UNIT – III

Electrical Properties of Solids

The electron theory of solids aims to explain the structures and properties of solids through their electronic structure; it was developed in three main stages:

(1) **Classical Free electron theory**: Drude and Lorentz developed this theory in 1900, which assumed that metals contain free electrons obeying the laws of classical mechanics.

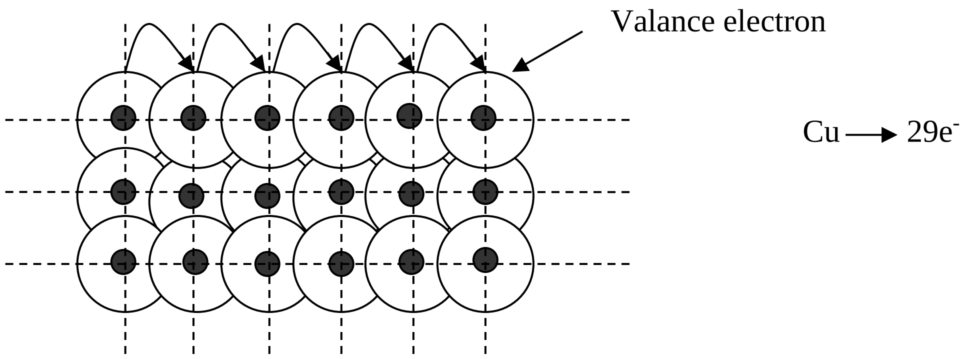
(2) **Quantum Free electron theory**: Sommerfeld developed this theory in 1928, which assumed that the free electrons obey quantum laws.

(3) **Zone theory**: In 1928, Bloch proposed this theory according to which the electrons move in a periodic potential provided by the lattice. This theory was able to explain almost all properties of materials. This theory was called as "Band theory of solids" because it explained the mechanism of superconductivity based on the band model.

Classical Free electron theory of metals [Drude – Lorentz classical theory/ Drude's model]:

The outstanding properties of metals are their high electrical and thermal conductivities. We can understand such important physical properties of metals in terms of the free electron model.

Drude, in 1900 postulated that the metal consists of positive ion cores with valence electrons moving freely among these cores. The electrons are however bound to move within the metal due to electrostatic attraction between the positive ion cores and the electrons. The potential field of these ion cores, which is responsible for such an interaction, is assumed to be constant throughout the metal and the mutual repulsion among the electrons is neglected. The behaviour of free electrons moving inside the metals is considered to be similar to that of atoms or molecules in a perfect gas. These free electrons are therefore referred as free electron gas. These electrons are responsible for conduction of electricity through metals. Since the conduction electrons move in a uniform electrostatic field of ion cores, their potential energy remains constant, normally taken as zero. Thus the total energy of conduction electrons is equal to its kinetic energy.



***<u>Assumptions of the classical free electron theory</u>*:**

1. A metal is imagined as a structure of 3 –dimensional array of ions, in between which there are freely moving valence electrons confined to the body of the material, and are called conduction electrons or free electrons.
2. These free electrons move in random directions and make collisions with either +ve ions fixed in the lattice or other free electrons. All the collisions are elastic and hence there is no loss of energy.
3. The free electrons are treated as equivalent to gas molecules, and thus they are assumed to obey the laws of kinetic theory of gases. Thus the energy is given by $\left(\frac{3}{2}\right)KT$ and it is related to kinetic energy as $\left(\frac{3}{2}\right)KT = \frac{1}{2}mv_{+n}^{2}$

   v_{+n} is the thermal velocity of the electrons.
4. The electric field due to the ionic cores is taken to be constant throughout the body of the metal and the effect of repulsion between the electrons is considered insignificant.
5. The potential energy of electrons moving through metals is constant, which for simplicity and mathematical convenience has been taken as zero. Therefore the total energy of electrons is equal to their kinetic energy.
6. The electric current in a metal due to an applied field is a consequence of the drift velocity in a direction opposite to the direction of the field.

Based on Drude's considerations Lorentz in 1909 postulated that electrons gas obey Maxwell – Boltzmann statistics under equilibrium conditions. The combined ideas of Drude and Lorentz constitute Drude – Lorentz theory.

Merits:

1) Successfully explains the validity of Ohm's law and electrical conductivity of metals.
2) Theory also explains the high luster and complete opacity of metals.
3) It could explain thermal conductivity of metals and Wiedemann-Franz law.

