UNIT-2

Chapter-1   ELECTRON THEORY OF METALS

FREE ELECTRON THEORY INTRODUCTION:-

Drudge and Lorentz developed classical free election theory to explain many special properties like conduction of electricity, thermal conductivity, magnetic properties etc of metals later Somerfield improved the version by applying quantum principles next Bloch started band theory which consider the interaction between the positive ions centers and the free electrons. The band theory could explain the behavior of solids with respect to the conduction of electricity through them.

Free electron theory is required because only electrons are responsible for conduction in metals such electrons which responsible for conduction phenomenon are called free electrons or conduction electron.

Classical free electron theory or electron gas model

Drudge and Lorentz proposed free electron theory of metals on the basis of some assumptions

1) In conductors (metals), there are large numbers of free electrons moving freely within the metal i.e. the free electrons or valence electrons are free to move in the metal like gaseous molecules, because nuclei occupy nearly 15% metal space and the remaining 85% space is available for the electrons to move.

2) Since free electrons behave like gaseous molecules, applying the laws of kinetic theory of gases. The mean K.E of a free E is equal to that of a gas molecule at same temperature.

3) In the absence of any electric field, the ES move randomly while undergoing scattering at +ve ion   centers. The collisions are regarded as elastic (no loss of energy).

4) The electron speeds are distributed according to the max well- Boltzmann distribution law.

5) When an electric filed is applied, the free electrons are accelerated in a direction apposite to that of the field.

6) The free electrons are cornfield to the metal due to surface potential.

7) The electrostatic force of attraction B/W the + ve ion cores and the free electrons is assumed to be negligible. The approximation is justified in the sense that the free electrons are move at a greater speed as they approach the electrons is also neglected in the concept of free electron theory.

RMS VELOCITY OF FREE ELECTRONS:-

RMS velocity $C = \frac{\sqrt{3kt}}{m}$

Relaxation time (TR):

As the electric filed is switched off, the electron speed gradually decreases with time due to the scattering of free electrons in the metal by +ve ions.

According to the law of decay of velocities, the velocity of the electrons at any instance `+` is given by the expression,

$V = voe^{-t/Tr}$

Here Tr is called mean or relaxation time Vo is the initial velocity at += 0.

A+ + = Tr, the above equation becomes

V= Vo/e

i.e the relaxation time is defined as the time required for the electrons to reduce its velocity to 1/e of its initial value (directional velocity)

RELATION BETWEEN RELAXATION TIME AND COLLISION TIME:-

Consider a conduction electron travelling inside a metal in the direction AB with a velocity `V` let it be scattered by
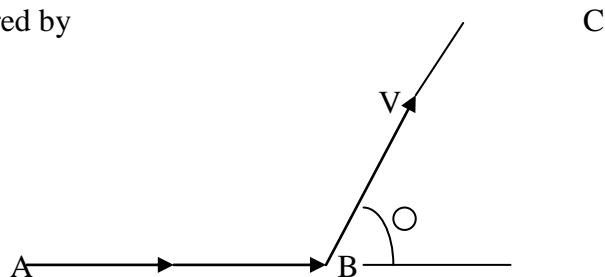
an ion core located by `B` as a result, the electron travels along BC With the same velocity

making an angle `Q` with the Original Direction `Q` is called scattering angle.

The value of `Q` is likely to be different for different collisions. The average value of coso taken avers Avery large number of collisions is represented by <coso>. Then the relaxation time Tr is related to the mean collision time according to the relation.

$$\text{Tr} = \frac{T}{1 - <coso>}$$

If the scattering is equally possible is all directions (symmetric scattering) then the average scattering angle of a large number of scattering will be $\cos\phi = 90^0$, then $<\cos\phi> = 0$ and Tr = T. i.e. the mean collisions time can be treated as relaxation time itself.

MEAN FREE PATH (∧):-

Let us consider S1, S2, and S3……. Etc are the free paths between the first, second, third etc. collisions, the mean free path `∧` is defined as the average of all the free paths.

$$∧ = (s1+s2+s3+………+Sn)/n$$

Mean free path is obtained as the product of rms velocity and mean time Tr.

$$\lambda = C^- \text{ x } T$$

$$\text{i.e } C^- = \frac{\sqrt{3kt}}{m} \text{ , } T = \frac{m}{\int ne^2}$$

$$\lambda = \frac{\sqrt{3kt}}{m} \text{ x } \frac{m}{\int ne^2}$$

$$\lambda = \frac{\sqrt{3mkT}}{\int ne^2} \text{ .}$$

From the above expression, the resistibility `S` is Proportional to square root of temperature in according with classical theory. But experimentally it is no true.

