1.11.FREE ELECTRON THEORY

Introduction:

- Electrons in outermost orbits of atoms in solids determine its Electrical, Magnetic, Thermal & Reactivity properties.
- Electron theory is applicable to all solids, both metals and nonmetals.
- The structure and properties of solids are explained by the free electron theory of solids which has been developed in 3-main stages:

  (i) Classical Free electron theory (or) Drude-Lorentz theory.

  (ii) Quantum free electron theory (or) Sommerfeld theory.

  (iii) Zone theory (or) Band theory (or) Bloch's theory.

(i) Classical Free Electron Theory of Solids

- During 1900, Drude proposed free electron theory for the metals using some basic assumptions, according to him, the valence e's of atoms, constituting a crystal, are free to move inside the metal just like the molecules/atoms in a perfect gas, named as free electron gas model.
- Later in 1909, H.A. Lorentz suggested that e's constituting the electron gas that obey Maxwell-Boltzmann statistics under the equilibrium conditions.
- Combining the ideas of Lorentz with Drude, the constituent theory is known as Drude-Lorentz theory.
- Since the theory is based on the classical ideas of Maxwell-Boltzmann statistics, it is called classical free electron theory.

Assumptions/Postulates/Salient features:

- Drude and Lorentz proposed the classical free electron theory for metals using some important assumptions, which are as follows.
- In crystalline solids, a large number of free electrons are moving freely in all possible directions and behave like gas molecules in a container, obeying the Law of kinetic theory of gases.
- Free electrons are -vely charged particles and obey Pauli's exclusion principle while the atoms or molecules of a perfect gas are mostly neutral.
- The behavior of free electrons moving inside a metal is like that of atoms or molecules in a perfect gas.
- In a metal, valence electrons move in a uniform potential field due to ions in the Lattice, the ion core and PE of electrons are constant.
- The total -ve charge of electrons is equal to the +ve charge of ion cores and hence, the metal remains electrically neutral.
- In the absence of electric field, the energy associated with each electron at a temperature 'T' is given by 3/2 KT and is related to Kinetic energy, K.E = 3/2 KT ------------(1)

- Since Potential energy =0, the total energy of the free electrons in a metal is almost equal to their Kinetic energy, K. E=$1/2mv^2$ -----------(2)
- **From (1) & (2)** => $3/2\ KT = 1/2\ mv^2$
- ***where:*** V => Thermal velocity

  K => Boltzmann constant

  T => Temperature

  m => Mass of electron
- When an electric field is applied to a metal, free electrons are accelerated in the direction opposite to the direction of the applied electric field with a drift velocity (V_d).
- $V_d = I / neA$
- In metals, the +ve ion cores are at fixed positions and free electrons move randomly and collide with the ion cores (or) other free electrons or with boundaries which are called elastic collisions with no loss of energy.

  <u>Merits/Advantages:</u>

  - It verifies Ohm's Law.
  - It derives Wiedemann - Franz Law
  - It explains electrical & thermal conductivities of metals.
  - It explains optical properties of metals.

  <u>Demerits/Drawbacks/Limitations:</u> It fails to explain

  - The electrical conductivity of semiconductors and insulators.
  - Acc. to this theory, $\sigma = ne^2\tau/m \rightarrow \rho = m/ne^2\tau$ which is not satisfactory.
  - The temperature variation of electrical conductivity at low temperature.
  - The concept of specific heat of metals and the mean free paths of the electrons.
  - The phenomenon like Photoelectric effect, Compton effect and Blackbody radiation
  - The temperature dependence of paramagnetic susceptibility and Ferromagnetism.
  - According to this theory, the relation between density and temperature is $\rho \propto \sqrt{T}$
  - But according to experiment, $\rho \propto T$ only. Which is not supported.

<u>(ii) QUANTUM FREE ELECTRON THEORY OF SOLIDS:</u>

- In 1928 Sommerfeld developed the Quantum free electron theory by applying the principles of Quantum mechanics.
- He explained this theory by choosing Fermi Dirac quantum statistics instead of Maxwell-Boltzmann statistics used by Lorentz.
- According to him, the free electrons move with a constant potential.

  <u>Assumptions/Postulates/Salient features:</u>
- Sommerfeld proposed the Quantum free electron theory of solids by using some important assumptions, as follows:

- Valence electrons move freely with a constant potential within the boundaries of metal and are prevented from escaping the metal at the boundaries. Hence electrons are trapped in a potential well.
- The distribution of e's in various allowed energy levels occurs as per Pauli Exclusion principle.
- The electrons can not have all energies but will have discrete energies of electron,
- $E_n = n^2h^2/8ma^2$, where: $n = 1, 2, 3...$

  a = dimension of metal.
- The attraction between the free electrons and lattice ions are ignored as well as the repulsion between electrons themselves are ignored.
- The distribution of energy among the free electrons is according to Fermi-Dirac statistics by F-D distribution function:

  $$F(E) = 1 / (e^{(E-Ef)/KT} + 1)$$
- The total energy depends only on the sum of the squares of quantum numbers like

  $$n^2 = n_x^2 + n_y^2 + n_z^2$$
- The different combinations of n_x, n_y and n_z integers may give different stationary states corresponding to the same energy value. These states of energy levels are known as degenerate states.
- The energy levels of free electrons are quantized.
- Schrodinger Time Independent wave Equation is applied to find the possible energy values of free electrons.
- The problem is like that of particles present in a 1-D potential box.

Merits/Advantages:

- It successfully explains the electrical and thermal conductivity of metals.
- It also explains temperature dependence & conductivity of metals.
- It explains the specific heat of metals and thermionic phenomena.
- It explains the magnetic susceptibility of metals, photoelectric effect, compton effect and black body radiation
- It gives the correct mathematical expression for the thermal conductivity of metals.
- It successfully explained the electrical conductivity of free electrons.

Demerits/Drawbacks/Limitations:

- It is unable to explain why the metallic properties exhibited by only certain crystals.
- It is unable to explain why the atomic arrays in metallic crystals should prefer certain structures only.
- This theory fails to distinguish between metal, semiconductor and insulator.
- It also fails to explain the +ve value of "Hall Coefficient".
- According to this theory, only 2-e's are present in the Fermi level, and they are responsible for conduction which is not true.