1. Electrical Properties of Materials

1.1. Introduction

It is essential to study the various electrical properties of solids for their specific applications. In terms of electrical properties, all solid state materials are classified as conductors, semiconductors and insulators. The selection of different applications depends on their electrical properties and the nature of the requirement (materials).Electrical phenomena caused by the motion of electrons in solids and find many applications in house holding and industrial applications. For example, electrons in metallic filament and the property of electrical resistivity of the material are used in incandescent lamps for heating. Similarly the mobility of electrons is being exploited in solar cells, lasers, in control of thermonuclear reactions, etc.

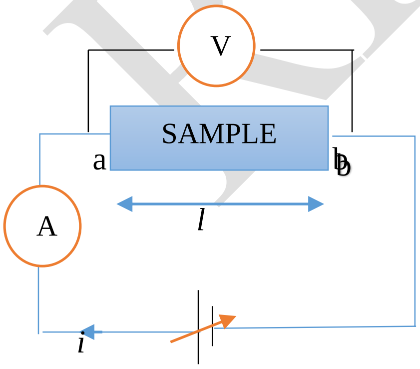
This chapter going to reveal the electrical conduction, thermal conduction, density of states, number of electrons per unit volume in a metal, etc. Besides, it also deals with classical free electron theory, quantum free electron theory, Energy bands in solids, tight binding approximation, electron effective mass and concept of the hole.

1.2 Arrival of Ohm's law in microscopic point of view.

If a battery is connected in series with an ammeter and a piece of some material (copper, Aluminium or such), a deflection in the ammeter will indicate a flow of charged particles (a current *i*) through the circuit (see Fig.1). Simultaneously there will be a voltage drop V across the sample as measured by a voltmeter. If the voltage of the battery is varied, *i* will vary proportionally with V. It can therefore be stated that if a voltage V is applied across a sample, a current proportional to it will flow:

$$V = iR \tag{1}$$

where *R* is the proportionality constant and is called the resistance of the sample. *Equation 1* is known as Ohm's law.



Ohm's law can be restated in a microscopic form to understand the phenomenon of conduction by concentrating attention on the sample. The fact that there is a potential difference V across the sample means that there is an electric field *E* in the sample. If the sample is uniform in geometry and quality, *E* will be constant, and it follows that

$$V_{ab} = V = \int_a^b E\,dl = El \tag{2}$$

Where *l* is the length of the specimen.

Given a certain potential difference (and therefore a certain *E*), the larger the cross-sectional area A of the sample, the larger the current will be. (Think of the analogy of a pipe with flowing water.) We can eliminate the geometric parameter A by introducing a new quantity, the current density *J*, defined as the current per unit cross-sectional area.

$$J = \frac{i}{A} (or) i = JA \tag{3}$$

Let us recollect the macroscopic Ohm's law ($V = iR$) and substitute the value of *i* as well as the value of *V* from equations (2) and (3), finally we get an equation as

$$El = JAR (or) E = J\frac{RA}{l}$$

where the quantity ρ = RA/*l* is called the electrical resistivity and has dimensions of ohm-meters (Ω-m). Ohm's law can be expressed another way by introducing the term electrical conductivity, (σ = 1/ρ), which has dimensions of reciprocal ohm-meters $(\Omega\text{-m})^{-1}$.

(or) $E = J\rho (or) E = \frac{J}{\sigma} [\because \rho = \sigma^{-1}]$

$$\therefore J = \sigma E \tag{4}$$

1.3 Relationship between current density (J), drift velocity (v_d) and mobility (μ).

Let *n* be the number of charge carriers per unit volume in a conductor of length *l* with uniform cross sectional area A. The current flow through the conductor is given by

$$i = \frac{Total\,charge(q)}{Time(t)} \tag{5}$$

Here the total charge depends on the number of electrons per unit volume (*n*), charge of one electron (*e*), Area of cross section (*A*) and length of the conductor (*l*). Hence equation (5) becomes

$$i = \frac{nAel}{t} = nAev_d \tag{6}$$

Here $v_d = l/t$ is called the drift velocity. It arises due to the movement of charges in the opposite direction of the electric field

We know that $J = \frac{i}{A}$ & Hence we can write $J = \frac{nAev_d}{A} (or) J = nev_d$ (7)

From equation (4), we get $\sigma E = nev_d$ (8)

(or) $\sigma = ne\frac{v_d}{E} (or) \sigma = ne\mu$ (9)

Where $\mu = v_d / E$ is called the mobility of the charge carrier. It is defined as the drift velocity per unit electric field. Its unit is $m^2V^{-1}S^{-1}$.

1.4. Free electron theory of solids

It is well known that the electrons in the outermost orbit of the atom determine the electrical properties of a solid. The free electron theory of solids explains the structure and properties of solids through their electronic structure. This theory is applicable to all solids, both metals and non-metals. It explains:

1. The behaviour of conductors, semiconductors and insulators.
2. The electrical, thermal and magnetic properties of solids.

1.4.1 Versions of free electron theory

1. **Classical free electron theory**
   The first successful attempt to understand the electrical properties of metals was presented by P. Drude in 1900 and was extended by H. A. Lorentz in 1909. According to this theory the free electrons are mainly responsible for electrical conduction in a metal. It obeys the laws of classical mechanics. Here, the free electrons are assumed to move in a constant potential.

2. **Quantum free electron theory**
   Many of the difficulties encountered by the classical free electron model were removed with the advent of quantum mechanics. In 1928, A. Sommerfeld modified the free electron model in two important ways:
   1. The electrons must be treated quantum mechanically. This will quantize the energy spectrum of the electron gas.
   2. The electrons must obey Pauli's exclusion principle; that is, no two electrons can have the same set of quantum numbers.
3. **Band theory of solids**
   This theory was proposed by Bloch in 1928. According to this theory free electrons move in a periodic potential. It explains electrical conductivity based on the energy bands.

1.5 Classical Free electron theory of metals

We know that an atom consists of a central nucleus with positively charged protons surrounded by the electrons of negative charge. The electrons in the inner shells are called core electrons and those in the outermost shell are called valence electrons. In a metal, when the valence electrons of each atom detach from the orbit, then they move freely throughout the metal. These electrons are known as free or conduction electrons

Assumption:

I. All the metals are composed of atoms. Each atom has central nucleus surrounded by number of electrons in the permissible orbits
II. The electrons in the metal are free to move in all possible directions about the whole volume of metal like molecules of a perfect gas in a container.

Absence of Electric field

I. All the electrons are move in random direction and collide with each other elastically without any loss of energy
II. The force between the conduction electron and ion core is neglected and the total energy of the electron is assumed to be Kinetic energy (Potential energy is zero)

Presence of electric field

I. The free electrons moves in a direction opposite to the direction of the applied field (drifted towards positive potential)
II. Since free electrons are assumed to be a perfect gas, they obey classical kinetic theory of gases and the free electron velocities in the metal obey Maxwell – Boltzmann statistics.

