(a+b)$. In regions where $b < x < a$ the potential energy is assumed to be zero, and in $-b < x < 0$ the potential energy is V_0 . Through this model Schrodinger eqn. can be solved in terms of elementary functions.

The Schrodinger eqn for two regions can be given by

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2} E \psi = 0 \quad \text{for } 0 < x < a \quad \rightarrow (1)$$

$$\text{and} \quad \frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2} (E - V_0) \psi = 0 \quad \text{for } -b < x < 0 \quad \rightarrow (2)$$

taking

$$\alpha^2 = \frac{8\pi^2 m}{h^2} E \quad \text{and} \quad \beta^2 = \frac{8\pi^2 m}{h^2} (V_0 - E)$$

eqn (1) and (2) will be,

$$\boxed{\frac{d^2\psi}{dx^2} + \alpha^2 \psi = 0} \quad \text{for } 0 < x < a \quad \rightarrow (3)$$

$$\boxed{\frac{d^2\psi}{dx^2} - \beta^2 \psi = 0} \quad \text{for } -b < x < 0 \quad \rightarrow (4)$$

eqn (3) and (4) is known as Bloch theorem, which

suggests that the solⁿ of Schrodinger eqn for a periodic potential will be of the form of a plane wave modulated with periodicity of the lattice.

It means the solution can be expressed as the product of two functions, a free particle wave function and a periodic function $u(x)$ that has same period as the lattice.

$$\psi(x) = u(x) e^{ikx} \rightarrow (5)$$

$$u(x) = u(x+a) \rightarrow (6)$$

The above wave functions are known as Bloch functions and change periodically with increasing x .

* Formation of energy bands:

If we put the above wave function in the Schrodinger eqn and solve it in the usual way, by applying periodic boundary conditions,

we get,

$$\frac{m a V_0 b}{\hbar^2} \frac{\sin \alpha \cdot a}{a} + \cos \alpha \cdot a = \cos k a \rightarrow (7)$$

where

$$\alpha = \frac{\sqrt{2mE}}{\hbar}$$

$\sin(\frac{ka}{\lambda})$ give the soln of schrodinger eqn.

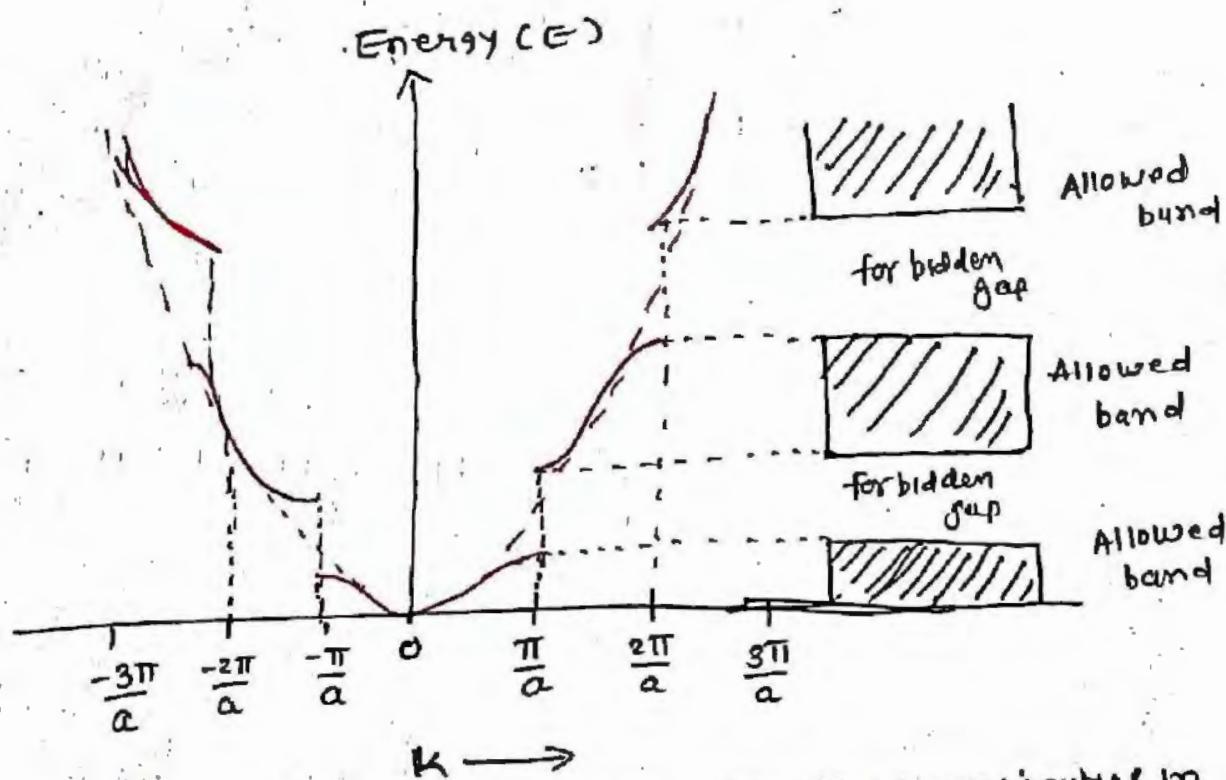
here trigonometric function is involved, that's why only certain values of k are possible.