Relation between relaxation time and mobility is

$$\mu = \frac{Tr}{m} = \frac{1}{\int ne}$$

DRIFT VELOCITY OF AN ELECTRON IN A METAL:-

When a current `I` is passed through a metallic wire, the electrons undergo multiple scattering with the + ve ions and move in a direction opposite to the current direction.
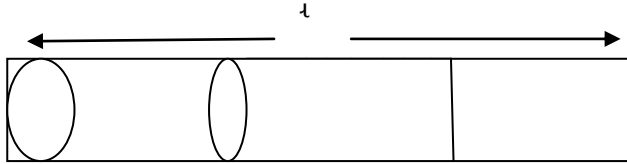
Let us consider a conductor of cross – sectional area `A` and length `l`, so that lA is the volume of the conductor .if there are length `N` Number of electrons for unit volume of the metal, then the total number of electrons in the specimen in ` NLA`. If `E` is the charge of the electron , then the total charge `Q` due to all the free electrons in the sample.

$$q = nAle.$$

Let `t` be the time taken by the e⁻ for moving from one end of the conductor to the other end. During this time, the charge crossed at any point in the conductor is q. the flowing through the conductor.

$$i = \frac{charge}{time} = \frac{q}{t} = \frac{nAle}{t}$$

If v is the drift velocity of the electron, then the time required for the electron to move from one end to the other end is t= distance / velocity = l/v.

Replace l/v = t

$$i = \frac{nAle}{(l/v)} = nAve.$$

$$\therefore \text{Drift velocity } V = \frac{i}{nAe}$$

But the current density J is defend as current flowing per unit cross sectional area,

$$J = \frac{i}{A}$$

$$\therefore V = \frac{J}{ne}$$

The drift velocity increases with the increase of current density or current and decreases with the increase of electron concentration `n`

RELATION BETWEEN DRIFT VELOCITY AND MOBILITY OF THE ELECTRON:-

According to the ohm`s law R = v/i , where `v` is the potential difference between the ends of a conductor, `i` is the current flowing though the conductor and `R` is the resistance.

The ohm`s law can otherwise be stated as E/J = P called microscopic ohm`s law . here `E` is the electric filed, `J` is the current density flowing through the conductor and `p` is the resistivity or specific resistance of the metal

V = j/ne   and   j = E/P

Substitute `J` in the expression foe `v` we get

$$V = \frac{E}{\int ne} .$$

i.e the drift velocity is proportional to applied electric field.

V∝E => V = μE

the proportionality constant μ is called the mobility of

$$\mu = \frac{1}{\int ne} .$$

when E = 1, then V = μ, mobility is defined as the drift velocity of e⁻ when the applied electric field is unity.

Expression for resistivity $\int = \frac{1}{\mu ne}$

Conductivity σ = μne.

FAILURE OF THE CLASSICAL FREE ELECTRON THEORY:-

1) **Heat capacities :-** the internal energy of a molar substances
$$U = \frac{3}{2} KTN$$
Molar specific heat + c v =3/2kn=3/2R.

'N' is the Alvarado number , K is Boltzmann constant and `R` is the universal gas constant .the molar specific heat is 1.5 R theoretically where as the experimental value obtained is too low . This is due to the fact that all free electrons do not contribute significantly to thermal or electrical conductivity.

There fore classical free e⁻ theory can`t hold good.

2) **Mean free path :-** It is calculated using the formula

λ = C⁻ x T

$$\lambda = \frac{\sqrt{3kt}}{m} \; X \; \frac{m}{\int ne^2}$$

39

$$\lambda = \frac{\sqrt{3kTm}}{\int ne^2} .$$

For cu at 20° c $\int$ = 1.69x 10⁻ 8 ohm-mλ

e⁻ concentration n = 8.5 x 10^{28}/m3.

The experimental `λ`was obtained nearly 10 times its theoretical valve . so classical theory could not explain the large variability in λ values

3) **RESISTIVITY:-**   According to the classical free electron theory ,the resistivity   is given by the equation.

$$\int = \frac{\sqrt{3mTk}}{\lambda ne^2}.$$

Which means the resistivity is proportional to the square root of absolute temperature. But according to the at room temperature it does not change up to 10K and in intermediate range of temperature $\int$ is proportional to T^5 .

4) The conductivity of semiconductors and Insulators can not be explained by the free electron theory.

QUANTUM FREE ELECTRON THEORY:-

In 1929, Somerfield stated to apply quantum mechanics to explain conductivity phenomenon in metal. He has improved the Drude ع Lorentz theory by quantizing the free electron energy and retaining the classical concept of free motion of electron at a random .