Drift velocity (v_d)

The average velocity acquired by the free electron due to the application of electric field in the direction opposite to the direction of electric field. $v_d = \frac{\lambda}{\tau_c}$

Mean free path (λ)

The average distance travelled by a free electron between any two successive collisions in the presence of an applied field is known as mean free path $\lambda = v_d \times \tau_c$

Collision time (τ_c)

The average time taken by a free electron between two successive collisions of the electrons is known as collision time $\tau_c = \frac{\lambda}{v_d}$

Relaxation time (τ)

The average time taken by a free electron to reach its equilibrium position from the distributed position due to application of an external electric field is called relaxation time. Generally the relaxation time is of the order of 10^{-14} sec

Electrical conductivity

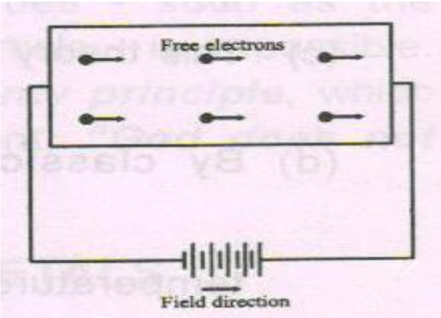
When an electric field (E) is applied between the extreme ends of a metallic rod, the electrons will move in opposite direction to the direction of applied field with a drift velocity V_d. If 'E' is the electric field applied on an electron of charge '*e*', then

Lorentz Force acting on the electron, F = eE (1)

This force accelerates the electrons and this accelerated electron collide with positive ion core and other free electrons elastically. After collision the electros losses its kinetic energy and velocity. Due to the driving force the electron will accelerated once again before its involve next collision.

Here, Acceleration (a) = $\frac{V_d}{\tau}$ (2)

here V_d – drift velocity; τ – Relaxation Time



From Newton II law of motion, Force on the electron, F = mass (m) x acceleration (a) (3)

Sub. (1) in (3), we get $F = \frac{mV_d}{\tau}$ (4)

From equations (2) & (4) $eE = \frac{mV_d}{\tau}$ (or) $V_d = \left(\frac{e\tau}{m}\right)E$ (5)

From ohm's law, the current density (J) is expressed in terms of electrical conductivity (σ) as

$J = \sigma E$ (6)

Also, the current density in terms of drift velocity can be written as $J = n e V_d$ (7)

Sub. (5) in (7), we get $J = ne\left(\frac{e\tau}{m}\right)E$ (or) $J = \frac{ne^2\tau}{m}E$ (8)

By comparing (6) and (8)

Electrical conductivity $\boxed{\sigma = \frac{ne^2\tau}{m}}$ (9)

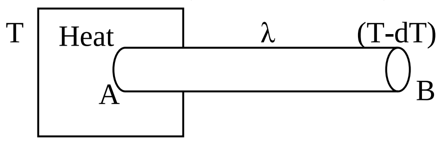
Thus, the amount of electrical charges (Q) conducted per unit time (t) per unit area (A) of a solid along unit applied electrical field (E).is called electrical conductivity

$$\boxed{\sigma = \frac{q}{tAE}}$$

Thermal Conductivity

"It is defined as the amount of heat (Q) flowing per unit time through the material having unit area of cross section and maintaining at unit temperature gradient (dT/dx)"

Consider A = 1m^2 & t = 1 sec,i.e., $Q = K\frac{dT}{dx}$ (or) $K = \frac{Q}{\frac{dT}{dx}}$ (10)



Consider two cross sections ‘A’ at high temperature (T) & ‘B’ at low temperature (T-dT) in a uniform metallic rod ‘AB’. Two cross sections ‘A’ and ‘B’ are separated by a distance ‘λ’. The conduction of heat takes place from ‘A’ to ‘B’ through electrons. During collision, electrons near ‘A’ lose their kinetic energy while electrons near ‘B’ gains the energy

Let the density of conduction electron be ‘n’ and velocity of electron be ‘v’.

At ‘A’ average kinetic energy of the electron = $\frac{3}{2}kT$ $\quad \because K.E = \left[\frac{1}{2}mv^2 = \frac{3}{2}kT\right]$ (11)

Where k – Boltzmann Constant and T – absolute temperature

At ‘B’ average kinetic energy of the electron = $\frac{3}{2}k(T-dT)$ (12)

$\therefore$ Excess Kinetic energy from A to B of an electron = $\frac{3}{2}kT$ - $\frac{3}{2}k(T-dT)$ = $\frac{3}{2}kdT$ (13)

Number of electrons crossing unit area per unit time from ‘A’ to ‘B’ = $\frac{1}{6}nv$ (14)

Excess energy carried from ‘A ‘to ‘B ‘for unit area in unit time = $\frac{1}{6}nv$ x $\frac{3}{2}kdT$ = $\frac{1}{4}nvkdT$ (15)

III^{rly}, Deficient energy carried from ‘B’ to’ A’ for unit area in unit time = -$\frac{1}{4}nvkdT$ (16)

Net amount energy transferred from ‘A ‘to ‘B’ $Q = \frac{1}{4}nvkdT - (-\frac{1}{4}nvkdT)$

(or) $Q = \frac{1}{2}nvkdT$ (17)

But, by definition $Q = K\frac{dT}{dx}$ (or)

$$\therefore K = \frac{1}{2}nvk\lambda \quad (18)$$

W.K.T for metals, relaxation time (τ) = Collision time (τ_c).

i.e., $\tau = \tau_c = \frac{\lambda}{v}$ (or) $\tau v = \lambda$ (19)

Sub. Eqn. (19) in (18), we get $\therefore K = \frac{1}{2} n v^2 k \tau$ (20)

This is the Expression for Thermal Conductivity

Wiedemann – Franz Law

Dividing equation (20) by (9), we get, $\frac{Thermal Conductivity}{Electrical Conductivity} = \frac{K}{\sigma} = \frac{\frac{1}{2} n v^2 k \tau}{\frac{ne^2 \tau}{m}}$

$$\text{(or) } \frac{K}{\sigma} = \frac{1}{2} \frac{mv^2 k}{e^2} \qquad (21)$$

W.K.T the kinetic energy of an electron is $\frac{1}{2} mv^2 = \frac{3}{2} kT$

Then, equation (21) becomes $\frac{K}{\sigma} = \frac{3}{2} \times \frac{kT \times k}{e^2} = \frac{3}{2}\left(\frac{k^2}{e^2}\right)T$

$$\text{(or) } \boxed{\frac{K}{\sigma} = LT}$$

Where L = $\frac{3}{2}\left(\frac{k^2}{e^2}\right)$ is a constant called Lorentz number. By substituting the value of

k = 1.38 x 10^{-23}JK^{-1}, e = 1.6 x 10^{-19}Coloumb, L = 1.12 x 10^{-8} WΩK^{-2}.

$$\boxed{\frac{K}{\sigma} \propto T}$$

Thus "The ratio of Thermal Conductivity to Electrical Conductivity of a metal is directly proportional to absolute temperature of the metal"

Success of classical free electron theory

i. It is used to verify Ohm's law
ii. It is used to explain electrical and thermal conductivities of metals
iii. It is used to derive Wiedemann – Franz law
iv. It is used to explain the optical properties of metal

Failure of classical free electron theory

i. Classical theory states that all free electrons will absorb the supplied energy. But quantum theory will absorb certain amount of supplied energy
ii. Electrical conductivity of semiconductors and insulators could not be explained by this theory

iii. The phenomenon such as photo – electric effect, Compton effect and black body radiation could not be explained by this theory
iv. The theoretical and experimental values of electronic specific heat and specific heat are not matched
v. The ratio of thermal to electrical conductivity is not constant at all temperature
vi. The experimental and theoretical values of Lorentz number are not matched.