The LHS of $\sin(\frac{ka}{\lambda})$ is cos function and can take values betw -1 and +1.

Therefore LHS is restricted between those two limits. So we can say that only certain values of k are allowed. That means energy E is restricted to lie within certain ranges.

The above mentioned concept can be best understood by drawing a graph of energy (E) as a function of wave number (k).

The parabolic relation betw E and k obtained in case of free electron is interrupted at a certain value of k shown by broken curve.



The Above figure shows discontinuity discontinuities in E . This discontinuity occurs at $ka = \pm n\pi$
 $k = \pm \frac{\pi}{a}, \pm \frac{2\pi}{a}, \pm \frac{3\pi}{a} \dots$

So the origin of allowed energy bands and forbidden gap is clear from above figure.

→ E-k diagram.

E-k diagram is a diagram which shows the relationship between energy (E) and momentum (k). It explains bandgap property.

Energy (E) of a free electron is

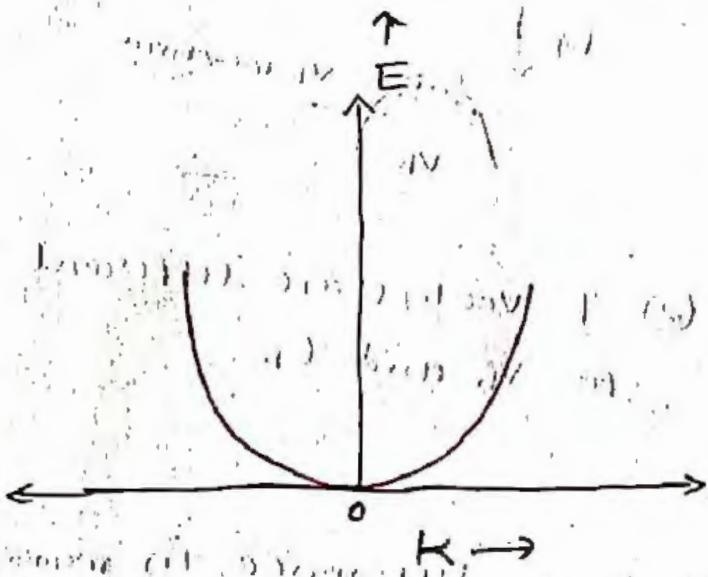
$$E = \frac{h^2 \cdot k^2}{2m} \rightarrow ①$$

where $k = \text{momentum}$

$m = \text{mass of free electron}$

$h = \text{Planck's constant}$

The graph of $E \rightarrow k$ is given below,



Eqn ① can be used

replacing m by m^*

$$E = \frac{h^2 \cdot k^2}{2m^*}$$

- Effective mass (m^*):

There is different mass of an electron in the vacuum and inside crystal because varying (periodic) potential inside crystal. So ele. mass altered due to varying potential. The altered mass is called effective mass (m^*) of electron.