ASSUMPTIONS:-

1) The electrons are free to move within the metal like gaseous molecules. They are confined to the metal due to surface potential.
2) The velocity distribution of the free electrons is described by Fermi-Divac Statistics because electrons are spin half particles.
3) The free electrons would be go into the different energy levels by following Pauli's exclusion Principle which states that no two electrons have same set of Quantum numbers.
4) The motion of electrons is associated with a complex wave called matter wave, according to Debroglie hypothesis.
5) The electrons cannot have all energies but will have discrete energies according to

the equation

$$E = n^2 h^2 / 8ma^2$$

'a' is the dimensions of the metal 'h' is plank's constant and 'n' is the integer starts from 1.

Energy levels – Fermi Dirac Distribution:

According to the Quantum theory Quantization leads to discrete energy levels. The electrons are distribution among these energy levels according to Pauli's exclusions principle it allows a maximum number of two electrons with spins in opposite directors in any energy level. The pair of electrons, one with sign up and the other with sign down occupy the lowest energy level. The next pair occupies the next level. This process goes on until all the electrons in the metal occupy their position.

But there will be many more allowed energy levels available for occupation. The highest energy level that can be occupied at ok is called Fermi energy level. I t is denoted by E f . When the metal is not under the influence of an external field, all the levels above the Fermi energy level are empty; those lying below are completely filled.

#Energy levels and order of filling levels in a metal.

The energy associated with Ef is called Fermi Energy.

The speed of the electron occupying the Fermi level is called Fermi Velocity.

Fermi – Dirac Distribution:

When the material is at a temperature higher than OK, it receives thermal energy from surroundings i.e. electrons are thermally excited. As a result, they move into the higher energy levels which are unoccupied at OK. The occupation obeys a statistical distribution called Fermi – Dirac distribution law.

According to this distribution law, the probability f(E) that a given energy state E is occupied at a temperature T is given by $\dfrac{1}{\exp(E-Ef)/KT \, +1}$

Here f(E) is called Fermi – Dirac probability function. It indicates that the fraction of all energy state (E) occupied under thermal equilibrium 'K' is Boltzmann constant.

Expression for Fermi Energy level(Ef)

$$Ef = 3.65 * 10^{-19} \, n^{2/3}$$

Where n is concentration of electrons.

Drawbacks of Quantum free electron theory :

(1) Lorentz Number : The Lorentz number in the Quantum free electron theory is given by

$$\underline{L} = \left(\frac{\pi^2}{3}\right)(K/e)^2$$

Here 'K' is Boltzmann constant and 'e' is charge of electron the observed Lorentz number is greater than the theoretical value as calculated from the above expression. i.e the Lorentz number is found to be vary with temperature. When metals are heated, the positive ions cores vibrate about their mean position and generate photons. The Phonons along with the free electrons carry some of the heat supplied to the metal. This must be the cause of large difference between observed and theoretical Lorentz number.

(2) Conductivity : According to Quantum free electron theory, the conductivity of a metal is

$$\sigma = \mu n e$$

Here 'μ' is the mobility of electron, 'n' is the free electron concentration and 'e' is the electron charge.
    According to the above equation, polyvalent metals like Aluminium (Al) should be more conductive than mono valent metals like copper (cu). But experimentally it is not so.

(3) Hall co efficient: According to the free electron theory, the hall coefficients for all metals is negative where as there are certain metals like Be, Cd, Zn for which the Hall coefficient is + ve

(4) Free electron theory could not explain why certain substances behave as insulators and some other substances as semiconductors, inspite of they have free electrons in them.

Chapter2:Band Theory of Solids

Introduction: According to Quantum free Theory of methods a conduction E in a metal experiences constant (or zero) potential and free to move within the crystal but will not come out the metal. This theory successfully explains electrical conductivity, specific heat etc but fails to explain many other physical properties, for example (I) Difference between conductors, insulators and semiconductors.

To overcome the above problems, the periodic potentials due to +ve ions in a metal have been considered.

Electrons in a periodic potential –Bloch Theorem:

   An E moves through + ve ions, it experiences varying potential. The potential of the E at the +ve ions site is zero and is maximum in between two +ve ions sites.