1.6 Quantum free electron theory (QFE)

Many of the difficulties encountered by the classical free electron model were removed with the advent of quantum mechanics. In 1928, A. Sommerfeld modified the free electron model in two important ways:

I. The electrons must be treated quantum mechanically. This will quantize the energy spectrum of the electron gas.
II. The electrons must obey Pauli's exclusion principle; that is, no two electrons can have the same set of quantum numbers.

As a result of these modifications, when we put an electron gas in a solid, we begin by putting the electrons in the lowest energy states available, while obeying the exclusion principle, until we have used all the available electrons. This is to be contrasted with the classical free electron gas in which the electrons can assume continuous energy values, with many electrons having the same energy. This has profound implications for the statistical distribution of energies (the average number of electrons having a certain energy E) that the electrons can have. Thus, whereas a classical gas will obey Maxwell-Boltzmann statistics, the quantum mechanical gas will follow a new type of statistical distribution known as the Fermi-Dirac distribution. This in turn will affect the way the electron gas can absorb energy from an external source, such as a heat source, and the way it responds to an electric field. Aside from these two key modifications, Sommerfeld kept most of the assumptions of the Drude model:

I. The valence electrons are free to move through the solid.
II. Aside from collisions with the ions, the electrostatic interaction between the electrons and the lattice ions is ignored.
III. The interaction between the electrons is also neglected.

Essentially, the valence electrons retain the main features of an ideal gas but a gas that must be treated quantum mechanically rather than classically.

Merits

I. This theory treats the electron quantum mechanically rather than classically.
II. It explains the electrical conductivity, thermal conductivity, specific heat capacity of metals, photoelectric effect, Compton effect, etc.,

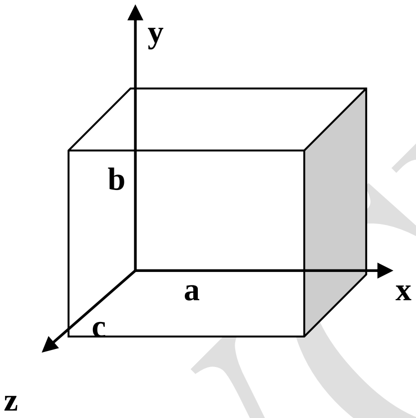
Demerits

I. It fails to state the difference between conductor, semiconductor and insulator
II. It fails to explain the positive value of Hall coefficient and some of the transport properties of the metals.

1.7 Electrons in metals - particle in a three dimensional box.

The Solution of one dimensional potential box can be extended for a three dimensional potential box. Here the particle can move in any direction in space. Hence instead of one quantum number ‘n’ three quantum numbers n_x, n_y ,n_z are considered corresponding to the three coordinating axis (x,y,z).

If a,b,c, are the length of the box as shown in figure along x,y,z axis ,then the energy of the particle $E_n = E_x + E_y + E_z$



Three dimensional potential box.

i.e., $E_{n_x,n_y,n_z} = \frac{n_x^2 h^2}{8ma^2} + \frac{n_y^2 h^2}{8mb^2} + \frac{n_z^2 h^2}{8mc^2}$

For a perfect cubic box a = b = c

Energy Eigen value is $E_{n_x,n_y,n_z} = \frac{h^2}{8m}\left[n_x^2 + n_y^2 + n_z^2\right]$ (1)

The corresponding normalized wave function of an electron in a cubical box can be rewritten as

$$\psi_{n_x,n_y,n_z} = \sqrt{\frac{2}{a}}\ \text{x}\ \sqrt{\frac{2}{a}}\ \text{x}\ \sqrt{\frac{2}{a}}\ .\sin\frac{n_x\pi x}{a}\ .\sin\frac{n_y\pi y}{a}\ .\sin\frac{n_z\pi z}{a} \qquad (2)$$

Degeneracy:

It is nothing but the quantum numbers having same Eigen value but different Eigen states. Such states and energy levels are called *Degenerate state*

Eg : if a state of quantum numbers are

$n_x = 1\,;\, n_y = 2\,;\quad n_z = 1$, $n_x = 1\,;\, n_y = 1\,;\quad n_z = 2$ &

$n_x = 2\,;\, n_y = 1\,;\quad n_z = 1$ have same Eigen values as $n_x^2 + n_y^2 + n_z^2 = 6$

$$E_{121} = E_{112} = E_{211} = \frac{6h^2}{8ma^2} \tag{3}$$

But the corresponding Eigen functions are

$$\left.\begin{aligned} \psi_{121} &= \sqrt{\frac{8}{a^3}}\,.\sin\frac{\pi x}{a}\,.\sin\frac{2\pi y}{a}\,.\sin\frac{\pi z}{a} \\ \psi_{112} &= \sqrt{\frac{8}{a^3}}\,.\sin\frac{\pi x}{a}\,.\sin\frac{\pi y}{a}\,.\sin\frac{2\pi z}{a} \\ \psi_{211} &= \sqrt{\frac{8}{a^3}}\,.\sin\frac{2\pi x}{a}\,.\sin\frac{\pi y}{a}\,.\sin\frac{\pi z}{a} \end{aligned}\right\} \tag{4}$$

Non - Degeneracy:

For various combinations of quantum numbers if we have same energy Eigen value and Eigen function then each states and energy levels are called *Non - Degenerate state*

Eg : for $n_x = 2\,;\, n_y = 2\,;\quad n_z = 2$ we have $E_{222} = \frac{12h^2}{8ma^2}$ &

$$\psi_{222} = \sqrt{\frac{8}{a^3}}\,.\sin\frac{2\pi x}{a}\,.\sin\frac{2\pi y}{a}\,.\sin\frac{2\pi z}{a}$$

1.8 Fermi- Dirac statistics

It deals with the particles having half integral spin like electrons. They are known as Fermi particles or fermions. Fermi distribution function gives the distribution of electrons among the various energy levels as a function of temperature.

Definition

‘The Probability F (E) of an electron occupying a given energy level at absolute temperature is called Fermi - Dirac distribution function

i.e., $F(E) = \dfrac{1}{1 + e^{\frac{(E - E_f)}{kT}}}$ where E – energy of the level whose electron occupancy is being considered; E_f – Fermi energy; k – Boltzmann constant; T – absolute temperature

The probability value of F(E) is always lies between 0 and 1.

If F(E) = 1, the energy level is occupied by an electron.

If F(E) = 0, the energy level is vacant and it is not occupied by an electron

If F(E) = 0.5, There is a 50% chance for the electron occupying in that energy level.