- In a semiconductor an electron in conduction band is similar to free ele. which can move in the crystal.

- But because of periodic potential eqn ① is not valid.

If (i) If we replace free electron mass in the eqn. by an effective mass m^*

(ii)

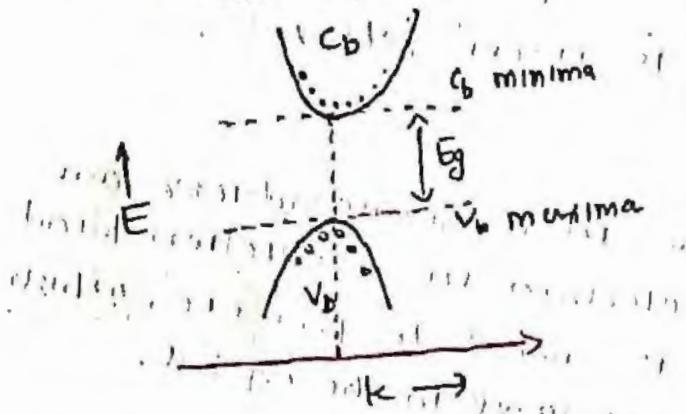
→ ②

→ Direct and indirect band gaps.

Band gap is it can be defined as the minimum energy difference between top of valence band and bottom of conduction band.

* Direct band gap.

D) In direct band gap, the max. energy level of V_b Aligns with min. energy level of C_b wrt momentum.



(2) k -vectors are same for V_b and C_b .

(The max of V_b and min of C_b is characterised by k -vector)

(3) When an electron from C_b recombines with hole from V_b the energy and momentum both conserved.

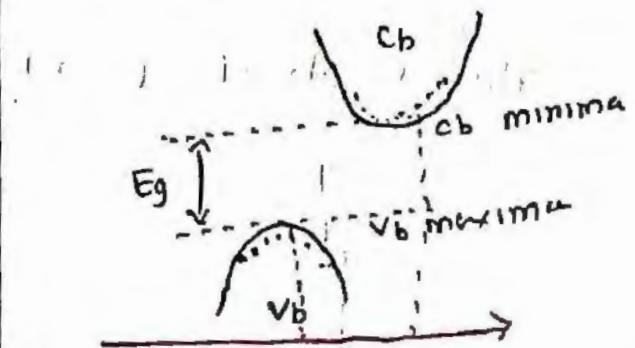
(4) The energy difference bet V_b and C_b released in form of photon.

(5) k -vectors of ele. and hole are same. so we can say momentum is conserved.

(6) Energy conserved by emitting photons. as they are radiative transitions.

* Indirect band gap

① In indirect band gap the max energy level of V_b do not Aligns with min energy level of C_b wrt momentum.



② k -vectors are different for V_b and C_b .

③ here difference in momentum the recombination is only possible after momenta align.

④ due to crystal imperfection, electron in C_b loses energy and momentum at sometime.

⑤ ele. Pass through intermediate state and transfer its momentum.

⑥ here energy emitted as heat so No Radiation.

- | | |
|--|---|
| ⑦ The probability of radiation recombination is very high. | ⑦ The probability of non-recombination is negligible. |
| ⑧ Efficiency factor is high. | ⑧ Efficiency factor is low. |
| ⑨ They are preferred for making optical devices like LED. | ⑨ They can't be used to make optical devices. |
| ⑩ Ex - Cr ₂ S, P | ⑩ Ex - Si, Ge. |

→ Types of Electronic material: ~~met~~ conductor, ~~semi~~ conductor, and insulator.

→ Types of electronic materials: Metal, Insulator, conductor, semi-conductor, superconductor.

