Semiconductor Physics & Computational Methods

UNIT-1

The Classical Free Electron Theory ⇒

Lorentz and Drude in the year 1900 developed this theory which assume that metals contains free electrons obeying the laws of classical mechanics. The important assumptions are as follows:

- Lorentz and Drude constructed this classical free e^- theory of metallic conduction by applying the highly sucessful Kinetic theory of gases to metals as a gas or cloud of electrons.
- In simple form, Kinetic theory treats the molecules of a gas as identical solid sphere which moves in a straight lines until they collide with one another.
- In simplest gases only one kind of particle present. But in metals there must be two type of particles, one for -ve charge e^- and metal is electrically neutral.
- Here it is assumed that when atoms of metallic element are closer to form a metal the valence e^- from each atom become detached and move freely through metals while metallic ion remain immobile.
- A single isolated atom of metallic element has a nucleus of charge eZa, where Za is the atomic number and 'e' is the magnitude of electronic charge surrounding the nucleus, there are 'Za' electrons of total charge $-eZa$. A few of these electrons 'Z' are the weakly bound valence electrons. The remaining $(Za-Z)$ electrons are tightly bound to nucleus and are known as core electrons. These isolated atoms condense to

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form the metallic ions and valence electrons allowed to wander far away. They are called conduction electron gas or cloud.

→ Inspite of strong $e^- - e^-$ and electron-ion electromagnetic interaction, the Drude model brodly treats the metallic electron gas by kinetic theory of neutral dilute gases as:-

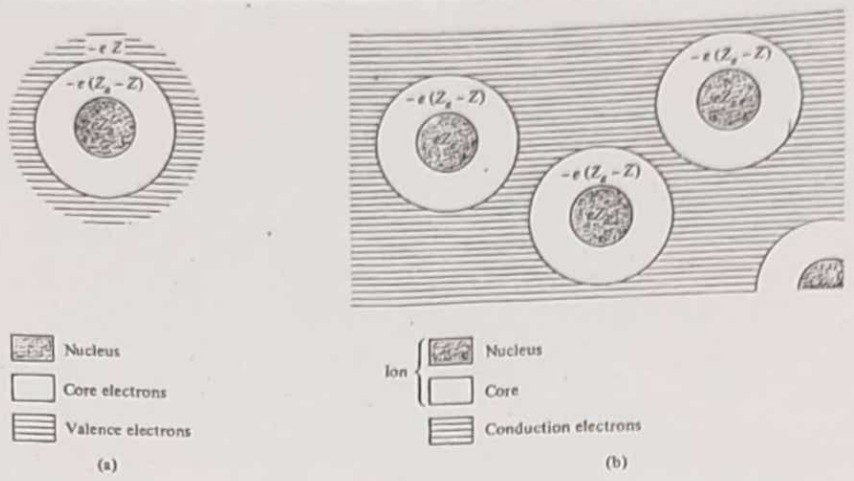

Fig. 1.2. Arrangement of atoms in a metal

→ (i) Between the collision the interaction of electron, both with electrons and ions are neglected. Thus in absence of externally applied electromagnetic fields, each electron move freely and collide with other free electron and positive ions. This collision is known as Elastic collision.

(ii) The neglect of electron-electron interaction between collision is known as independent electron approximation and neglect of electron-ion interaction is known as free electron approximation.

(iii) In the presence of externally applied electromagnetic field the electrons acquires some energy from field and directed to move with a constant velocity known as Drift velocity.

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1. Drude in 1900 constructed ...
them.

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➡ The electron experiences a collision with a probability per unit time $1/\tau$. So the probability of an electron undergoing collision in any infinite time interval of length ds is ds/τ.

➡ The τ is known as the relaxation time, the collision time or the mean free time. It is defined as the time taken by an electron between two successive collisions.

Success of classical free electron theory :-

1. It is used to verify Ohm's Law
2. It is used to explain the electrical and thermal conductivity of metals.
3. It is used to explain the optical properties of metals.
4. Ductility and malleability of metals can be explained by this model.

Drawbacks / Failure of classical free electron theory :-

1. This theory can not explain the electrical conductivity of semiconductors or insulators using this model.
2. From this theory theoretical value of paramagnetic susceptibility is greater than experimental values.
3. Ferromagnetism can not be explained by this theory.
4. At low temperature the electrical conductivity and thermal conductivity vary in different ways. So $K/\sigma T$ is not constant, but by classical theory it is constant.
5. The photo-electric effect, Compton Effect and Black body radiation can not be explained by classical free e^- theory.
6. From classical theory specific heat of metal is 4.5R, but experimental value of specific heat equal to 3R.

