This was developed by Drude and Lorentz.

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

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

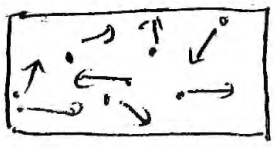
where $f[E]$ = probability that a particle will have energy E

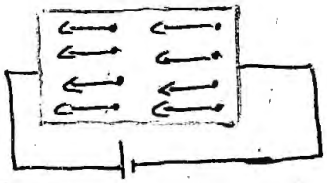
A = Normalization const.

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 electron move in uniform potential field due to ions fixed in lattice.
3. in absence of ele. field ($E=0$) electron 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 obeys laws of classical theory of gas.
6. free electrons obey maxwell-Boltzmann statistics





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* Basic terms involved in free electron theory

① Drift velocity (v_d) –

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

$$v_d = \frac{l}{T} \quad m/sec$$

② mobility (μ) –

it is drift velocity acquired by electron per unit electrical field.

$$\mu = \frac{v_d}{E} \quad m^2/V.sec$$

③ Relaxation time –

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

$$\tau = \frac{l}{v_d} \quad (sec)$$

④ mean collision time (τ_c)

The average time between two successive collision

$$\tau_c = \frac{\lambda}{v_d} \quad (sec)$$

⑤ mean free path (λ)

The average distance travelled by electron between two successive collisions.

* Electrical conductivity (σ) :

when ele. field is applied the electron experience a force e.E. due to which they are accelerated

$$F = e \cdot E$$

But

$$F = ma$$

$$\therefore \quad ma = e \cdot E \qquad \therefore \quad a = \frac{e \cdot E}{m} \rightarrow (1)$$

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Suppose that the electron only collide with positive ion core. So electrons are truly random in 3 direction (because collision destroy its tendency to drift).

The next collision would change the ele. velocity by V_d.

$\therefore V_d = a \cdot \tau$ (τ mean free path)

$\therefore V_d = \frac{e \cdot E}{m} \cdot \tau$

current density $J = n \cdot e V_d$

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

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

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

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

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

A = cross sectional area of conductor

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

$$k = \frac{n V \cdot k_B \lambda}{2}$$

where n = density of ele.

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

k_B = Boltzmann const

λ = mean free path.

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* Wiedemann- Franz law

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

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

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

L = Lorentz number.
$= 2.44 \times 10^{-8}\ W\text{-}\Omega/K^2$

we know that

$$\sigma = \frac{ne^2 \cdot \lambda v}{3 K_B T}$$

and $$k = \frac{n v K_B \lambda}{2}$$

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

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

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

→ 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 Wiedmann- Franz Law.
(5) It explains optical properties of metals.

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Disadvantages of free electron theory.

① The theoritical values of specific heat of metal and obtained by this theory is do not match.

② Electrical conductivity of insulator can't be explain by this theory.

③ The theoritical 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 $K/\sigma T$ 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.

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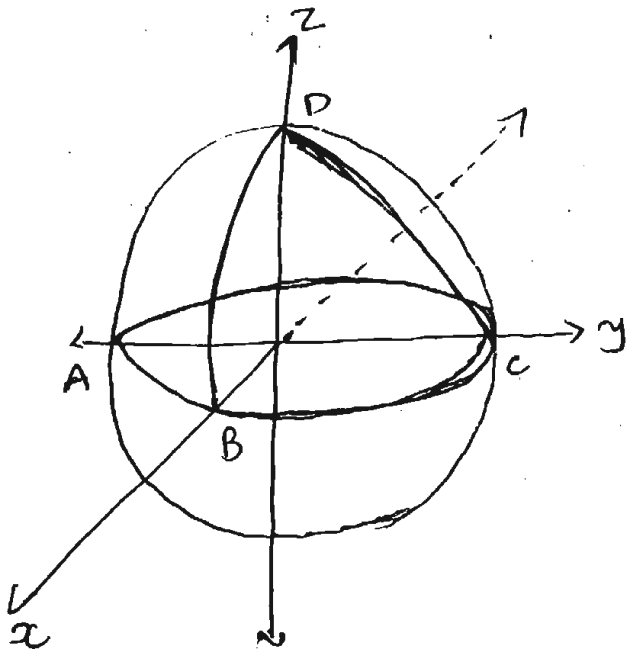
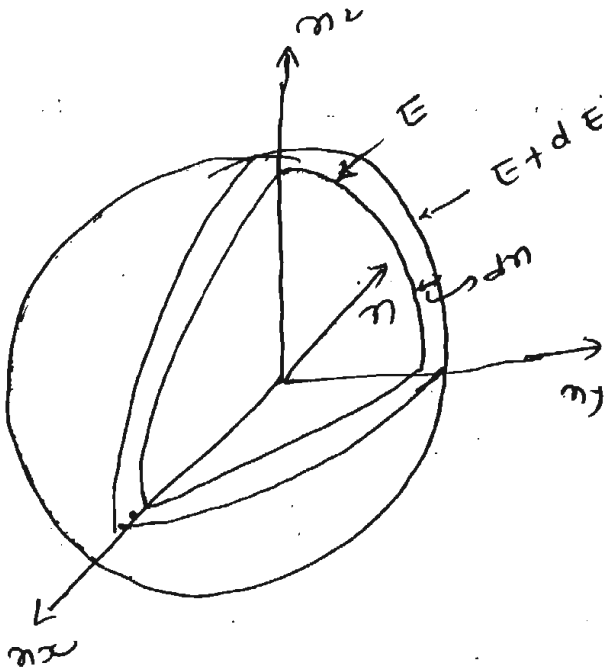
Density of states