Effect of temperature on Fermi function

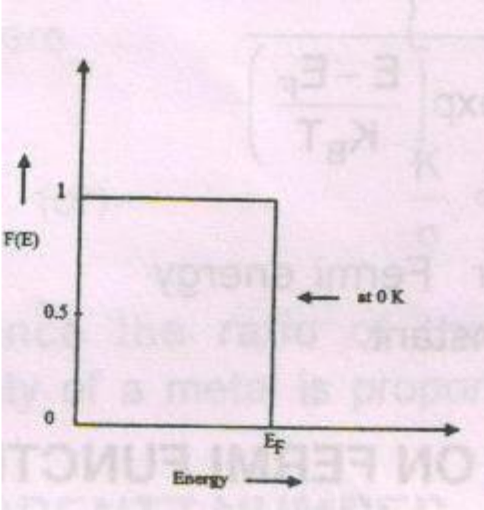
The dependence of Fermi distribution function on temperature and its effect on the occupancy of energy level is shown in fig. (5) and (6)

Case 1: at T = 0 K for E < E_f , $F(E) = \dfrac{1}{1 + e^{\frac{(Some - VeValue)}{0}}} = \dfrac{1}{1 + e^{-\alpha}} = \dfrac{1}{1} = 1$

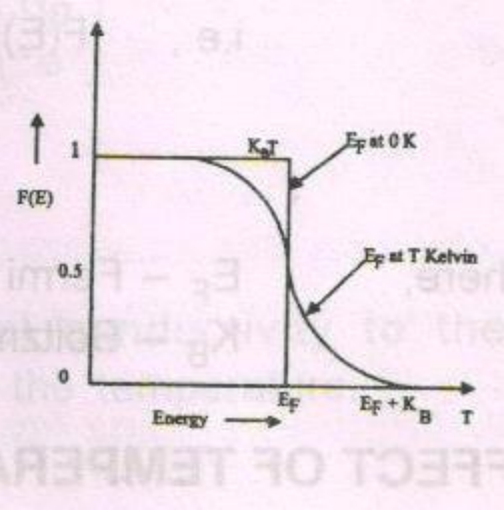
$\therefore$ F(E) = 1Thus, there is a 100% chance of electron occupy below the Fermi energy of the energy level

Case 2: at T = 0 K for E > E_f , $F(E) = \dfrac{1}{1 + e^{\frac{(Some + VeValue)}{0}}} = \dfrac{1}{1 + e^{\alpha}} = \dfrac{1}{1 + \alpha} = \dfrac{1}{\alpha} = 0$

$\therefore$ F(E) = 0 Thus, there is a no chance of electron occupy above the Fermi energy of the energy level



Fig(5)



Fig(6)

Case 3: At any temperature other than 0K and E= E_f , $F(E)=\frac{1}{1+e^{0}}=\frac{1}{1+1}=\frac{1}{2}=0.5$

There is a 50% chance for the electron to occupy Fermi energy level

With increase in Temperature, i.e., T>0K, Fermi function F (E) varies with 'E' as shown in figure (5)

At very high temperature when (thermal energy) kT >>E_f (or) T → α, electron lose their quantum mechanical behavior and the Fermi distribution function reduces to classical Boltzmann distribution.

Uses:

(i) It gives the probability of the electron occupation at the given energy state at given temperature

(ii) It is used to calculate the number of free electrons per unit volume at given temperature

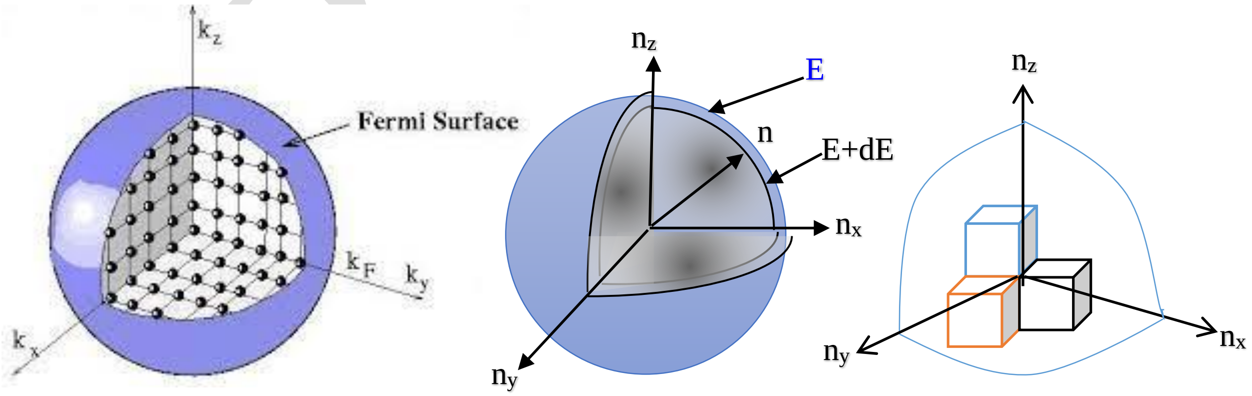
(iii) It is used to calculate the Fermi energy of the metal.

Fermi energy level

It is the energy level at any finite temperature above zero Kelvin at which the probability of electron occupation is ½ (or) 50%

It is also the energy level of maximum energy of the filled states at zero Kelvin.

1.8. Density of states



It is defined as the number of available electron states per unit volume in an energy interval E and E+dE. It is denoted by Z(E)

$$Z(E)=\frac{Number\ of\ available\ energy\ states\ between\ E\ \&\ E+dE\ in\ a\ metal\ piece\ (N(E)\ dE)}{Volume\ of\ the\ metal\ piece\ (a^{3})}$$

Let us consider a cubical metal piece of side 'a'. The electron will behave as a wave in this metal and confined with the allowed energy levels.

The energy of the electron in three dimensional potential well is $E = \frac{h^2}{8ma^2}\,(n_x^2 + n_y^2 + n_z^2)$ (1)

where the energy of an electron is determined by sum of the square of quantum numbers (n_x, n_y, n_z). For this, A imaginary sphere is constructed with quantum numbers n_x, n_y, n_z as three coordinate axes in a three dimensional space. A radius vector 'n' is drawn from the origin 'O' to a point n_x, n_y, n_z.. It is observe that, all the points lie on the surface of this sphere will have same energy 'E'.

Thus, $n^2 = \mathbf{n_x^2 + n_y^2 + n_z^2}$ denotes the radius of the sphere with energy 'E'. This sphere is further divided into many shells. Each shell represents a particular combination of quantum numbers and therefore represents particular energy value

Let us consider two such energy values E and E+dE. The number of available energy states between E and E+dE can be determined by finding the number of energy states between the shells of radius n and n+dn.