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Salient features of Classical Free Electron theory

1. Drude in 1900 constructed this classical free electron theory of metallic conduction by applying the highly successful kinetic theory of gases to metal, considered as a gas of electrons.

2. In this Drude model we shall assume that when atoms of a metallic element are brought together to form a metal, the valence electrons from each atom become detached and wander freely through the metal, while the metallic ions remain intact and play the role like immobile positive particles.

3. A single isolated atom of metallic element has a nucleus of charge eZ_a, where Z_a is atomic number & 'e' is the magnitude of electronic charge surrounding the nucleus. A few of these electrons 'Z' are the weekly bound electron. The remaining $(Z_a - Z)$ electrons are tightly bound to nucleus and are known as <u>core electrons</u>. These isolated atoms condense to form the metallic ion and valence electrons allowed to wander far away. They are called <u>conduction electron gas or cloud</u>.

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4. The density of electron gas can be calculated as

$$n = \frac{N}{V} = 6.023 \times 10^{23} \times \frac{\rho_m Z}{A}$$

where ρ_m = mass density, A = atomic mass & Z = no. of electrons

5. Drude Model brodly treats the metallic electron gas by kinetic theory of neutral dilute gas with modifications -

(i) Between collission the interaction of electron, both with electron and ions are neglected. Thus in absence of extenall

applied electromagnetic field, each electron move freely and collide with other free electron & positive ions. This collision is known as Elastic collision.

(ii). The neglect of electron-electron interaction between collision is known as independent electron approximation, and neglect of electron-ion interaction is known as free electron approximation.

(iii). In the presence of externally applied electromagnetic field the electrons acquire some energy from field and directed to move with a constant velocity known as drift velocity.

6. The probability of an electron undergoing collision in any infinitesimal time interval of length ds is ds/τ. The time 'τ' is known as relaxation time. the relaxation time 'τ' is defined as the time taken by electron between two successive collision.

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- Merits of classical free Electron theory :⇒

(i) It is used to verify ohm's Law.

(ii). It is used to explain the electrical and thermal conductivity of metals.

(iii). It is used to explain the optical properties of metals.

(iv). Ductility and malleability of metals can be explained by this model.

- Demerits of classical free electron theory :⇒

(i) This theory cannot explain the electrical conductivity of insulator or semiconductors.

(ii). From this theory theoretical value of paramagnetic suscep-tibility is greater than experimental value.

(iii). Ferromagnetism can not be explain by this theory.

(iv). At low temp. the electrical conductivity and thermal conductivity vary in different way. So $K/\sigma T$ is not constant. But by classical theory it is constant.

(v). The photoelectric effect, Compton Effect and black body radiation can not be explained by this classical theory of electrons.

* Salient features of Quantum free Electron theory :⇒

(i). In 1928 Sommerfield proposed this theory. He remain the concept of free electron moving in uniform potential within metal as classical theory but treated electrons obey the ~~New~~ Law of Quantum Me

(ii). Based on De-broglie wave concept he assumed that a moving electron behaves as if it were a system of wave. (Matter Wave).

(iii). According to quantum mechanics the energy of an electron in metal is quantized. The electrons are filled is a given energy level according to Pauli's exclusion principle.

(iv). Each energy level can provide only two states namely, one with spin up and one with spin down and hence only two electrons can be occupied is a given energy level. So permissible energy levels of free electron can determined.

(v). It is considered that valence electrons travel in constant potential inside the metal but they are prevented from escaping the crystal by very high potential barriers at the end of crystal.

(vi) In quantum theory the spacing between the consecutive energy levels of electrons is very less and thus distribution of energy levels seems to be continuous.

* Merits of Quantum Free Electron theory :⇒

(i). According to classical theory all free electrons gain energy, which follow Maxwell - Boltzman statistics. But according to quantum theory only one percent of free electron can absorb energy. So the resulting specific heat and paramagnetic susceptibility values are in much better agreement with experimental value.

(ii) According to quantum free electron theory both experimental and theoretical values Lorentz number are in good agreement with each other.

* Demerits or Drawback of Quantum Free electron theory :⇒

(i). It fails to explain why some crystals have metallic properties and others do not have.

(ii). It fails to explain why the atomic arrays in crystal including metal should prefer certain structure not other.