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

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

→ assume that the sphere is devided of into number shells.

each shell is known as (n_x, n_y, n_z)

and will have their energy

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

the radius of the sphere is with

energy E is

$$n^2 = n_x^2 + n_y^2 + n_z^2 \longrightarrow (2)$$

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The Schrodinger can for two regions can be g

Number of energy states within a sphe
of radius n = volume of the sphere

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

→ 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 (1/8 th).

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

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

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

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

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

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

from eqn (1), (4)

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

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

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

$$(n+dn)^3 = n^3 + dn^3 + 3n^2dn + 3ndn^2 \longrightarrow (3)$$

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

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

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Neglecting the higher power of dn like dn^2, dn^3,

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

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

$$\therefore N(E)\,dE = \frac{\pi}{2} n\cdot(n\,dn) \longrightarrow (7)$$

→ Suppose a cubic metal with cube edge

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

$$\left(\because E = \frac{h^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2) \right.$$

$$\left. E = \frac{h^2 n^2}{8mL^2} \right)$$

From above eqn

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

$$n = \left(\frac{8mL^2 E}{h^2}\right)^{1/2} \longrightarrow (9)$$

• taking differentiation

$$2n\,dn = \frac{8mL^2}{h^2} dE \longrightarrow (10)$$

$$n\,dn = \frac{8mL^2}{2h^2} \cdot dE \longrightarrow (11)$$

putting the value of n and $n\,dn$ from the eqn (9) (11) into eqn (7)

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

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

$$\boxed{N(E)\,dE = \frac{\pi}{4}\left(\frac{8mL^2}{h^2}\right)^{3/2} \cdot E^{1/2}\,dE}$$

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a^3 = volume of metal piece

from pauli's exclusion law

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

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

$(\because a^3 = 1)$ → (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 state per unit volume $a^3 = 1$

density of state

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

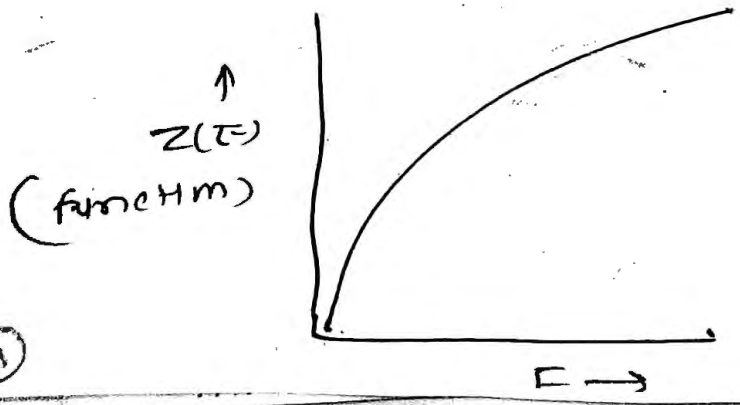
putting value of $N(E)dE$ and $V = a^3 = 1$