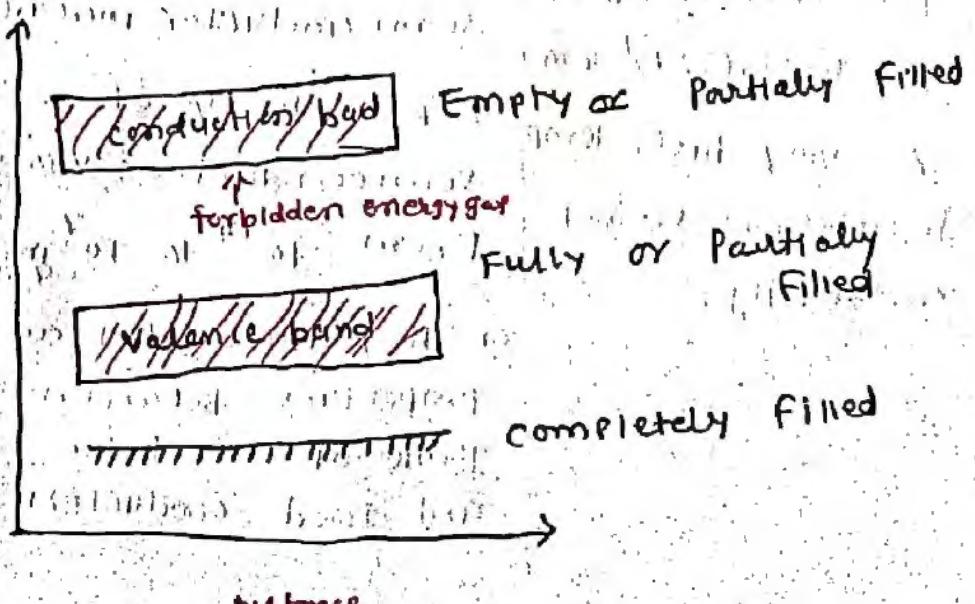
few basic defⁿ

① Energy band diagram: it is a graphical representation of energy level associated with top energy band and the next lower energy band in a solid.

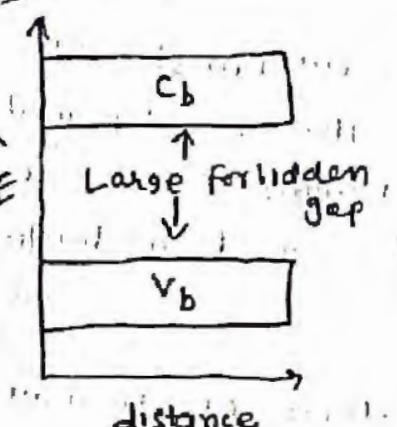
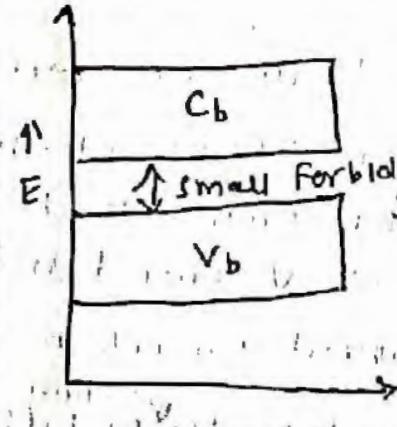
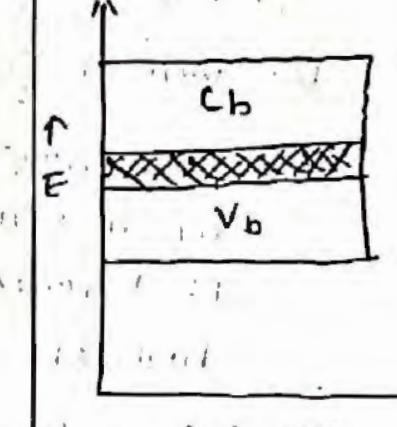
② Valence band: The electrons in outermost shell are known as valence electrons. The band formed by a series of energy levels containing valence ele. is known as Valence band. (or a band having highest occupied energy.)

③ Conduction band: In certain metals valence electrons are tightly attached to nucleus, even at ordinary temp. Some valence ele. left valence band. This ele. are free electrons. These are responsible for conduction of current in a conductor, so they are also called as conduction electrons. The band contains occupied by these free electrons is known as conduction band. (or a band having lowest unfilled energy band.)

④ Forbidden energy gap: The energy separation between conduction and valence band, is known as forbidden energy gap.