* Fermi Energy (E_F) :⇒

"Fermi energy is the energy of states at which the probability of electron occupation is 1/2 at any temperature above 0K. It is the maximum kinetic energy that a free electron can have at 0K. So the energy of the highest occupied level at absolute zero temp. is called Fermi Energy or Fermi Level". The Fermi Energy at 0K for metal is

$$\boxed{E_F = \left[\frac{3N}{\pi}\right]^{2/3}\left(\frac{h^2}{8m}\right)} = \frac{h^2}{8m}\left[\frac{3N}{\pi}\right]^{2/3}$$

when temperature increases the fermi Energy or Level decreases.

Fermi-Dirac Distribution Function $f(E)$ & Effect of temperature :→

The distribution of electrons among the levels is usually described by the distribution function $f(E)$. It is defined as the probability of an electron occupying an energy level 'E'.

Free Electron gas obey Fermi-Dirac Statistics. Consider an assembly of fermions, ~~there~~ $M(E)$ are allowed quantum states in energy range between E & $E+dE$ and $N(E)$ are the number of particles, So the Fermi-Dirac Distribution function is

$$f(E) = \frac{N(E)}{M(E)} = \frac{1}{1+\exp(E-E_F)/KT} = \frac{1}{1+e^{(E-E_F)/KT}}$$

Thus if level is certainly empty then $f(E)=0$, $f(E)$ has value between zero and unity.

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The distribution function for electrons at absolute zero has different form :-

(i). When $E < E_F$ (i.e.) for energy levels lying below E_F, $(E-E_F)$ is a negative quantity and hence

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

So, All the levels below E_F are occupied by electrons.

(ii). When $E > E_F$ (i.e.) for energy levels lying above E_F, $(E-E_F)$ is a positive quantity and hence

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

So, All the levels above E_F are vacant.

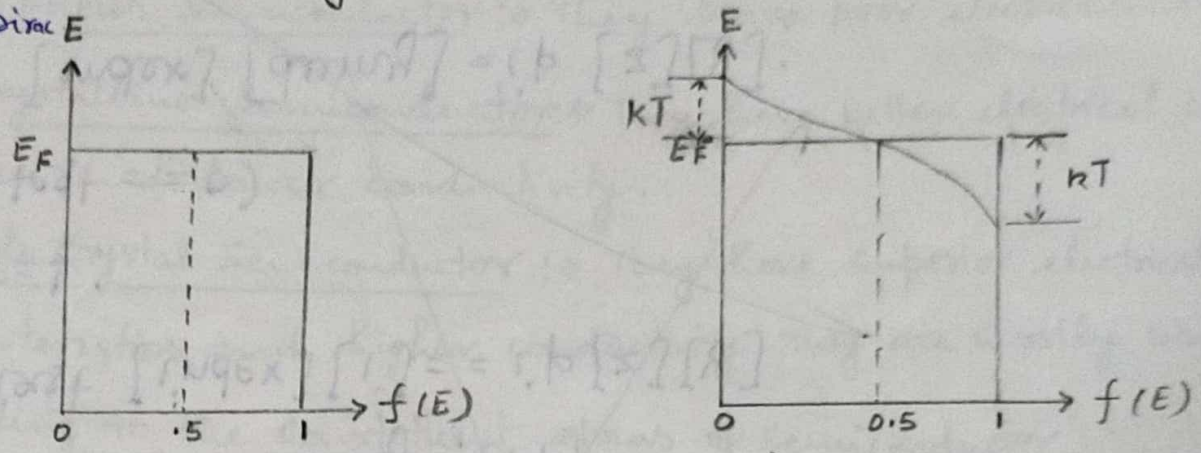
Thus At absolute zero, all levels below E_F are completely filled and all levels above E_F are completely empty. The level that divides these two state is known as Fermi Energy level.

(iii). When $E = E_F$

$$f(E) = \frac{1}{1+e^0} = \frac{1}{1+1} = \frac{1}{2} \text{ at all temperatures.}$$

Thus the probability of finding an electron with energy equal to the fermi energy in a metal is 1/2 at any temperature.

Fermi-Dirac



(a) At T=0K (b) when T>0K

(a)- At T=0 all energy level upto E_F are occupied & above E_F are empty.

(b) At T>0K some level above E_F are filled & below E_F are partially empty.

Semiconductors :⇒ Semiconductors are materials whose electronic properties lies inbetween those of metals and insulators. These intermediate properties are determined by the crystal structure, bonding characteristics and electronic energy bands. They are a group of materials having conductivities between those of metals and insulators.

At room temperature semiconductor behave like insulators but when some energy like thermal energy given to it it behave like conductor.

Classification :⇒

According to the nature of current carriers, semiconductor are two

(i) Ionic Semiconductor :⇒ In this type of semiconductor conduction takes place through the movement of ions and accomplished by mass transport.