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

↳ eqn for density of energy states

from above eqn

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



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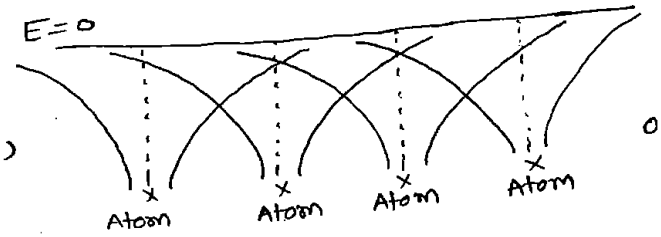
In order to find the allowed energy of ele in solid we have to apply Schrodinger eqn. in lattice.

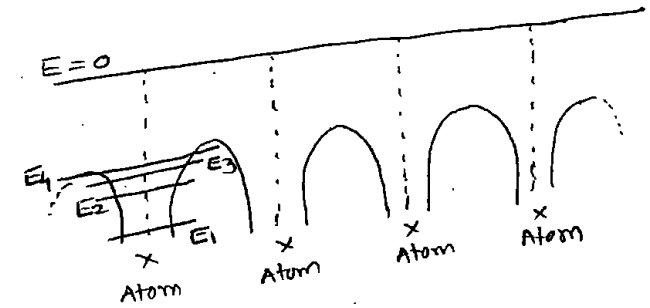
It is assumed that the potential energy of electron is zero near the nucleus of positive ion and maximum when it is halfway between adjacent nuclei.

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

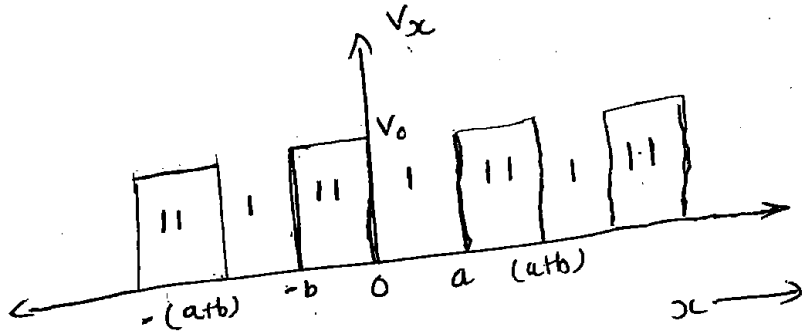
Defn:- The one-dimensional representation of periodic lattice is known as kroning-penny model.



over lapping 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 $0 < x < a$ 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 ~~...~~ ... terms of ~~...~~ elementary functions.

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The schrodinger eqn for two regions can be

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

and

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

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,

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

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

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

which 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.

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

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

The above wave functions are known as bloch function 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 boundry conditions,

we get,

$$\frac{maV_0 b}{\hbar^2} \cdot \frac{\sin \alpha a}{a} + \cos \alpha a = \cos ka \longrightarrow (7)$$

where

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

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eqn (7) gives the soln of schrodinger eqn.