Number of energy states within a sphere of radius 'n' = $\frac{4}{3}\pi n^3$ **(1)**

Since the quantum number n_x,n_y,n_z have only +ve integer value, we have to take only one octant of sphere $\left(\frac{1}{8}\right)$

∴ No. of available energy states within one octant of sphere of radius 'n' Corresponding to energy 'E' $\Big\}$ $= \frac{1}{8} \times \left[\frac{4}{3}\pi n^3\right]$ (2)

lll^rly No. of available energy states within one octant of sphere of radius 'n+dn' corresponding to energy 'E+dE' $\Big\}$ $= \frac{1}{8} \times \left[\frac{4}{3}\pi (n+dn)^3\right]$ (3)

No. of available energy states between the shell of radius 'n' & 'n+dn'

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

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

$$\therefore \text{N(E)} = \frac{1}{8} \times \frac{4\pi}{3}\left(n^3 + dn^3 + 3n^2 dn + 3n dn^2 - n^3\right)$$

Neglecting higher power of *dn* which is very small, N (E) dE $= \frac{1}{8} \times \left[\frac{4}{3} 3n^2 dn\right]$ (or)

N (E) dE $= \left[\frac{\pi}{2} n^2 dn\right]$ (or) N (E) dE $= \left[\frac{\pi}{2} n(ndn)\right]$ (4)

We know that, the particle in a one dimensional box of radius ‘a’ in Schrödinger’s wave equation is

$$E = \frac{n^2 h^2}{8ma^2} \tag{5}$$

(or) $n^2 = \frac{8ma^2 E}{h^2}$ (6)

(or) $n = \left[\frac{8ma^2 E}{h^2}\right]^{\frac{1}{2}}$ (7)

Differentiating eqn (6) w.r.t *n* & E, we get $2ndn = \frac{8ma^2}{h^2} dE$ (8)

(or) $ndn = \frac{8ma^2}{2h^2} dE$ (9)

Sub the value of Eqn(4) & Eqn (7) in Eqn. (9) , we get

N (E) dE = $\frac{\pi}{2} \times \left[\frac{8ma^2 E}{h^2}\right]^{\frac{1}{2}} \times \left[\frac{8ma^2}{2h^2}\right] dE$

(or) N (E) dE $= \frac{\pi}{2} \times \frac{1}{2} \times \left[\frac{8ma^2}{h^2}\right]^{\frac{3}{2}} \times E^{\frac{1}{2}} dE$

Pauli’s exclusion principle states that’ two electrons of opposite spins can occupy each state’

∴ N (E) dE $= 2 \times \frac{\pi}{4} \times \left[\frac{8ma^2}{h^2}\right]^{\frac{3}{2}} \times E^{\frac{1}{2}} dE = \frac{\pi}{2} \times \left[\frac{2 \times 2^2 m}{h^2}\right]^{\frac{3}{2}} \times a^3 \times E^{\frac{1}{2}} dE$

∴ N (E) dE = $\frac{4\pi}{h^3} \times (2m)^{\frac{3}{2}} \times a^3 \times E^{\frac{1}{2}} dE$ (10)

Density of states is number of energy states per unit volume

∴ Z (E) dE = $\frac{N(E)dE}{V} = \frac{\frac{4\pi}{h^3} \times (2m)^{\frac{3}{2}} \times a^3 \times E^{\frac{1}{2}} dE}{a^3}$

∴ Z (E) dE $= \frac{4\pi}{h^3} \times (2m)^{\frac{3}{2}} \times E^{\frac{1}{2}} dE$ (11)

This is the density of charge carriers in the energy interval ‘E’ & ‘E+dE’. It is used to calculate carrier concentration in metals and semiconductors.

Carrier Concentration

Normally all the energy states are not filled. Hence the probability of filling the electron is done by Fermi distribution function (E). The number of electrons per unit volume (or) density of electrons is called carrier concentration

Carrier concentration of electrons in energy bands $n_c = \int Z(E).F(E)dE$

(or) $n_c = \frac{4\pi}{h^3} \times (2m)^{\frac{3}{2}} \times \int\limits_{energyband} E^{\frac{1}{2}} dE.F(E)$ (12)

(or) $n_c = \frac{4\pi}{h^3} \times (2m)^{\frac{3}{2}} \times \int\limits_{energyband} E^{\frac{1}{2}} \frac{1}{1+e^{\frac{(E-E_f)}{kT}}} dE$ (13)

n_c is known as carrier distribution function

Fermi energy at 0 Kelvin

We know that 0 K maximum energy levels that can occupied by the electron is called Fermi energy level (E_{f_0})

(i.e.,) at 0 K for E<E_f and therefore F (E) = 1

∴ Integrating equation 12 within the limits 0 to E_{f_0} , then the carrier concentration is

$$n_c = \int_0^{E_{f0}} \frac{4\pi}{h^3} \times (2m)^{\frac{3}{2}} \times E^{\frac{1}{2}} dE. \qquad = \frac{4\pi}{h^3} \times (2m)^{\frac{3}{2}} \times \int_0^{E_{f0}} E^{\frac{1}{2}} dE.$$

(or) $n_c = \frac{8\pi}{3h^3} \left(2mE_{f_0}\right)^{\frac{3}{2}}$ (14)

(or) $E_{f_0} = \left(\frac{h^2}{2m}\right) \times \left(\frac{3n_c}{8\pi}\right)^{\frac{2}{3}}$ (15)

This is the Fermi energy of electrons in solids at absolute zero. Thus, Fermi energy of a metal depends only on the density of electrons of that metal.

When the temperature increases .Fermi level (or) Fermi energy slightly decreases

It can be shown that $E_f = E_{f_0}\left[1 - \frac{\pi^2}{12}\left[\frac{kT}{E_{f_0}}\right]^2\right]$

Importance:

- It is the level which separates the filled valence energy level and vacant conduction energy levels
- It determines the energy of the particle at any temperature

Average energy of electron s at 0K

Average energy of electron (E_{avg}) = $\dfrac{\text{Total energy of electrons at 0K } (E_T)}{\text{Number of Energy States at 0K } (n_c)}$ (16)

Here, Total Energy of electrons at 0K = Number of Energy states at 0K x Energy of the electron

$$E_T = \int_0^{E_{f0}} Z(E)dE.E$$

$$\therefore E_T = \frac{4\pi}{h^3} \times (2m)^{\frac{3}{2}} \int_0^{E_{f0}} E^{\frac{1}{2}}.E.dE$$

(or) $E_T = \frac{4\pi}{h^3} \times (2m)^{\frac{3}{2}} \times \frac{E_{F_0}^{\frac{5}{2}}}{\frac{5}{2}}$

(or) $E_T = \frac{8\pi}{5h^3} \times (2m)^{\frac{3}{2}} \times E_{F_0}^{\frac{5}{2}}$ (17)

Substituting Eqn (13) & (15) in (14), we get

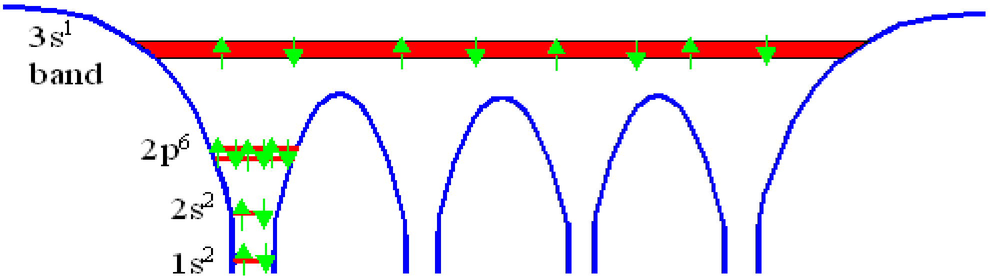
$$E_{Avg} = \frac{\frac{8\pi}{5h^3} \times (2m)^{\frac{3}{2}} \times E_{F_0}^{\frac{5}{2}}}{\frac{8\pi}{3h^3}(2m)^{\frac{3}{2}} \times E_{F_0}^{\frac{3}{2}}} = \frac{3}{5} E_{F_0}^{\frac{5}{2}} - E_{0F}^{\frac{3}{2}}$$

$\therefore$ The average energy of electron at 0K is $E_{Avg} = \frac{3}{5} E_{f_0}$

1.9. Electron in periodic potential

Band theory of solid (Zone theory)

The free electron theory explains the properties like thermal conductivity, electrical conductivity and specific heat of most of the metals. But it fails to explain why some solids are conductors, some are insulators and others are semiconductors. A solution to this problem was given by band theory of solids and is called zone theory. According to this theory, the potential energy of the electron inside the crystal through which an electron move is supposed to be constant (zero). So it is completely free to move about in the crystal, restrained only by the surface of the crystal.