On the basis of forbidden gap, insulator, semiconductor and conductor are described as below.

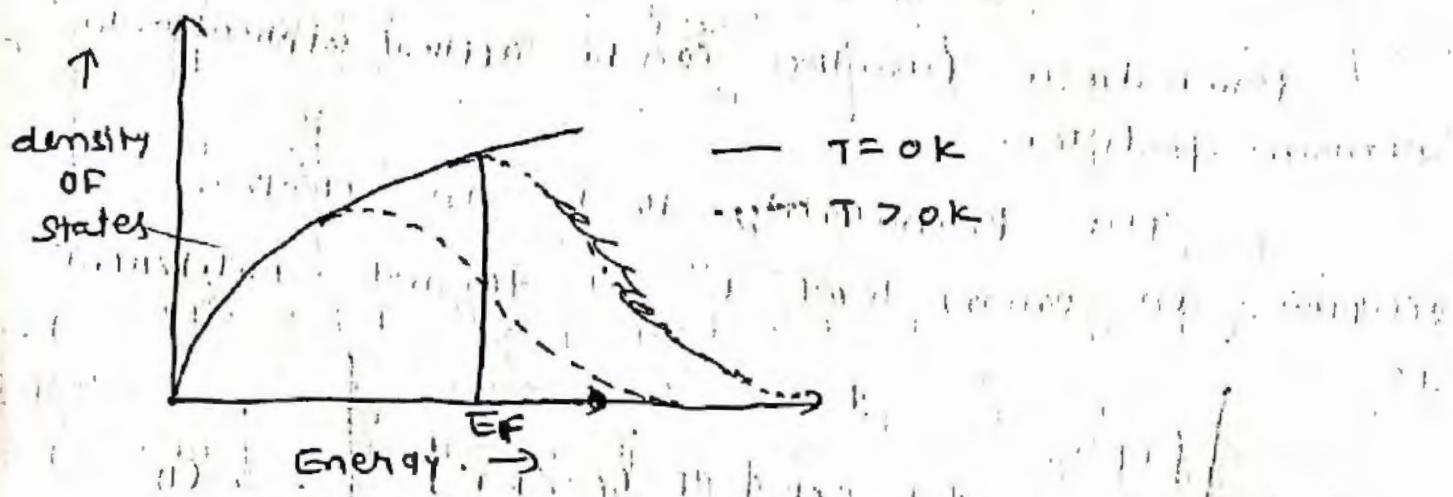
Insulators	Semiconductors	conductors.
 <ul style="list-style-type: none"> → forbidden gap is very wide → Even in presence of ele. Field No ele moves from V_b to C_b. → They have full Valence band → They have empty C_b. → forbidden gap is very large (~ 5 to 10 eV) → The resistivity is very high ($\sim 10^7 \Omega \cdot m$) → At very high temp they show small conductivity. 	 <ul style="list-style-type: none"> → forbidden gap is very small. → in presence of small ele field ele. moves from V_b to C_b. → They have empty C_b and filled V_b. → Small forbidden gap for $Ge = 0.91$ eV, $Si = 1.1$ eV → When temp. increases the conductivity of semi conductor increases. → Resistivity of Semiconductors varies from 10^{-14} to $10^7 \Omega \cdot m$ → They have electrical properties between those of insulator and good conductors. 	 <ul style="list-style-type: none"> → No forbidden gap. → due to overlapping of V_b, C_b a slight potential difference will produce current flow. → plenty of free ele are available for ele. electrical conduction. → There is no forbidden energy gap. Valence and conduction band overlap each other. (No energy gap between two bands) → There is no structure to establish holes. → Total current in conductors is mainly due to flow of electrons.

→ Density of states and occupation probability:

As we know that the density of state in the interval E and $E+dE$ is given by

$$z(E)dE = \frac{\pi^2}{2} \left(\frac{8m}{\hbar^2}\right)^{3/2} E^{1/2} dE$$

and graph of density of states \rightarrow Energy is given by



This graph is parabolic. The area under curve represents the number of electrons in the metal.