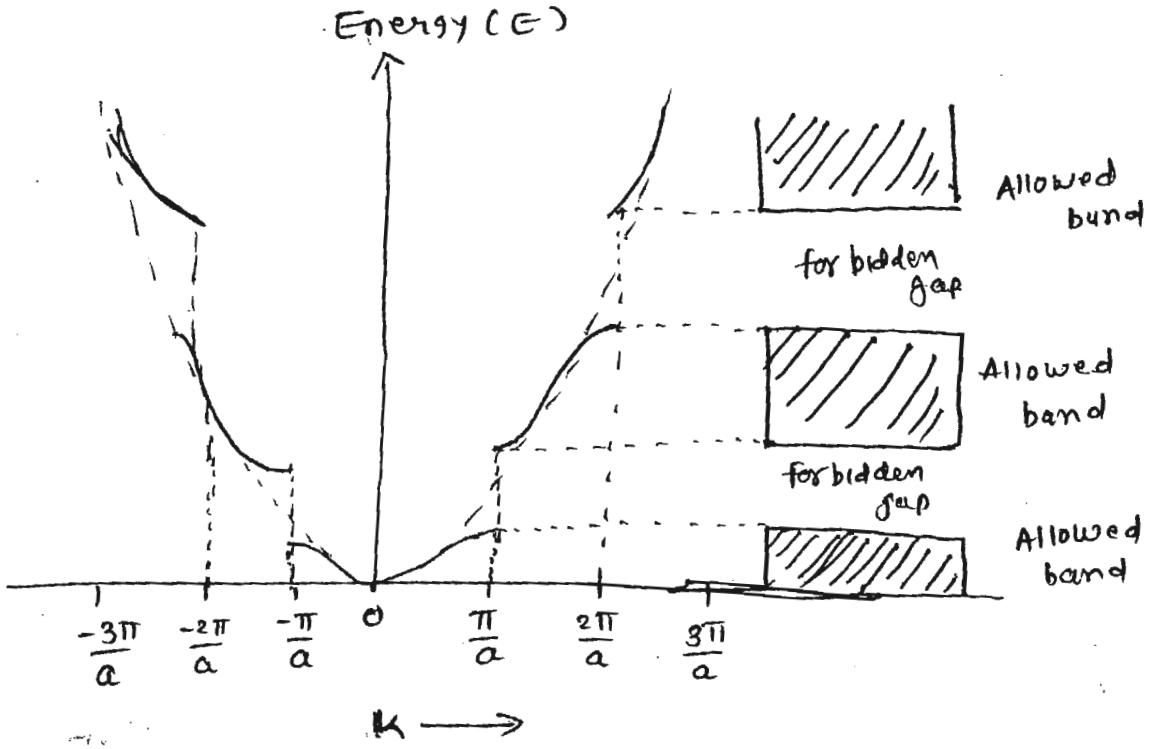
here trigonometric function is involved, thats why only certain values of α are possible.

The RHS of eqn (7) is cos function and can take values betn -1 and $+1$.

Therefore LHS is restricted between those two limits. So we can say that only certain values of α 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 betn 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 discontinuities in E. The discontinuities occurs at $ka = \pm n\pi$

$$k = \pm \frac{\pi}{a}, \pm \frac{2\pi}{a}, \pm \frac{3\pi}{a} \text{ ------}$$

So the origin of Allowed energy bands and forbidden gap is clear from Above figure.

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

It explains bandgap properly.

Energy (E) of a free electron is

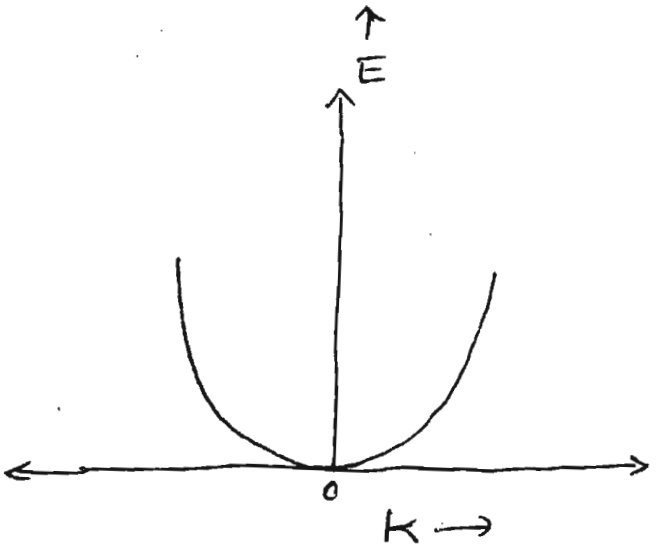
$$E = \frac{h^2 \cdot k^2}{2m} \rightarrow (1)$$

where k = momentum

m = mass of free electron.

h = planks constant

The graph of E → k is given below



- In a semiconductor an electron in conduction band is similar to free ele. which can move in the crystal.
- But because of periodic potential of nuclei eqn (1) is not valid.

Eqn (1) can be used if (i) if we replace free electron mass in the eqn. by

(ii) an effective mass m^*

replacing m by m^*

$$\boxed{E = \frac{h^2 \cdot k^2}{2m^*}} \rightarrow (2)$$

- Effective mass (m^*) :-

There is diffrent 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

(1)

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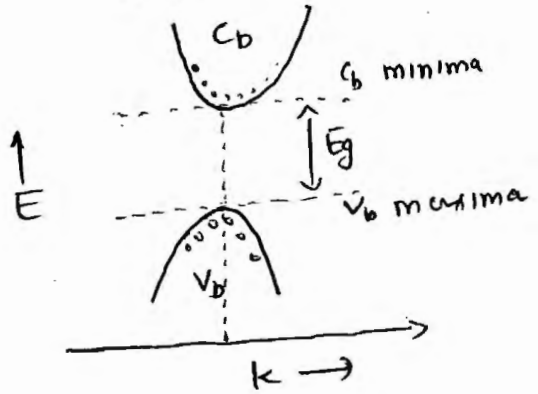
Band Gap :- It can be defined as the minimum energy difference between top of valence b and bottom of conduction band.