Postulates:

I. According to band theory, potential energy of electron within the crystal is periodic due to periodicity of the crystal. i.e., free electron move inside periodic lattice field.

II. The potential energy of the solid varies periodically with the periodicity of space lattice *'a'* which is nothing but the interatomic spacing.

Inside a real crystal, the electrons (-) move through periodic arrangement of positively charged holes (+). Let us imagine one dimensional periodic potential distribution for a crystal (Fig). Here the potential energy of the electron at the positive ion site is zero and is maximum when it is half way between the adjacent nucleui.

Brillouin zones *are the boundaries that are marked by the values of propagation vector* $\bar{k}$ *in which the electrons can have allowed energy values without diffraction. since k is a vector, it has different values along different directions.*

Explanation:

The relationship between the wave vector and the energy of the electron in constant potential field can be got as follows.

We know, in a length of potential box *'l'* the energy of the electron in a constant potential field.

$$E = \frac{n^2h^2}{8ma^2} \qquad (1)$$

Also, we know that wave vector $k = \frac{n\pi}{a}$ (or) $a^2 = \frac{n^2\pi^2}{k^2}$ (2)

Substituting equation (2) in (1) we get $E = \frac{k^2h^2}{8m\pi^2}$ (3)

a plot is made between the total energy *'E'* and the wave vector *k*, for different values of *k* with $n = \pm 1,\ k = \pm\pi/a.\quad n = \pm 2,\ k = \pm 2\pi/a$, *etc.,* For the above values of *k*, the curve is obtained as shown in figure. which is in the form of a parabola with discontinuities.

From the figure it can be seen that the energy of the electron increases continuously from *0* to $\pm\pi/a$ then the electron meets the wall and is reflected. This range of allowed energy values in te region between - π/a to π/a is called first Brillouin zone. The second allowed energy values consists of two parts: one from π/a to $2\pi/a$ and another from - π/a to -2 π/a is called second Brillouin zone and so on.

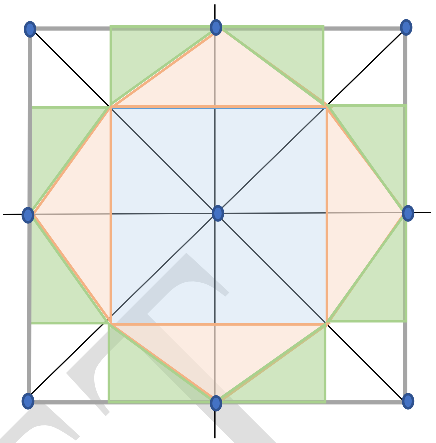
Therefore we can conclude that the electron can go from one Brillouin zone to the other only if it is supplied with an energy equal to forbidden gap energy. This forbidden gap is the one which decides whether the solid is an insulator, semiconductor (or) conductor.

Brillouin zone can be constructed by drawing vectors from the origin to the nearest lattice point and then draw Bragg planes perpendicularly between these two points. The region below this plane are said to Brillouin zone.

🟦 First Brillouin Zone ($-\pi/a$ to π/a)

🟧 Second Brillouin Zone ($-2\pi/a$ to $-\pi/a$ & $2\pi/a$ to π/a)

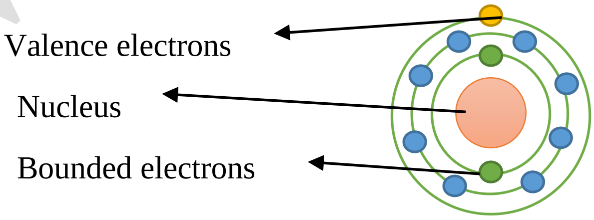
🟩 Third Brillouin Zone ($-3\pi/a$ to $-2\pi/a$ & $3\pi/a$ to $2\pi/a$)



1.10 Energy bands in solids

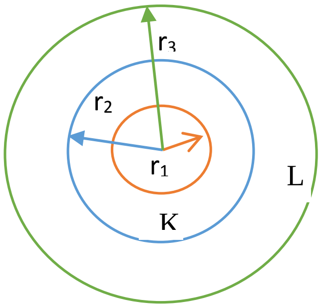
(i) Free and bound electrons

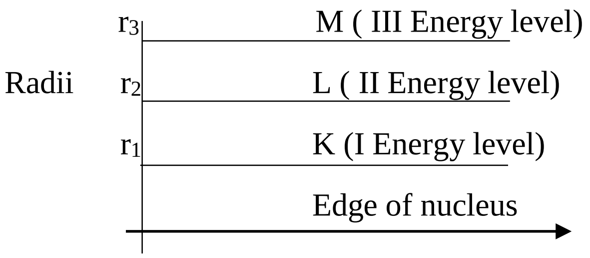
In an isolated atom all the electrons are tightly bounded with the central positive nucleus and revolves around various orbits. The number of electrons the outermost orbit are called *valence electrons*. In the outermost orbits, the attractive force between the nucleus and electrons will be very less, so that the electrons can be easily detached from the nucleus. These detached electrons from the outermost orbits are called *free electrons*. But as far as the innermost orbits are concerned, the electrons are tightly bounded with positive nucleus, and hence they are termed as *bound electrons*.



(ii) Energy levels

We know that each orbit of an atom has fixed amount of energy associated with it. The electrons moving in a particular orbit possess the energy of that orbit. The larger the orbit, the greater is its energy. So, the outermost orbit electrons possess more energy than the inner orbit electrons. A convenient way of representing the energy of different orbits are called *energy levels* as shown in figure. Let E_1 be the energy level of *K* shell, E_2 be the energy level of *L* shell, E_3 be the energy level of *M* shell and so on. The larger the orbit of an electron, the greater is its energy and higher is the energy level.