(iii). Electronic Semiconductor :⇒ In this type conduction takes place through the movement of electrons and no mass transport is involved.

According to the Structure of Semiconductor, it is of three type -

(i). Amorphous Semiconductor :⇒ They have poor electrical characteristic

(ii). Polycrystalline Semiconductor :⇒ They have better electrical characteristics and lower conductivity.

(iii). Single crystal Semiconductor :⇒ They have superior electrical characteristics and higher conductivity. They are mostly used.

According to the Constituent atoms of Semiconductor

(i). Element Semiconductor :⇒ All the constituent atoms are of same kind i.e. composed up of single species of atoms. Exp. Ge & Si

(ii). Compound Semiconductor :⇒ They are composed of two or more element. Exp. GaAs, AlAs.

* Intrinsic Semiconductor :⇒ When the semiconductor crystal is in pure form i.e. free from any kind of impurity, then the resultant crystal is known as Intrinsic Semiconductor.

Extrinsic Semiconductor :⇒ When impurity atoms are added to the pure semiconductor then the resultant semiconductor is known as Extrinsic Semiconductor. The addition of impurity increases the carrier concentration and hence conductivity of conductor.

Doping :⇒ The process of mixing impurity to the pure semiconductor crystal or others is known as doping.

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Fermi Energy Formula for an Intrinsic Semiconductor :⇒

In intrinsic semiconductor the conduction is due to the intrinsic characteristics of the crystal without impurity. The electrons are excited from the top of the valence band to the bottom of the conduction band by thermal energy. The no. of electrons excited across the gap can be calculated by Fermi-Dirac Distribution function

$$f(E) = \frac{1}{1 + \exp^{(E-E_F)/k_BT}} \quad \text{——— (1)}$$

The fermi Level E_F for intrinsic semiconductor lies midway in forbidden gap as shown in fig.. The probability of finding an electron here is 50%. Then $(E-E_F)$ in eqn. (1) is equal to $E_g/2$, where E_g is magnitude of energy gap.

For exp. Silicon has $E_g = 1.1\,eV$, so $(E-E_F) = .55\,eV$, which is twenty times higher than thermal energy $k_BT = .026\,eV$.

The factor unity in denominator can be ignored, so the probability $f(E)$ of an electron occupying energy level E

$$f(E) = \exp(-E_g/2k_BT) \quad \text{——— (2)}$$

So for the number of electron (n) promoted across gap

$$n = N \exp(-E_g/2k_BT) \quad \text{——— (3)}$$

where N = no. of electrons available for excitation for top of valence band.

The electron across the gap leaves some vacant electron site in valence band., These are called holes. An intrinsic semiconductor have equal no. of holes in valence band and electrons in conduction band, $n_e = n_h$.

Under externally applied field the excited electrons can accelerate using the vacant states available in conduction band.

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At the same time holes in valence band also move but in opposite direction of electrons. Conductivity of intrinsic semiconductor depends upon charge carriers n_e and n_h. Like drift velocity in case of metal we have mobility of conduction electron and holes μ_e and μ_h as drift velocity. So the conductivity σ of intrinsic semiconductor as:

$$\sigma_i = n_e e \mu_e + n_h e \mu_h \quad \text{——} \quad (4)$$

where e = electronic charge and n_e and n_h are concentration of electrons & holes.

Fermi Level :⇒ The no. of free electrons per unit volume in an intrinsic semiconductor is

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

The no. of holes per unit volume is an intrinsic semiconductor is

$$p = 2\left[\frac{2\pi m_h kT}{h^2}\right] \exp\left(\frac{E_v - E_F}{kT}\right)$$

Since $n = p$ in intrinsic semiconductor

$$2\left(\frac{2\pi m_e kT}{h^2}\right)^{3/2} \exp\left(\frac{E_F - E_c}{kT}\right) = 2\left(\frac{2\pi m_h kT}{h^2}\right)^{3/2} \exp\left(\frac{E_v - E_F}{kT}\right)$$

$$(m_e)^{3/2} \exp\frac{(E_F - E_c)}{kT} = (m_h)^{3/2} \exp\frac{(E_v - E_F)}{kT}$$

$$e^{2E_F/kT} = \left(\frac{m_h}{m_e}\right)^{3/2} \exp\left(\frac{E_v + E_c}{kT}\right)$$