* Direct band gap

① In direct band gap the max. energy level of V_b Aligns with min. energy level of C_b wrt momentum.



② k-vector is 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.

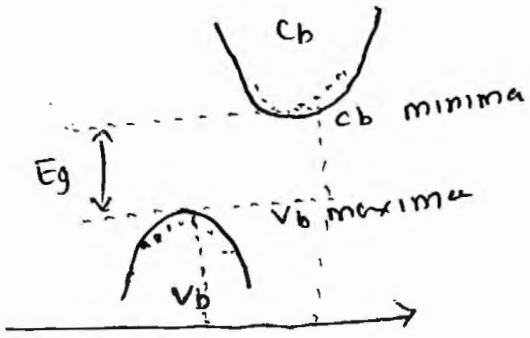
④ The energy difference bet^n V_b and C_b released in form of photon.

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

⑥ energy conserved by emitting photons.

* Indirect band gap

① In indirect band gap the max energy level of V_b do not Align 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 often momenta Align.

④ due to crystal imperfection, electron in V_b C_b loses energy and momentum at same time.

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

⑥ here energy emited as heat so no Radiation.

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the probability of radiation recombination is very high	⑦ The probability of radiative recombination is negligible.
⑧ Efficiency factor is high	⑧ Efficiency factor is Low.
⑨ They are preffered for making optical devices like LED.	⑨ They cant be used to make optical devices.
⑩ Ex - GaAs, P	⑩ Ex. Si, Ge.

→ ~~Types of Electronic material: Metconducter, Semiconductors, and insulators.~~

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Few basic defⁿ

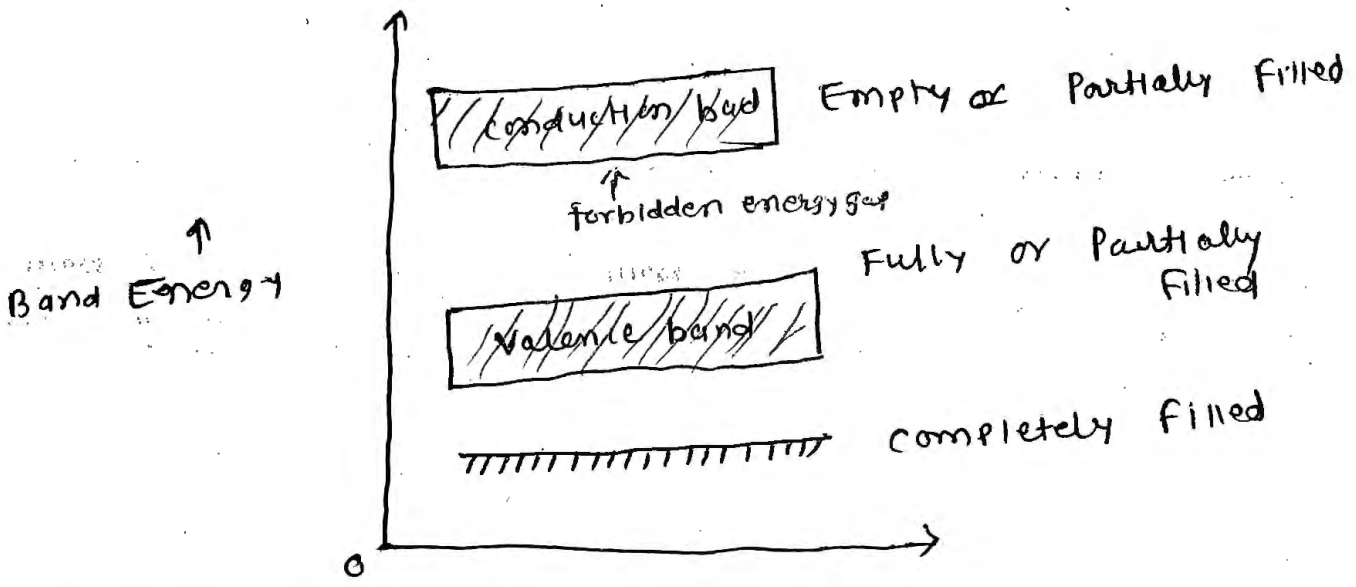
① Energy band diagram :- it is a graphical representation of energy level associated with top energy band and the next lower energy band in a solid.