Number of available energy levels at lower ends of parabola is considerably less than at higher energies.

The plot of $z(E) \rightarrow E$ at $T=0$ drops abruptly to zero at $E=E_F$. The electrons can't crowd in lower energy state because they obey Pauli's exclusion principle. They start with lowest energy level and go on occupying higher and higher energy states until all of them accommodate. The highest energy occupied is E_F .

The plot $z(E) \rightarrow E$ at much higher temp. is also shown in figure. The area under curve shows the number of electrons in metal, the area under two curves must be equal. It is seen that at very high temperature the distribution curve changes only very slightly.

→ occupation probability

we need to know how electrons are distributed among the various energy level at given temp. we can't apply Maxwell-Boltzmann distribution to elec. because ① they obey exclusion ~~principle~~ principle
② They are indistinguishable particle.

Fermi-Dirac function can be applied applicable to quantum particles.

The probability that an electron occupies an energy level E at thermal equilibrium is

$$f(E) = \frac{1}{1 + \exp[(E - E_f)/kT]} \rightarrow ①$$

where $f(E)$ = Fermi function

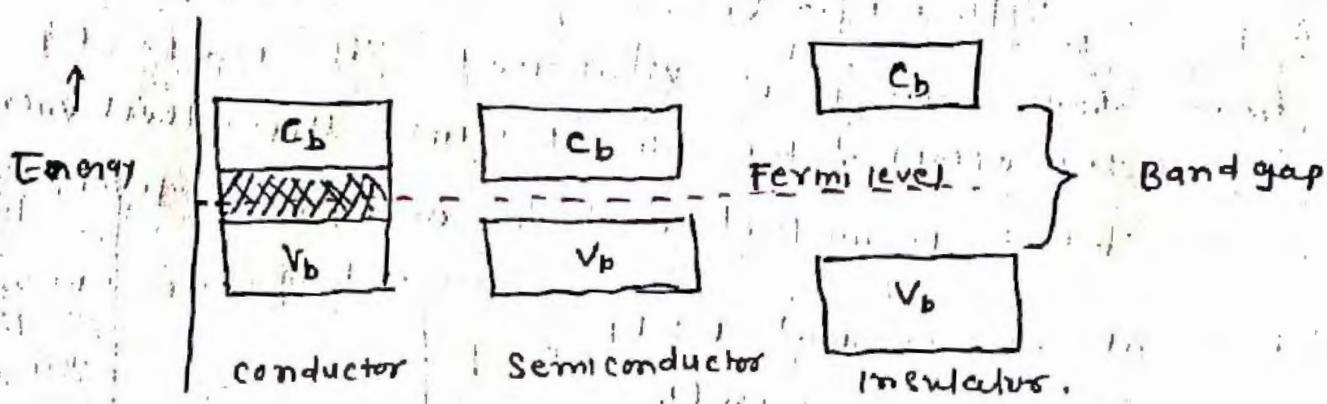
equation ① is known as Fermi-Dirac distribution function. It is the probability of electron to occupy in energy state E , increases with temp.

In general, E_f may or may not correspond to energy level, but it provide reference with which other energy can be compared.

2. Occupation number: The number of electrons in a particular energy level depends upon the temperature and pressure. This will be related to probability of electrons occupying a particular energy level. Let us consider a system consisting of N number of particles. The probability of finding n electrons in a particular energy level is given by

→ Fermi Level, Effective mass, Phonons :-

- ① Fermi Level :- The fermi level is highest energy level which an ele. can occupy at $T=0K$ if it is between V_b and C_b .



- In a conductor Fermi level is inside the conduction band. In semiconductor it'll between C_b and V_b . In insulator very large energy gap between C_b and V_b . so electron can't cross it.
- The fermi function is known as Fermi-Dirac probability function, which is

$$f(E) = \frac{1}{1 + e^{\frac{(E - E_F)}{kT}}} \rightarrow ①$$

where

k = boltzmann const. eV/k

T = Absolute temp

E_F = Fermi level for crystal

E = Energy level for allowed state

In above eqn ① $f(E)$ lies between 0 to 1. so there are three probability

$f(E)=1$ 100% probability to occupy the energy level by ele.