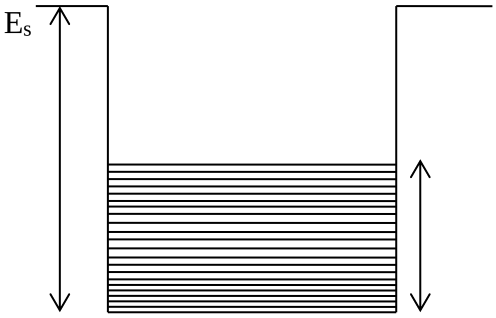
Drawbacks/Failures/Limits of classical free electron theory:

The drawbacks of the classical free electron theory are listed as follows:

1) The theory predicts that resistivity varies as $\sqrt{T}$, but actually it is found to vary linearly with temperature.
2) Theory predicts that conductivity $\sigma \alpha n$, but it does not hold good. Where n →e^- concentration.
3) At low temperatures, the electrical conductivity, σ and thermal conductivity, k varies in different ways. Therefore, the ratio (k/ σT) is not a constant at these temperatures, but according to classical free electron theory it is constant.
4) Classical theory states that all free electrons absorb the total supplied energy, but quantum theory states that only few electrons absorb the supplied energy.
5) The electrical conductivity of semiconductors and insulators cannot be explained by this theory.
6) The concepts of Photoelectric effect, Compton effect and black body radiation cannot be explained on the basis of this theory because these phenomenon are based on quantum theory.
7) Classical theory failed to explain the paramagnetic susceptibility (χ) of the conduction electrons. According to theory, χ is inversely proportional to temperature. But, experimental results show that paramagnetism is independent of temperature. Also Ferromagnetism cannot be explained by this theory.

Quantum free electron theory:

In 1928, by applying quantum mechanical principles, Sommerfeld succeeded in overcoming many of the drawbacks of the classical free electrons theory while retaining all its essential features. He realized the role played by Pauli's Exclusion principle in restricting the energy values of electron and the theory proposed by him is known as Quantum free electron theory. He suggested that Maxwell – Boltzmann statistics is classical and it is applicable only for ordinary gas not to electron gas. He suggested that Fermi – Dirac statistics holds good for electron gas. The velocity and energy distribution of the free electrons are governed by the Fermi-Dirac distribution function. An electron in a metal finds itself in the field of all nuclei and other electrons. The potential energy for such an electron may therefore be expected to be periodic. The periodicity is being that of the lattice. As per Sommerfield model, the interior of the metal can be represented by potential energy box of depth 'E_s' as shown in fig. It consists of discrete set of energy levels, i.e., energy levels of electrons are quantized. Potential energy of an electron inside the metal is lower than that of an electron outside the metal.



Assumptions/Postulates of Quantum free electron theory:

1. The energy values of the conduction electrons are quantized. The allowed energy level values are realized in terms of a set of energy levels.
2. The distribution of electrons in the various allowed energy levels occurs as per Pauli Exclusion Principle.

   However, the following assumptions of classical free electron theory continue to be applicable in quantum free electron theory also.
3. The free electrons travel in a constant potential inside the metal, but stay confined within its boundaries.
4. The attraction between the free electrons and the lattice ions, and the repulsion between the electrons themselves are ignored.

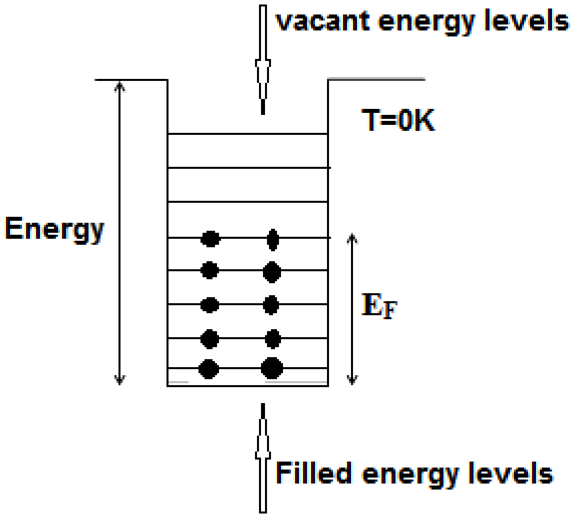
Fermi energy:

Fermi energy level is the maximum energy level upto which the electrons can be filled at 0K and the energy corresponding to this level is called as Fermi energy, E_F.

$$E_{F_o} = \left(\frac{h^2}{8m}\right)\left(\frac{3n}{\pi}\right)^{2/3} = Bn^{2/3}$$

where B= $\left(\frac{h^2}{8m}\right)\left(\frac{3}{\pi}\right)^{2/3}$ is constant

B = 5.85 x 10^{-38} J.



We know that for a metal containing N atoms there will be N allowed energy levels in each band. As per the Pauli Exclusion Principle, each energy level can accommodate a maximum of two electrons, one with spin up, ↑ and other one with spin down, ↓ as shown in above Fig.

The important features of Fermi energy level are as follows:

(1) Fermi level acts as reference level that separates the vacant and filled states at 0K.

(2) At absolute zero, all the quantum states below E_F are occupied while all the quantum states having energies greater that E_F are unoccupied.