Taking log on both sides

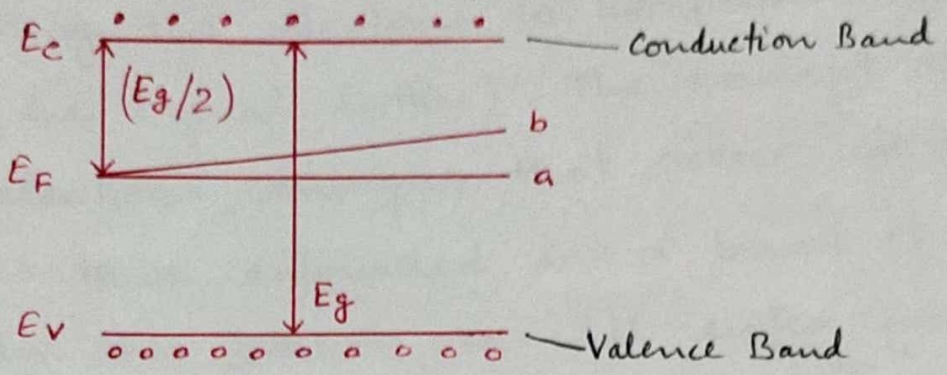
$$\frac{2E_F}{kT} = \frac{3}{2}\log_e\left(\frac{m_h}{m_e}\right) + \log_e\left[\exp\left(\frac{E_v + E_c}{kT}\right)\right]$$

$$\frac{2E_F}{kT} = \frac{3}{2}\log_e\left(\frac{m_h}{m_e}\right) + \left(\frac{E_v + E_c}{kT}\right)$$

$$E_F = \frac{3kT}{4}\log_e\left(\frac{m_h}{m_e}\right) + \left(\frac{E_v + E_c}{2}\right)$$

If we assume $m_e = m_h$ $\Rightarrow$ $E_F = \left(\frac{E_v + E_c}{2}\right)$ $\quad (\log_e 1 = 0)$

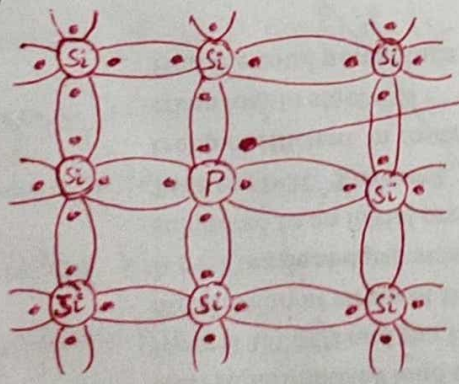
Thus the fermi level is located half way between valence and and conduction band and is independent of temperature. Since $m_h > m_e$, E_F is just above the middle and rise slightly with increase in temperature.

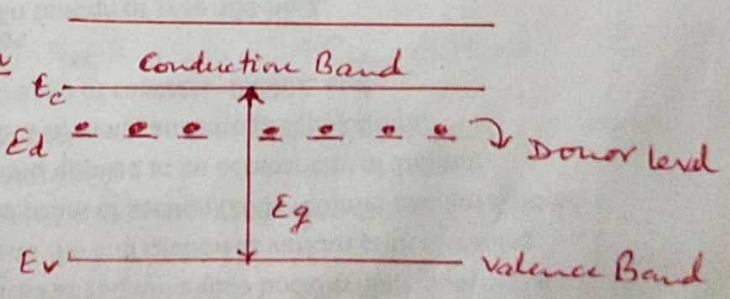


Position of Fermi level in an intrinsic Semiconductor at Various temperature → (a) At T=0, (b) As temp increases E_F shift

⇒ **N-type of Semiconductor** ! ⇒ When small amount of pentavalent impurity such as P, As, Sb is added to the intrinsic semiconductor, n-type semiconductor is formed.

⇒ When fifth column element phosphorus substitute for a Silicon atom, four of the five electrons in the outermost orbit of Phosphorus atom take part in tetrahedral bonding with four silicon atom. The fifth electron cannot take part and it is loosely bound. It revolve around the +ve charged P ion.





⇒ The electron of phosphorus atom is moving in the electric field of Silicon crystal and not in free space.