$f(E)=0$ No probability to occupy the energy level by ele. so & empty

$f(E)=0.5$ So, 50% probability to finding ele. in energy state.

we need to see 4 cases

case-1 probability occupation at $T=0\text{ K}$ and $E \leq E_f$

Putting it in eqn (1) $f(E) = \frac{1}{1+e^{\frac{E-E_f}{kT}}} = \frac{1}{1+e^0} = \frac{1}{2} = 1$

$\therefore [f(E)=1] \rightarrow \textcircled{2}$

from above can it is clear that at $T=0\text{ K}$ - E_f
- is fully occupied by ele. leaving upper level vacant
- So below fermi level electron occupation in levels

case-2 at $T=0$ and $E > E_f$

Putting this in eqn (1)

$$f(E) = \frac{1}{1+e^{\frac{E-E_f}{kT}}} = \frac{1}{1+e^{\infty}} = \frac{1}{\infty} = 0$$

$\therefore [f(E)=0] \rightarrow \textcircled{3}$

from above can we say that at $T=0\text{ K}$ the energy level below Fermi level E_f is unoccupied.

case-3 at $T=0$ and $E=E_f$

Putting this in eqn (1)

$$f(E) = \frac{1}{1+e^0} = \frac{1}{1+1} = \frac{1}{2} = 0.5$$

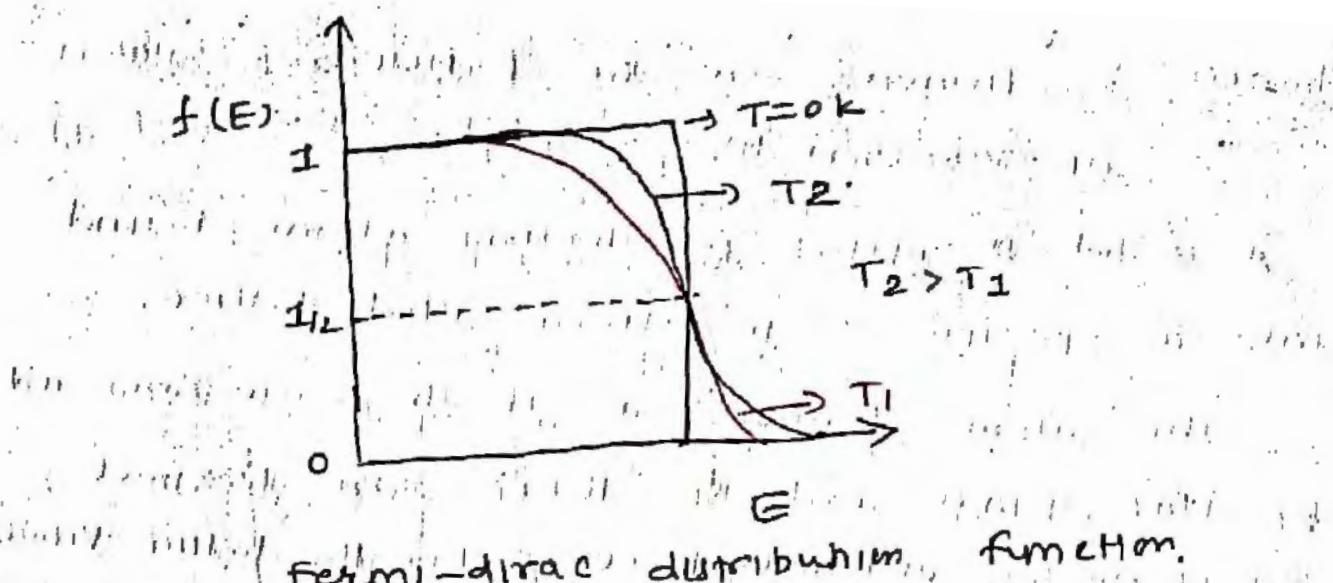
$\therefore [f(E)=0.5] \rightarrow \textcircled{4}$

from above can we say that at $T=0\text{ K}$ there is a 50% probability for the electrons to occupy the Fermi energy level.