(3) When the temperature is increased, few electrons gain the thermal energy and jump to the higher unoccupied energy levels.

(4) Fermi energy denotes the maximum kinetic energy that can possess at 0K.

(5) Fermi energy levels are used to explain the flow of electrons when two metals are brought into contact.

Fermi factor:

Effect of temperature on the occupancy of energy levels can be discussed with the help of Fermi – Dirac statistics. It is apparent that, for temperature greater than 0K, Fermi level may not be the topmost filled level. Since some of the electrons from the filled energy levels may be excited to the higher levels. Thus some of the levels below E_{Fo} would be empty. While some above it would be occupied.

Fermi has shown that the probability that a particular quantum state is occupied is given by so called Fermi factor 'f (E)' given by

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

Fermi factor is the distribution function which gives the probability of occupancy of a given energy state for a material in thermal equilibrium in terms of the Fermi energy, Boltzmann constant and the temperature.

Effect of temperature on Fermi factor (Dependence of Fermi factor on temperature and effect on occupancy of energy levels):

The dependence of Fermi factor on temperature and the effect on occupancy of energy levels is as shown in below Fig. Let us consider the different cases of distribution as follows:

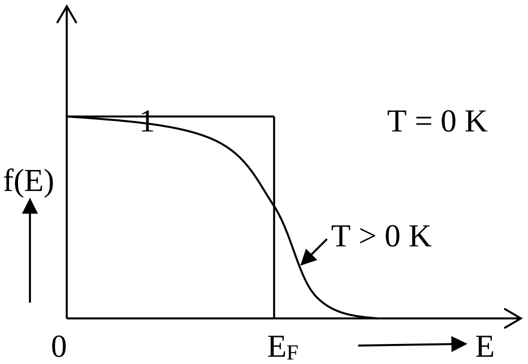
i) Probability of occupancy for E < E_F at O K

When T=0K and E < E_F, we have for the probability,

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

$f(E) = 1$ for $E < E_F$

∴ At T= 0 K, all the energy levels below the Fermi level are occupied.



ii) Probability of occupancy for E > E_F at T = 0 K

When T=0K and E > E_F, we have for the probability,

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

∴ $f(E) = 0$ for $E > E_F$

∴ At T = 0 K, all the energy levels above Fermi level are unoccupied.

In view of the above two cases, at T = 0 K, the variation of f(E) for different energy values, becomes a step function, as shown in Fig.

iii) Probability of occupancy at ordinary temperatures

At ordinary temperatures, though the value of probability remains 1 for $E \ll E_F$ it starts decreasing from 1 as the values of E become closer to E_F (in Fig. see the curve corresponding to T>0K).

The value of f(E) becomes ½ at $E = E_F$.

This is because, for $E = E_F$,

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

Further, for $E > E_F$, the probability value falls off to zero rapidly.

This means to say that, the highest occupied energy levels in metal at absolute zero has an energy equal to E_F.

As temperature increases from absolute zero, electrons occupying states lying near E_F can gain sufficient thermal energy to move into the higher unoccupied states. The actual change in energy is very small. Since an electron can gain only few 'KT' of energy. Resulting change in the curve is also shown in Fig.

Fermi energy at T > 0 K

The Fermi energy E_F, at any temperature T in general can be expressed in terms of 'E_{Fo}' through the relation.

$$E_F = E_{F_o}\left[1 - \frac{\pi^2}{12}\left(\frac{KT}{E_{F_o}}\right)^2\right]$$

Except at extremely high temperatures, the second term within the brackets is very small compared to unity.

$\therefore E_F \approx E_{Fo}$

Hence, the values of E_{Fo} can be taken to be essentially equal to E_F itself.

Density of States:

- The quantity which represents the number of allowed electron or hole states per volume at a given energy is called density of states

- The Fermi function does not by itself gives us the number of electrons, which have certain energy. It gives us only the probability of occupation of an energy state by a single electron.

- Since even at the highest energy the difference between neighboring energy levels is as small as 10^{-6} eV, we can say that in a macroscopically small energy interval dE, there are still many discrete energy levels.

- To know the actual number of electrons with a given energy, one must know the number of states in the system, which has the energy under consideration.

- Then by multiplying the number of states by the probability of occupation, we get the actual number of electrons.

Fermi temperature (T_F):

It is the temperature at which the average thermal energy of the free electron in a solid becomes equal to the Fermi energy at 0 K. But the thermal energy possessed by electrons is given by the product kT.

$\therefore$ when $T = T_F$, the equation $E_{Fo} = kT_F$ is satisfied. But for all practical purposes, $E_{Fo} \approx E_F$

$$\therefore kT_F = E_F \qquad \text{or } T_F = \frac{E_F}{k}$$

The Fermi temperature is only a theoretical concept, since at ordinary temperatures; it is not possible for the electrons to receive thermal energy in a magnitude of E_F.