⇒ this brings in dielectric constant of crystal into orbit calculation and the radius of electron orbit here turn out to be very

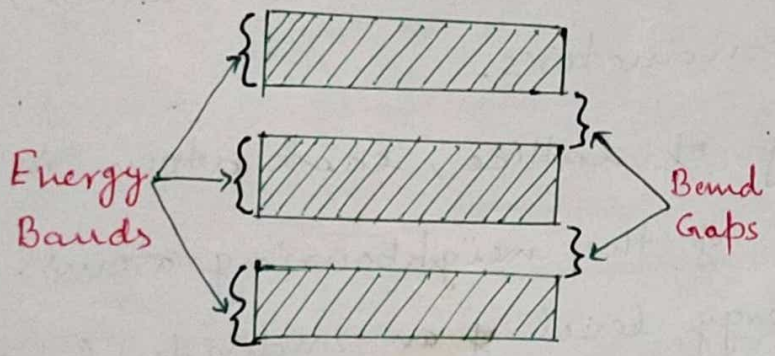
Band Theory of Solids :- The electrical properties of many metals, semiconductor can not be explained on the basis of free electron theory. This can done only by considering the electrons to be present in a periodic potential (i.e crystal lattice). The concept of discrete allowed electrons energies that occur in a single atom, has to be expanded in a band of allowed energies. In this process we will enter into a more valid discription of electrons in a periodic lattice, namely energy band theory.

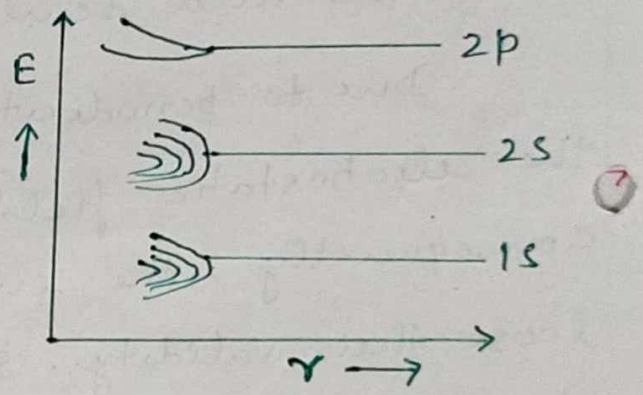
The energy band theory is now a basic principle of semiconductor physics and is used to explain the difference in electrical properties between metals, insulators and semiconductors.

Due to periodicity of lattice, each atom is in the electrostatic field of the neighbouring atoms. Consequently, the energy level of an individual atom loose their validity. If the crystal contains N-atoms then due to interaction between the atom, each discrete energy level in an individual atom splits into N-close sublevels. As N is very large, the seperation between sublevels is very small so that these dense levels are almost continuous and are said to form an energy band. These energy bands are in general seperated by regions which have no allowed energy levels.

These regions are called forbidden bands or band gaps.

In some crystals the adjacent energy bands overlap. The no. of levels in such a merged band is equal to the sum of the no. of the levels into which both levels of the atoms split up. Moreover the amount of splitting is not the same for different levels. Those filled up by the valence electron in an atom are distributed most, while those filled by inner electrons disturbed only slightly. Figure represents the splitting off levels as a function of distance r between atoms. The energy band structure of solid and the occupation of energy bands by electrons determine the electrical properties of that solids.





Classification of Solids on the basis of Energy band Gap theory :- The concept of energy bands helps us in understanding the division of solids into three groups

Conductor :- In some solids an upper vacant band overlaps the valence band or the valence band itself is half filled. It means that electrons in valence band have easy access to levels in the upper vacant band.

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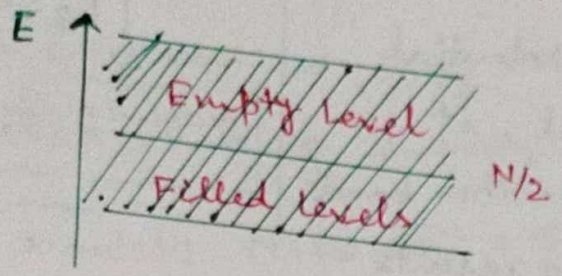
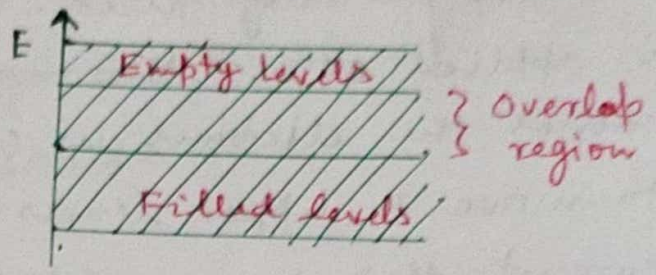
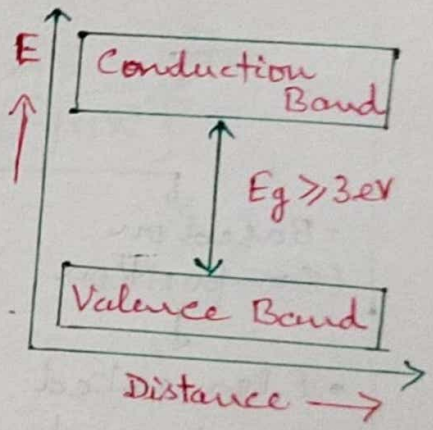
For this reason, very large no. of electrons available for conduction, even at extremely low temperature.