② Valence band :- The electron in outer most cell are known as valence electron. The band formed by a series of energy level containing valence ele. is known as valence band. (or a band having highest occupied energy.)

③ Conduction band :- In certain metals valence electron are loosely 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 contain occupied by these electrons are is known as conduction band. (or a lowest unfilled energy band.)

④ Forbidden energy gap :- The energy seprartion between conduction and valence band is known as for bidden energy gap.



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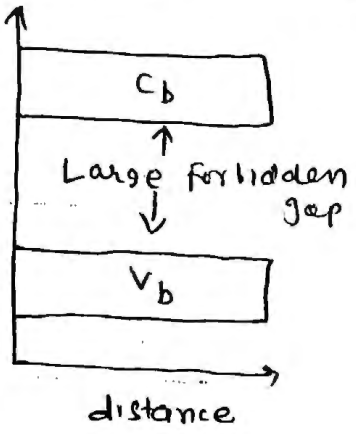
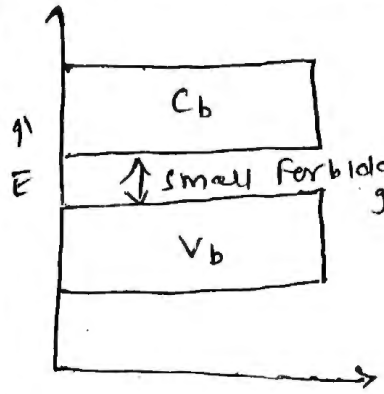
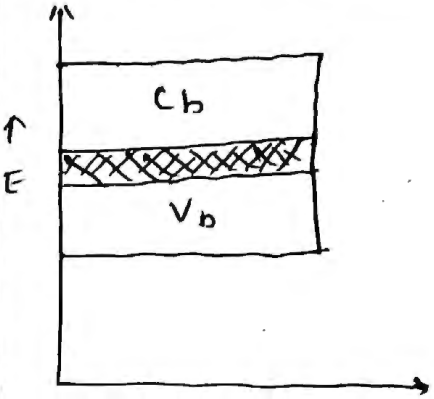
on the basic of forbidden gap, insulator, semiconductor a... conductor are discribed as belowd.

Insulators	Semiconductors	conductors.
		
Forbidden gap is wide	→ Forbidden gap is very small.	→ No forbidden gap.
Even in presence of E-fied No ele moves from V_b to C_b.	→ In presence of small ele field ele. moves from V_b to C_b.	→ due to overlapping of V_b, C_b a sligel potential difference will produce current Flow.
They have full Valence band	→ They have empty C_b and filled V_b	→ plenty of free ele are avaible for ele electrical conduction.
They have empty C_b.	→ small forbidden gap for Ge = 0.7 eV, Si = 1.1eV	→ There is No forbidden energy gap valence and conduction band overlap each other. (No energy gap between two bands)
forbidden gap is very large (~5 to 10 eV)	→ when temp increases the conductivity of semi conducter increases	→ There is NO structure to establish holes.
The resistivity is very high ($\sim 10^7$ Ωm)	→ Resistivity of semiconductors varies from 10^{-14} to 10^7 Ωm.	→ Total current in conductors is simply due to flow of electrons.
At very high temp they show small conductivity.	→ They have electrical properties between those of insulator and good conductors.	