Fermi velocity:

The energy of the electrons which are at the Fermi level is E_F. The velocity of the electrons which occupy the Fermi level is called the Fermi velocity V_F.

$$\therefore E_F = \tfrac{1}{2} m v_F^2$$

$$\text{or } V_F = \left(\frac{2E_F}{m}\right)^{1/2}$$

Quantum expression for electrical conductivity:

Sommerfeld realized that, the free electrons obey Fermi – Dirac statistics. Hence by applying Fermi – Dirac statistics and by using Boltzmann transport equation, the expression for electrical conductivity of metals is obtained as,

$$\therefore \sigma = \frac{ne^2\lambda}{m^*V_F}$$

Where m^* – effective mass of electrons

λ – mean free path

V_F – Fermi velocity

Similarly electrical resistivity of the metal is given by

$$\therefore \rho = \frac{m^*V_F}{ne^2\lambda}$$

Merits of quantum free electron theory:

This theory explains most of the drawbacks of the classical free electron theory.

1) **Specific Heat:**

Only those electrons close to E_F can absorb the heat energy. We can show using quantum free electron theory that,

$$C_v = \left(\frac{2k}{E_F}\right)RT$$

Taking a typical value of E_F = 5 eV (For metals E_F varies from 1 to 10 eV), we get

$$\left(\frac{2k}{E_F}\right) = 10^{-4}$$

$\therefore C_v = 10^{-4}$ RT, which confirms the experimentally observed values.

Thus the quantum free electron theory is successful in explaining the low specific heat value for conduction electrons.

2) **Temperature dependence of electrical resistivity.**

The experimentally observed fact is that the electrical resistivity has dependence on T, but not on $\sqrt{T}$.

As per quantum free electron theory, the electrical resistivity for metals is given by

$$\therefore \rho = \frac{m^* V_F}{ne^2 \lambda} \quad \text{--------- (1)}$$

Also as per theory E_F and V_F are independent of temperature. But λ (mean free path) is dependent on temperature.

If 'r' is the amplitude of vibration of ions in all the direction, then the area of cross section that blocks the electron is πr^2. If this area is more, then λ becomes small.

$$\therefore \lambda \, \alpha \, \frac{1}{\pi r^2} \quad \text{----------- (2)}$$

Now considering the facts that,

i) The energy of vibrating body is proportional to r^2

ii) The energy of ions is due to thermal energy, and

iii) The thermal energy is proportional to T, so

$$r^2 \, \alpha \, T \qquad \Rightarrow \qquad \lambda \, \alpha \, \frac{1}{T} \quad \text{------ (3)}$$

So equation (1) becomes,

$\therefore \ \rho \, \alpha \, T$ Which is true experimentally.

3. Electrical conductivity and electron concentration

According to classical free electron theory σ α n, the concentration of electrons. But Aluminium and Gallium, which has 3 free electrons / atom have lower conductivity than metals such as copper and silver which posses only 1 free electron / atom.

As per quantum free electron theory,

$$\sigma = \frac{ne^2}{m^*}\left(\frac{\lambda}{V_F}\right)$$

From the above equation it is clear that, the value of 'σ' depends on both n and the ratio $\left(\frac{\lambda}{V_F}\right)$.

If we compare the cases of copper and aluminium, the value of n for aluminium is 2.13 times higher than that of copper. But the value of $\left(\frac{\lambda}{V_F}\right)$ for copper is about 3.73 times higher than that of aluminium. Thus the conductivity of copper exceeds that of aluminium.

Electron concentration (n):

The number of free electrons per unit volume (n) can be calculated using the relation

$$\mathrm{n} = \frac{\text{number of free electrons per atom} \times \mathrm{N_A} \times \mathrm{D}}{\text{atomic weight}}$$

Where N_A is Avogadro's number = 6.025 x 10^{26} / k mole

D is density of the material

Some of the terms and formulas used are:

1. Electrical conductivity: $\sigma = \frac{ne^2}{m}\left(\frac{\lambda}{V_F}\right) = \sigma = \frac{ne^2\tau_r}{m}$

τ_r is relaxation time

2. Drift velocity: The average velocity acquired by an electron in the presence of an electric field is known as drift velocity.

$$v_d = \frac{eE\tau_r}{m}$$

3. Relaxation time (τ_r): The average time taken by electron to attain steady-state velocity from zero velocity is called relaxation time.

4. Mean free path (λ): In the absence of electric field, the average distance travelled by the electron between any two successive collisions is known as mean free path,

$$\lambda = v\tau_r$$

5. Mobility (μ): The mobility of charge carrier is defined as the average velocity of the carge carrier per unit applied electric field intensity.