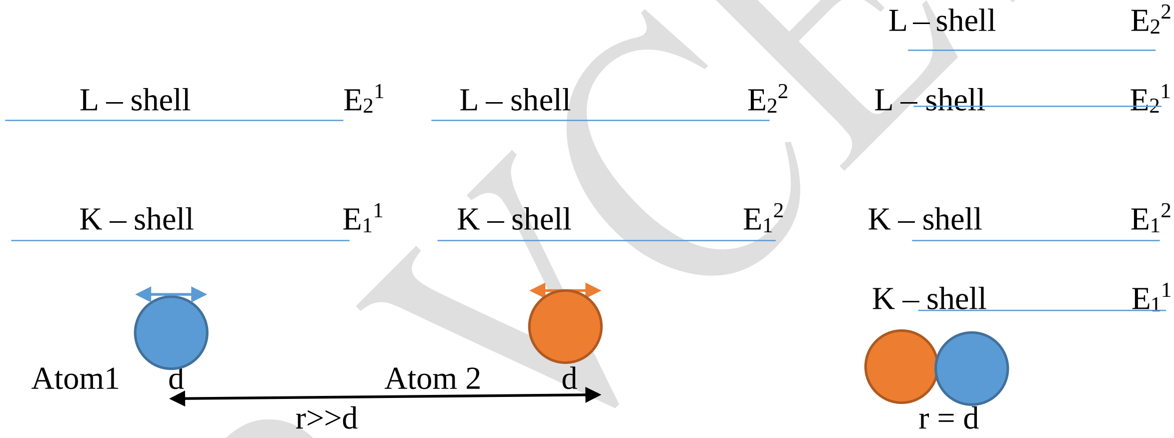


From the figure it is clear that the electrons can revolve only in certain permitted orbits of radii r_1, r_2 *and* r_3 *etc.*, and not in any arbitrary orbit. Since the electrons are not allowed in between the radii r_1 *and* r_2 or between the radii r_2 *and* r_3 etc., there won't be any electronic energy levels in between those radii so called *forbidden radii.* These unallowed energy levels are called *forbidden energy levels.*

(iii) Energy bands

It has to be noted that as long as the atoms are widely separated, they have identical energy levels. But, once the atoms are brought together the interatomic force of attraction between the atoms in the solid may modify the energy levels of a solid as energy bands. Now let us discuss how energy levels of single free atom becomes bands in solids.

Let us consider two identical atoms of diameter (*d*) separated at a distance (*r*), so that the electronic energy levels of one atom [E_1^1*(K – shell) and* E_2^1*(L – shell)*] do not affect the electronic energy levels of the other atom [E_1^2*(K – shell) and* E_2^2*(L – shell)*] as shown in figure



Now when the atoms are bring closer to each other, some force of attraction occurs between them and according to quantum mechanics, their wave functions will start overlapping. Therefore when two atoms are brought closer, it does not remains as two independent atoms, rather it forms a **single two – atom** system with two different energy levels to form energy band as shown in figure.

Origin of energy band formation in solids

We know that when two atoms of equal energy levels are brought closer to eachother, the original energy levels *viz* E_1 *and* E_2 splits each into two energy levels. i.e., the *K*- shell energy E_1 splits in to E_1^1 *and* E_2^1. Similarly the *L* – shell energy E_2 splits in to E_1^2 *and* E_2^2. *Now when* three atoms are brought closer together, the original energy levels *viz* E_1 and E_2 splits each into three energy levels *viz* E_1^1 E_1^2 *and* E_1^3*and* E_2^1 E_2^2 *and* E_2^3respectively. These type of transformations from the original energy levels into two (or) more energy levels is known as *Energy level splitting*

Energy bands

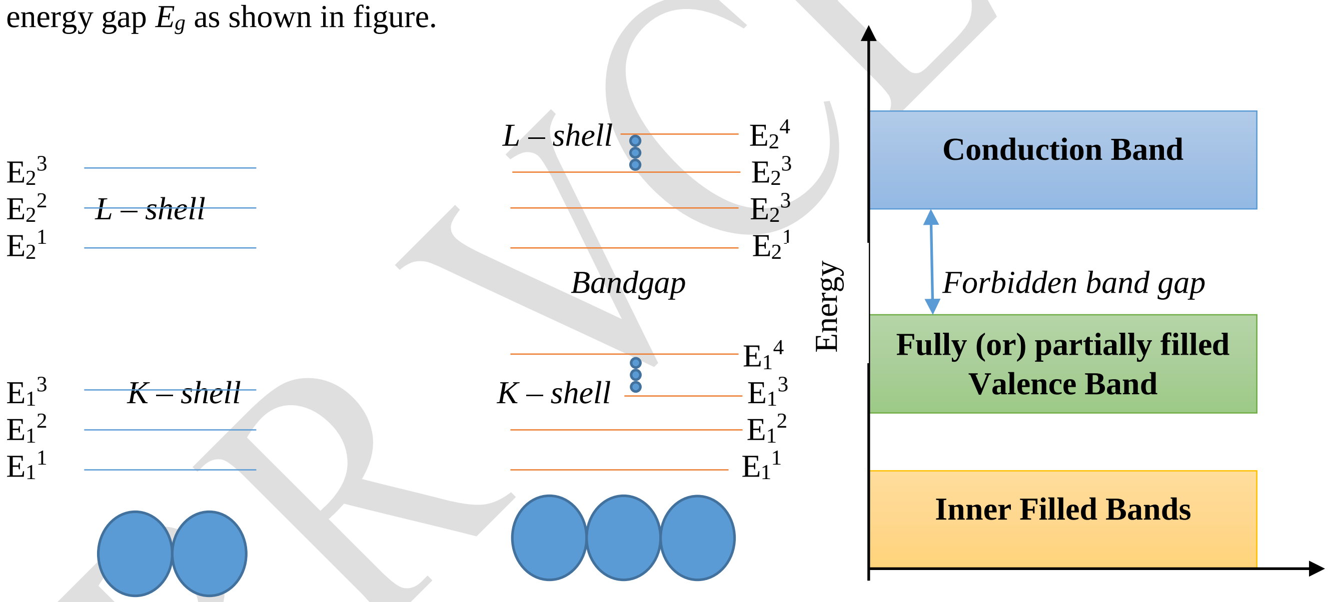
Therefore, if ‘*N*’ number of atoms of equal energy levels are brought closer to from a solid, then it forms a closely spaced continuous energy levels, so called **energy bands**.
Hence an energy band can be defined as, *the range of energies possessed by an electron in a solid*. The magnified view of the energy band which consists of a large number of very closely spaced energy levels as shown in figure.

Inner Filled Bands, Valence band and Conduction band

During the formation of energy bands, the inner filled energy levels forms a energy band called *Inner filled bands*. Similarly the electrons in the outermost shells of atoms forms an energy band called *valence band*. The valence band will be of completely filled (or) partially filled with electrons, based on the type of materials.
If an electron comes out from valence band for conduction, then they form an energy level corresponding to the energy band called *conduction band*

Forbidden gap

While referring to energy bands, they are separated by small regions which does not allow any energy levels. Such regions between the energy bands are called forbidden gaps (or) forbidden energy gap E_g as shown in figure.



Based on band theory and the presence of forbidden band gap the materials are classified in to three categories viz:

(i) **Metals (or) Conductors**

Here, there is no forbidden band gap. Hence the valence band and conduction band overlap with each other. Since the free electron are relatively available in large number, even a small external field induces the electrons from the valence band to conduction band and hence conduction easily occurs.

Example: Copper, Aluminium, etc.

(ii) **Semiconductors**

Here, the forbidden band gap is small (say 0.5 to 1.5 eV) and hence the width of forbidden gap is smaller than allowed energy bands. Generally, the free electrons in valence band is comparatively less compared to conductors because of finite forbidden gap and hence the semiconductor requires external field with energy greater than or equal to this forbidden gap energy such that conduction process occurs.

Example: Germanium, Silicon, etc.

(iii) **Insulators**

Here the width of the forbidden gap is wider (say 3 to 5.47 eV) and hence the width of forbidden gap is larger than allowed energy bands. Therefore in case of insulator, a sufficiently large energy is required for conduction to occur.