The potential experienced by an e⁻, then it passes though +ve ions shown in life.
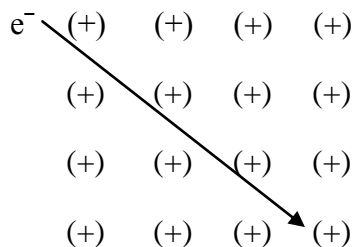
i.e The potential experienced by an E's in shown in Fig known as real periodic potential variation
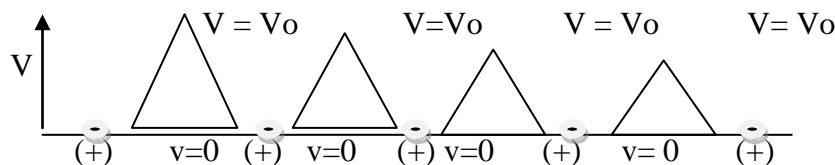
To study the motion of E in lattice and the energy states it can occupy, Schrodinger equation is necessary

For making simplicity, Koenig-penny introduced a simple model for the shape of potential variation. The potential inside the crystal is approximated to the shape of rectangular steps.

KRONIG PENNY MODEL:-

Kronig – penny consider a periodic management of potential walls and barriers to represent the potential variation exhibited by the E , Known as Ideal-periodic square well potential as shown in figure. New forms of boundary conditions are developed to obtain a simple solution known as cyclic or periodic boundary conditions.

Conclusion From Kronig –Penny Model:

1).The Energy spectrum of E consists of an infinite number of allowed energy bonds separated by intervals in which, there are no allowed energy levels. These are known as forbidden regions.

2). When α a increase, the first term of eq(1) on LHS decrease , so that the width of the allowed energy bonds is increased and forbidden energy regions become narrow.

3). The width of the allowed bond decrease with the increase of p value. When p → α, the allowed energy regions become infinity narrow and the energy spectrum becomes line spectrum.

Validity ∴ when p ⟶ o, cos α a = cos k a

$$i.e\ x^2 = x^2$$

$$i.e\ \frac{8\pi^2 m}{h^2}\ E = k^2$$

$$\Rightarrow E = \frac{h^2\ k^2}{8\pi^2 m}$$

Here k = $\frac{2\pi}{\lambda}$, $\Rightarrow E = \frac{h^2}{8\pi^2 m}\ \frac{4\pi^2}{\lambda^2}$

$$i.e\ E = (\frac{h^2}{2m})\frac{1}{\lambda^2}$$

Here $\lambda = \frac{h}{p}$, ie E = $(\frac{h^2}{2m})\ \frac{p^2}{h^2}$

Here p = mv_1 $\Rightarrow$ E = $(\frac{h^2}{2m})\ \frac{m^2\ v^2}{h^2}$

$$E = \frac{1}{2}\ mv^2.$$

The wave functions associated with this model can be calculated by solving Schrödinger's eq for two regions 1 and 2.

(1) ie $\frac{d^2 4}{dx^2} + \frac{8\pi^2 m}{h^2}\ E\ 4 = 0,\ 0 < x < a$

$\frac{d^2 4}{dx^2} + x^2\ 4 = 0,\ x^2 = \frac{8\pi^2 m}{h^2}\ E$

(2) $\frac{d^2 4}{dx^2} = \frac{8\pi^2 m}{h^2}\ (v_0)\ 4 = 0\ ,\ -b < x < o$

(3) $\frac{d^2 4}{dx^2} - \beta^2\ 4 = 0\ ,\ \beta^2 = \frac{8\pi^2 m}{h^2}\ (v_0 - E)$

These two eq are solved by using Block and Koenig-penny models, and applying Boundary conditions the solution is

$$\frac{\beta^2 - \alpha^2}{2\alpha\beta} \sin\alpha a \, \sin h \, \beta b + \cos\alpha a \, \cosh\beta b = \cos k(a+b)$$

To provide simplest solution, Koenig-penny assumed that   b→o

$$\sin h \, \beta b \longrightarrow \beta b$$

$$\cos h \, \beta b \longrightarrow 1$$

i.e $\frac{\beta^2 - \alpha^2}{2\alpha\beta} \sin\alpha a \, \beta b + \cos\alpha a = \cos k \, a$

here $\beta^2 - \alpha^2 = \frac{8\pi^2 m}{h^2}(v_0 - 2E) = \frac{8\pi^2 m}{h^2} v_0$, since $v_0 \gg E$

i.e $\left(\frac{8\pi^2 m}{h^2} \frac{v_0}{2\alpha\beta}\right) \sin\alpha a \, \beta b + \cos\alpha a = \cos k \, a$

i.e multiplying this eq with $\frac{\alpha a}{\alpha a}$ then

$\frac{m v_0 ba}{h^2} \frac{\sin\alpha a}{\alpha a} + \cos\alpha a = \cos ka$

i.e $p \, \frac{\sin\alpha a}{\alpha a} + \cos\alpha a = \cos ka$ ——————— 1

Here $p = \frac{m v_0 ba}{h^2}$ is scattering power

And 'v_0 b' is known as barrier strength.