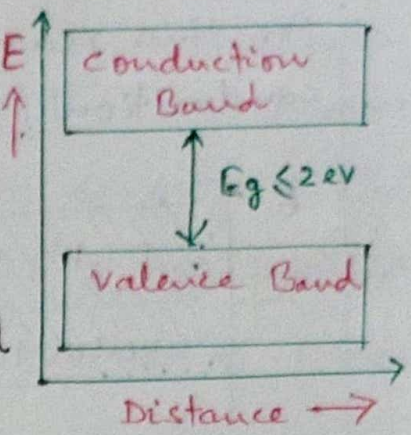
When electric field is impressed across the solids electrons readily jump into upper unoccupied energy levels of the vacant band and current flows into large measure in solids. Therefore these solids exhibits good electrical conductivity and are called conductors.

Insulators :- Some solids have band gap that are very wide ($E_g > 3eV$). It would require the acquistion of very large amount of energy to cause an electron to jump from the valence band to the conduction band. very few electrons can get this large amount of energy to jump from valence band to conduction band at ambient temperature. Hence there are very few electron in the conduction band. When a voltage is applied across the solid, negligible current flows and the solid exhibits very low electrical conductivity. These solids are called insulators.



Semiconductors :- In some solids the band gap is narrow and of order of 2eV or less. Acquistion of small amount of energy from the vibration of atoms can raise

electrons from the valence band to the conduction band. The conduction band is then partially filled. If a potential is applied across the material, it causes the electrons in conduction band to move to upper levels. As a results current flow in a modest measure in solids. Such solids are called semiconductors.



Classification of Semiconductors

Semiconductors are classified mainly on three w's based on the composition of materials, purity of materials and nature of band gap of materials.

Semiconductor

- Based on composition
  - Elementized
  - Compound
- Based on impurity
  - Intrinsic
  - Extrinsic
    - p-type
    - N-type
- Based on Bandgap
  - Direct Bandgap
  - Indirect Band Gap

Density of States :- It is defined as the no. of energy states per unit range. In other words density of states for electrons in band gives the no. of orbitals (states) in a given energy range. Hence the no. of filled states having energy range E & E+dE is

$$N(E)\,d(E) = E(E)\,f(E)\,dE \qquad \text{—— (I)}$$

From energy relation

$$E = \frac{\hbar^2 K^2}{2m} \qquad \text{—— (II)}$$

The no. of electrons

$$N = \frac{V}{3\pi^2} K^3 \quad \text{OR } K^3 = \frac{3\pi^2 N}{V} \quad [V = L^3]$$

where E = Total energy, N = no. of electrons so from above eqn.

$$E = \frac{\hbar^2}{2m}\left[\frac{3\pi^2 N}{V}\right]^{2/3} \qquad \text{—— (III)}$$

or

$$\frac{3\pi^2 N}{V} = \left[\frac{2mE}{\hbar^2}\right]^{3/2} = \left[\frac{2mE}{h^2/4\pi^2}\right]^{3/2}$$

This eqn. in terms of N

$$N = \frac{8\pi V}{3h^3}(2mE)^{3/2} \qquad \text{—— (IV)}$$

By differentiating eqn. (IV) w.r. to E

$$\frac{dN}{dE} = \frac{8\pi V}{3h^3}(2m)^{3/2}\cdot\frac{3}{2}E^{1/2} = \frac{8\pi m V (2mE)^{1/2}}{h^3}$$

or

$$\frac{dN}{dE} = \frac{V}{2\pi^2}\left[\frac{2m}{\hbar^2}\right]^{3/2} E^{1/2} \quad [\text{In terms of } \hbar = \tfrac{h}{2\pi}]$$

The quantity dN/dE is frequency referred to as density of available states d(E), which on multiplication with probability of occupation f(E) gives the density of states N(E) as in fig.