case-4 at very high Temp i.e $T > 0\text{ K}$ i.e

$$KT \gg E_f \quad \text{or} \quad E_f \ll kT$$

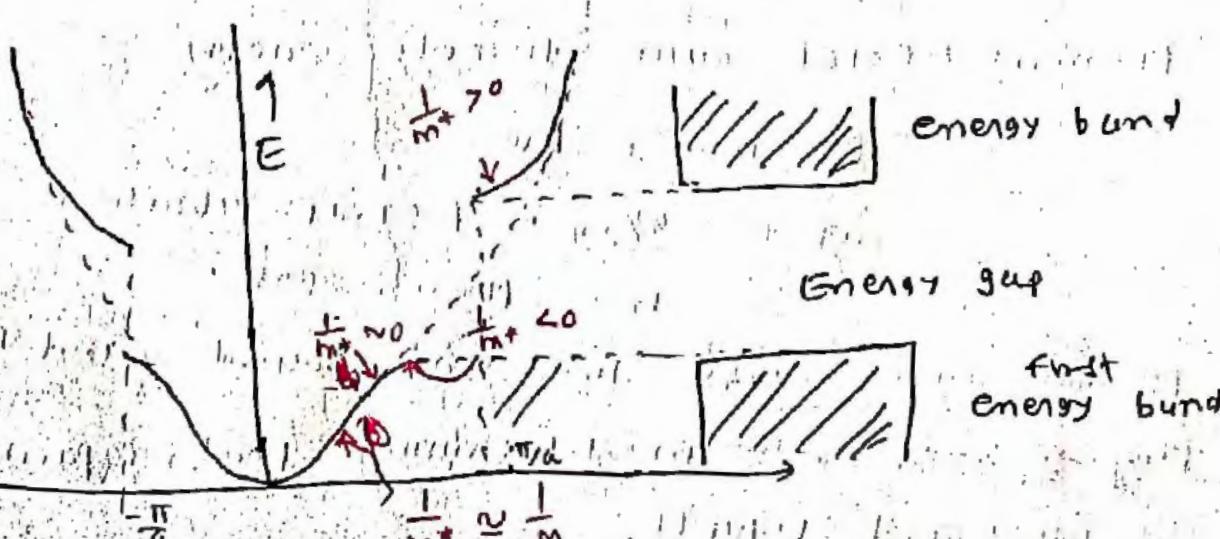
At high temp ele are excited above Fermi level which are vacant so most ele are in cb.



Fermi-Dirac distribution function.

② Effective mass: Generally we consider that effective mass of ele. in solid is similar to mass of free electron. but few experiments have prove that mass of free electron is higher than mass of electron in solid. This experimentally determined electron mass is known as m^* (effective mass). So m^* is inversely proportional to curvature of an allowed energy band.

$$\text{Effective mass} m^* = \frac{\hbar^2}{d^2E/dx^2}$$



- Near the bottom of band $m = m^*$
- Near top of allowed band $dE/dx < 0$ so m^* is negative
- At middle $dE/dx = 0$ so $m^* = \frac{1}{0} = \infty$

③ Phonons : Phonons are the particle representation of vibration in a crystal.

- A Solid ~~is~~ crystal is having atoms bound into a specific 3-D pattern called lattice.
 - The atoms behave as if they are connected by tiny springs and, so their own thermal energy ~~or~~ or outside force makes the lattice vibrate.
 - This generates mechanical wave that carry heat and sound through the material.
 - A packet of these wave can travel through the crystal with definite energy and momentum.
- These waves are treated as a ~~part~~ particle called "Phonons".

(Also) we can say phonons can be defined as a discrete unit of vibrational mechanical energy.

- Phonons can be created or destroyed in collisions.
- Phonons exist with discrete energy
$$E = h\omega = h\nu$$
 where $\omega/2\pi = \text{freq. of vibration}$
 $h = \text{Planck's const.}$
- Phonon can carry heat and sound and they play a major role in determining heat capacities of solid and liquids.