The LHS and RHS of eq (1) are equal, then LHS of eq(1) on y-axis of a function of αa,in value p=3 /2. The RHS of 1. i.e' cos ka can take values between +1to-1.so the LHS of each 1. Is also restricted to vary between =1.

Chapter 3 SEMICODUCTORS

Energy bond Formation in solids:

- In isolated atom, the e⁻s are tightly bond and have discrete, shape energy levels.


E_1
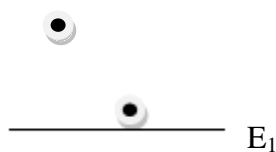
- When two identical atoms are brought closed the outermost orbits of these atoms overlap and intersects the wave functions of the E of the different atoms begin to overlap, then the energy levels corresponding to those wave functions split in to two.

E_1
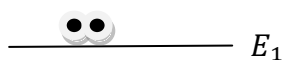
$$\underline{\qquad\qquad} E_2$$

- If more atoms brought together more levels are formed and for a solid of N atoms, each of these energy levels of an atoms splits into N levels of energy.

GE
N atoms
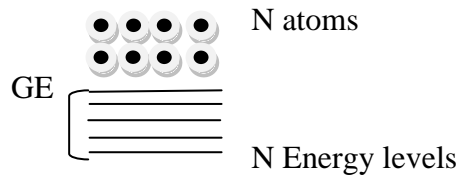
N Energy levels

The levels are so close together that they form almost continuous bond.

-The E first occupies lower energy bonds and are no importance in determining many of the physical properties of solid.

-These E present in higher energy bonds are important in determining many of the physical of solids.

-These two allowed energy bonds are called as valence and conduction bonds.

-The bond corresponding to the outermost orbit is called conduction bond and the gap between those two allowed bonds is called forbidden energy gap are bond gap.

Classification of solids:

Solids are classified into three types based on energy gap.

(1) Conductors(metal)
(2) Insulators
(3) Semiconductors

-In case of conductors, valence bond and conduction bond almost overlap each other and no significance in energy gap. The two allowed bond are separated by semi energy level.

-Here there is no role in Eg, as a result conducting is high.

CB

VB
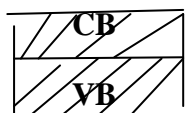
-In case insulator, valence bond and conduction bond are separated by large energy gap, Hence conductivity is zero.

-In case semiconductors, the valence bond and conduction bond are separated by relatively narrow energy gap, hence the conductivity lies in between conductors and insulators.

Effective mass of the E moving in a crystal lattice:

-Consider a crystal (metal) be subjected to an electric field 'E', so the experienced by an E of charge E is Ee.

-Acceleration of the E in the crystal is given by a=f/m=Ee/m

-But acceleration of the E is not constant because of the velocity changes i.e The E move faster near the +ve ions in the crystal. Since the electric field and charge of the E are invariant, the effective mass Mh of the E to change accordingly.

i.e F=mha   (1)

-Consider a particle velocity 'v' is equal to group velocity 'vg' of a wave packet, then

$V = vg = \frac{dw}{dk}$, w= angular frequency, k= wave propagation vector

$W = 2\pi v$ $dw = 2\pi dv$

Frequency of the complex wave v=E/n   dv=1/ndE

$dw = 2\pi \, de/h = de/h$

$\therefore V = dw/dk = 1/h \, de/dk$

SO, $a = \frac{dk}{dt} = \left(\frac{1}{h}\right) \frac{d^2E}{dk\,dt}$

$a = \frac{1}{h} \frac{d^2E}{dk^2} \left(\frac{dk}{dt}\right)$

Wove propagation vector $k = \frac{2\pi}{\lambda}$

$$k = \frac{2\pi}{h} \quad P = \frac{p}{h}$$

`P` is momentum, `$\lambda$` is debrogle   wave length

$\therefore \frac{dk}{dt} = \frac{1}{h} \left(\frac{dp}{dt}\right) = \frac{f}{h}$

Sings $\frac{dp}{dt}$ is the rate of change of momentum, which is nothing but force `F`

$a = \frac{1}{h} \frac{d^2E}{dk^2} \frac{1}{h} \, F$

$a = \frac{f}{h^2} \left(\frac{d^2E}{dk^2}\right)$

i.e $F = \frac{h^2}{\frac{d^2E}{dk^2}} \, a$-----2

Compare 1 & 2

Effective mass $m^v = \dfrac{h^2}{\frac{d^2E}{dk^2}}$