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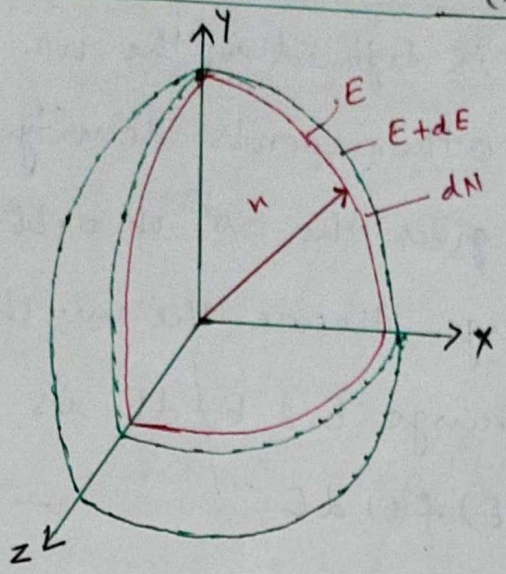

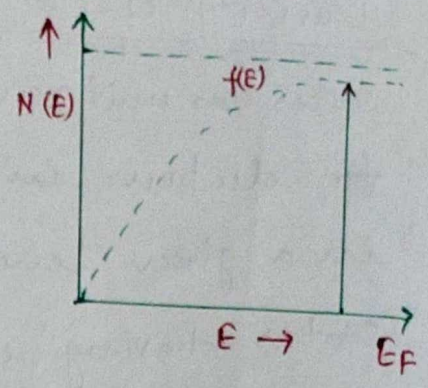

Thus the no. of electrons whose energy lie between E & E+dE is given by

$$N(E)\,dE = \frac{dN}{dE} f(E)\,dE$$

$$\boxed{N(E)\,dE = \frac{8\pi V m}{h^3}(2mE)^{1/2} \cdot \frac{dE}{1+e^{(E-E_F)/kT}}}$$

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Direct & Indirect Band Gap :-

In Semiconductor physics, the Band gap of Semiconductor can be of two basic type –

1- Indirect Band Gap

2- Direct Band Gap

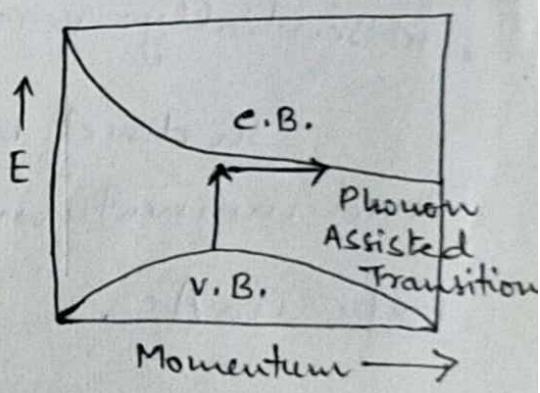
1. **Indirect Band Gap** :⇒ The minimum energy state in conduction band and the maximum energy state in valence band are each characterised by a certain e^- crystal momentum (K-vector) in Brillouin zone. If the K-vector is different for these two energy state for different material, then the band gap is called indirect band gap.

In indirect band gap phonon assisted transition occur which is horizontal in nature. The momentum of phonon is compratively large. In indirect band gap the bottom of C.B. and top of V.B. lies for different value of K.

In indirect band gap transition only energy is conserved.

Exp. Si, Ge

In an indirect band gap a photon can not be emitted. Because the e^- must passes through an intermediate state and transfer momentum to crystal lattice.



Indirect Band Gap

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2. Direct Band Gap : ⇒ The Bandgap is called direct band gap, if the crystal momentum vector (K-vector) of e^- and holes in both the minimum energy state of conduction band and maximum energy state of valence band is same.

An e^- can directly emit a photon.

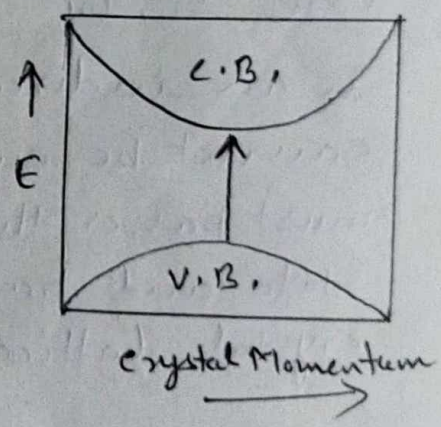
In this case e^- can shift from highest energy state in valence band to lowest energy state in conduction band without change in crystal momentum vector. The transition in which a photon excite an e^- from V.B. to C.B.

OR in other words in direct band gap the bottom of conduction band & top of valence band lies for same value of crystal momentum $K = 0$.

In direct band gap photon assisted transition occurs. Photons are massless entities and carry little momentum & this kind of transition is essentially vertical in E-K diagram.

In direct band gap the energy and momentum are conserved.

Exp. GaAs.



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