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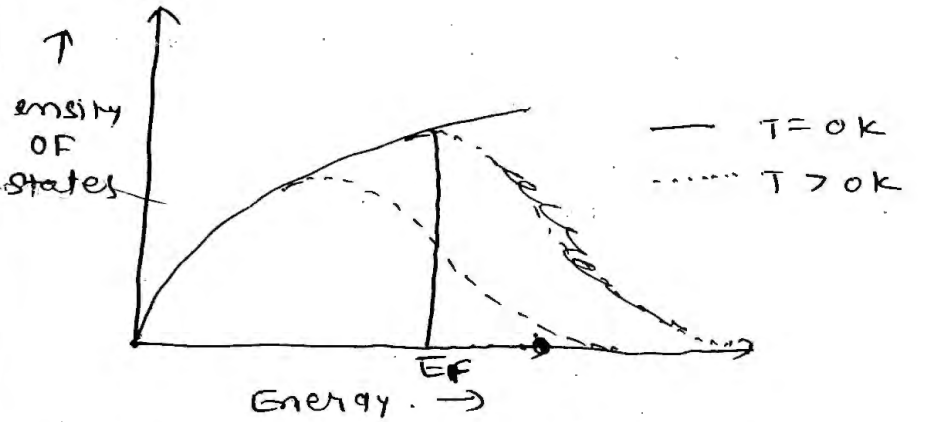
As we know that the density of state in the interval E and E+dE is given by

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

and graph of density of states → Energy is given by



This graph is Parabolic. The area under curve represents the number of electron 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) → E at T=0 drops abruptly to zero at E = EF. The ele 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 state until all of them accomodate. The highest energy occupied is EF.

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

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→ 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 ele. because ① they obey expulsion principle

② They are indistinguishable particle.

Fermi-dirac function can be applicable to quantum particles.

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

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

where $f(E)$ = Fermi function.

eqn (1) is known as fermi-dirac distribution function.

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 refrence with which other energy can be computed.

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

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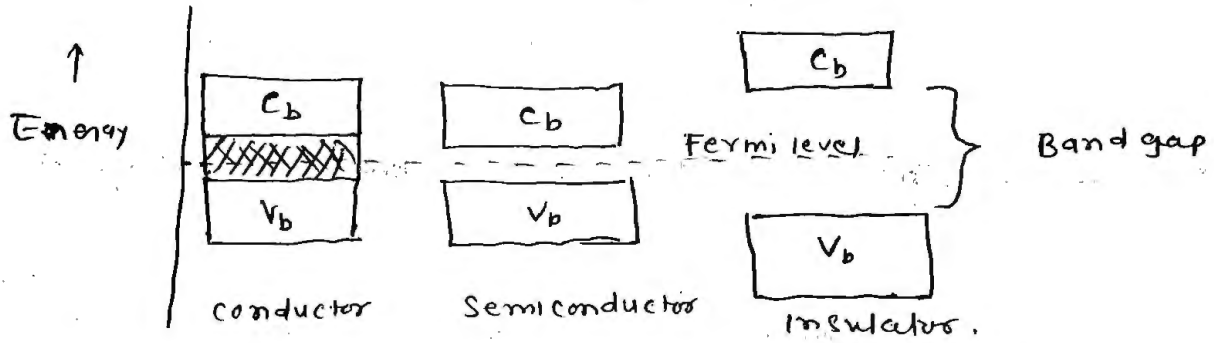
Fermi Level, Effective mass, Photon

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



- In a conductor fermi level is inside the conduction band. In semiconductor it is between C_b and V_b. In insulator very large energy gap betn 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 is empty

f(E) = 0.5 50 % probability to finding ele. in energy

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we need to see 4 cases

case:-1 Probability occupation at $T=0$ K and $E < E_f$

Putting it in eqn (1) $f(E) = \frac{1}{1+e^{-\infty}} = \frac{1}{1} = 1$

$\therefore \boxed{f(E)=1} \rightarrow (2)$

from above eqn it is clear that at $T=0$ K. E_f is fully occupied by ele leaving upper level vacant.

— So below fermi level electron occupy ∞ in levels.

Case:-2 at $T=0$ and $E > E_f$

Putting this in eqn (1)

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

$\therefore \boxed{f(E)=0} \rightarrow (3)$

from above eqn we can say that at $T=0$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)

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

$\therefore \boxed{f(E)=0.5} \rightarrow (4)$

from above eqn we can say that at $T=0$k there is a 50% probability for the electrons to occupy the fermi energy level.

Case-4 at very high Temp $T > 0$k ie

$KT >> E_f$ or E_f or $T = \infty$

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

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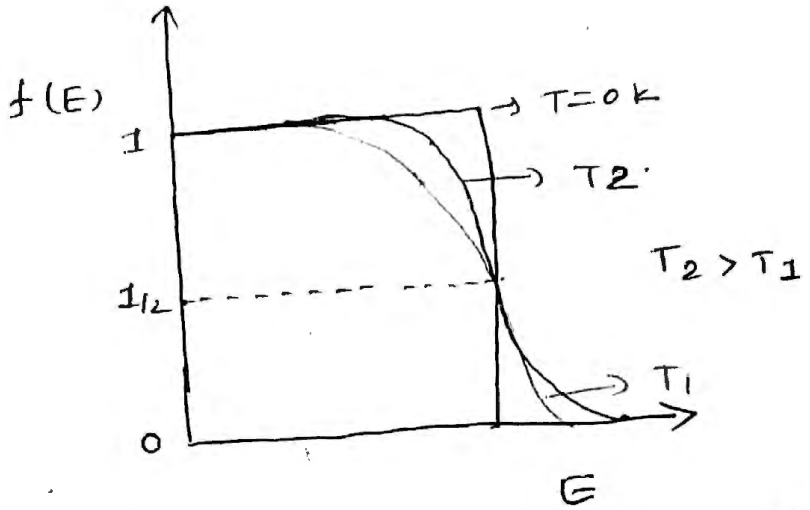
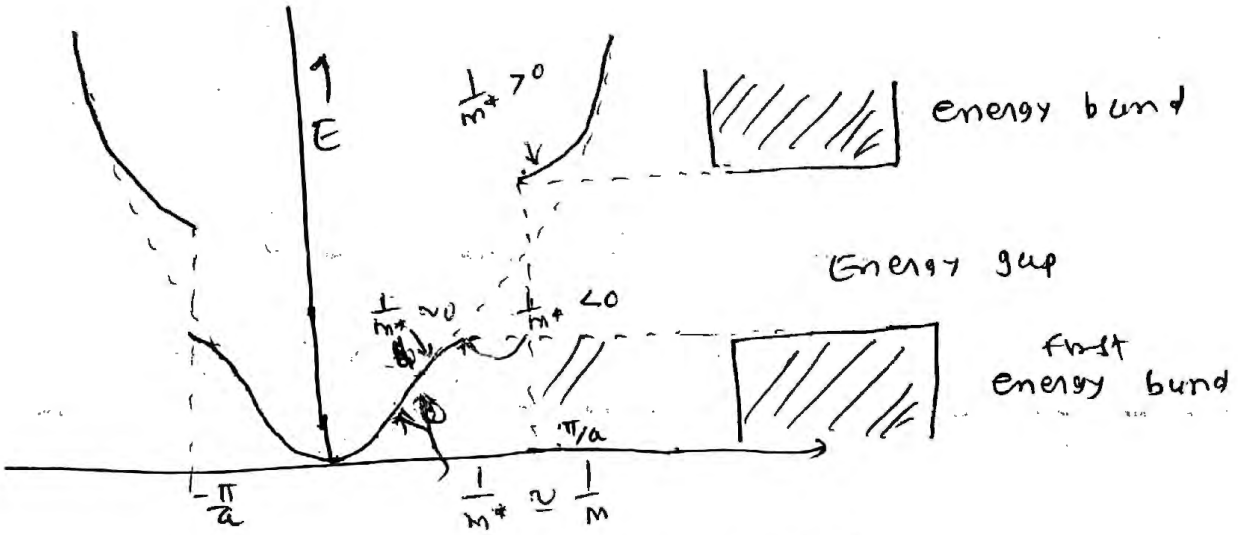


Fermi-dirac distribution function.

② Effective mass : Generally we consider that 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 ele in solid. This experimentally determined electron mass is known as m^* (effective mass)

effective mass is inversely proportional to curvature of an allowed energy band.

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



- Near the bottom of band $m = m^*$
- Near top of allowed band $d^2E/dk^2 < 0$ so m^* is negative

At ... 1st ... dec ...

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

- A solid 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 outside force makes the lattice vibrate
- This generates mechanical waves that carry heat and sound through the material.
- A packet of these wave can travel throughout the crystal with definite energy and momentum.

"These waves are treated as a particle called Phonons".

- So 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

$$E = \hbar\omega = h\nu.$$

where $\omega/2\pi$ = freq. of vibration

h = Plank's const.

- Phonon can carry heat and sound and they play a major role in determining heat capacities of solids and liquids.

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