Example: Diamond, Dielectrics, etc,

1.11 Free electron approximation

We know in solids there exists the ionic cores which are tightly bounded to the lattice location, while the electrons are free to move here and there throughout the solid. This is called free electron approximation.

In free electron approximation the following points are observed:

(i) The potential energy of the electron is assumed to be lesser than its total energy.

(ii) The width of the forbidden bands (E_g) are smaller than the allowed bands as shown in the figure

(iii) Therefore, the interaction between the neighbouring atoms will be very strong.

(iv) As the atoms are closer to each other, the inter atomic distance decreases and hence the wave functions overlap with each other as shown in figure

1.12 Tight binding approximation

Tight binding approximation is exactly an opposite approach of discussing the atomic arrangements, when compared to free electron approximation.

Here instead of beginning with solid core, we begin with the electrons, i.e., All the electrons are bounded to the atoms. In other way we say that the atoms are free, while the electrons are tightly bounded. Hence, this is called tight binding approximation

The following points are observed in tight binding approximation:

(i) The potential energy of the electron is assumed to be almost equal to its total energy.

(ii) The width of the forbidden bands (E_g) are larger than the allowed bands as shown in the figure

(iii) Therefore, the interaction between the neighbouring atoms will be weak.

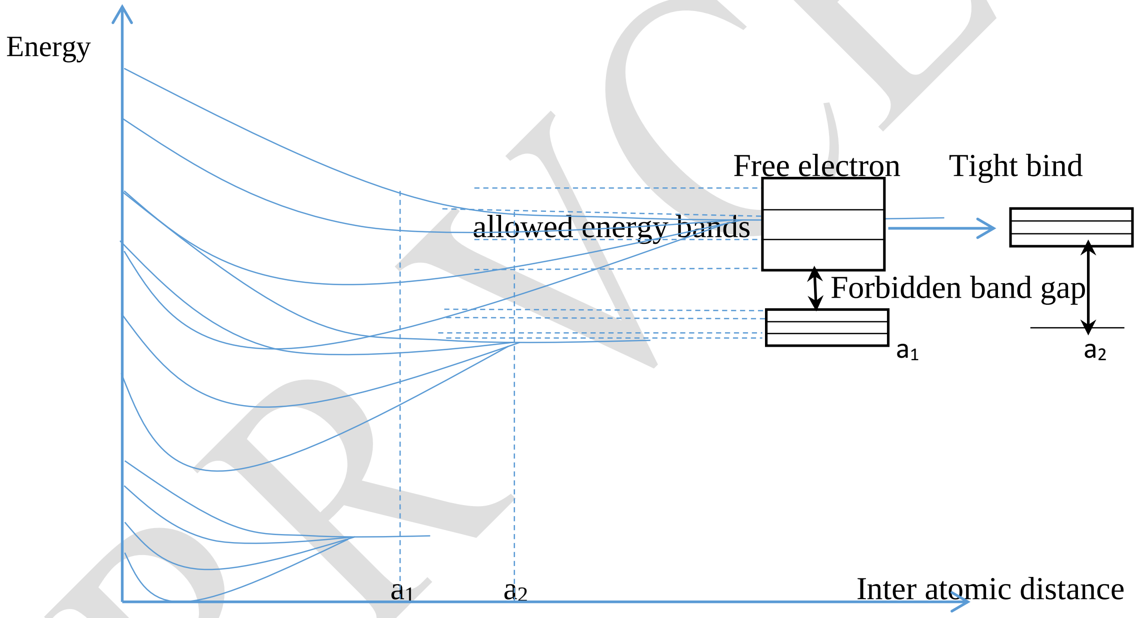
(iv) As the atoms are not closer, the inter atomic distance increases and hence the wave functions will not overlap with each other as shown in figure

Explanation

Let us consider the atoms with larger inter atomic distance (a_2) as shown in figure. Here the atoms are far apart, and all the bounded electrons have fixed energy levels. Therefore when a solid is formed by using the same element, then the energy levels occupied by the electrons in each atom will be identical, which lead to *tight binding approximation*.

Now, when we bring the atoms closer to each other to form the solid, then inter atomic distance (a_1) decreases. Therefore, the outer shell electrons begin to overlap and the energy levels also splits as shown in figure.

If the inter atomic distance is further reduced, then the splitting of energy level happens for the inner shall electrons also, which lead to *free electron approximation*.



1.13 Effective Mass and Concept of Hole

Effective mass of an electron is the mass of the electron when it is accelerated in a periodic potential and is denoted by m^*

When an electron of mass m is placed in a periodic potential and if it is accelerated with the help of an electric or magnetic field, then the mass of the electron is not constant, rather it varies with respect to the field applied. That varying mass is called as *effective mass* (m^*)

To study the effect of electric field on the motion of an electron in one dimensional periodic potential, let us consider the Brillouin zone which contains only one electron of charge e in the state k, placed in an external field *'E'*. Due to the field applied the electrons gains a group velocity quantum mechanically and therefore the acceleration changes.

The group velocity with which the electron can travel is $V_g = \frac{d\omega}{dk}$ (1)

Where $k \rightarrow$ wave vector; $\omega \rightarrow$ angular velocity of electron $\omega = 2\pi\upsilon$ (or) $\omega = \frac{2\pi E}{h}$ (2)

Substituting equation (2) in equation (1) we get

Group velocity $V_g = \frac{2\pi}{h} \times \frac{dE}{dk}$ (or) $V_g = \frac{1}{\hbar} \times \frac{dE}{dk}$ (3)

If the electron moving in a crystal lattice with momentum P, then the wavelength associated is $\lambda = \frac{h}{p}$ (or) $p = \frac{2\pi}{\lambda} \times \frac{h}{2\pi}$ (or) $P = \hbar k$ (4)

Differentiating equation (4) w.r.t to t $\frac{dP}{dt} = \hbar \frac{dk}{dt}$ (5)

(or) $F = \hbar \frac{dk}{dt}$ (or) $\frac{F}{\hbar} = \frac{dk}{dt}$ (6)

we know acceleration $a = \frac{dV_g}{dt} = \frac{d}{dt}\left[\frac{1}{\hbar} \times \frac{dE}{dk}\right]$

$$= \frac{1}{\hbar}\frac{d^2E}{dk^2} \times \frac{dk}{dt} \qquad (7)$$

Substituting equation (6) in equation (7), we get

$$a_g = \frac{1}{\hbar}\frac{d^2E}{dk^2} \times \frac{F}{\hbar} \text{ (or) } a_g = \frac{1}{\hbar^2}\frac{d^2E}{dk^2}F \text{ (or) } F = \frac{\hbar^2}{d^2E/dk^2}a_g \qquad (8)$$

Equation (8) resembles with newton's force equation

i.e., $F = eE = m^*a$ (9)

Where m^* is the effective mass of the electron.

Comparing equation (7) and (8), we can write $m^* = \frac{\hbar^2}{d^2E/dk^2}$ (10)

Equation (10) represents the effective mass of an electron in a periodic potential, which depend on $\frac{d^2E}{dk^2}$

Special cases:

(i) If $\frac{d^2E}{dk^2}$ is +ve, then effective mass $m^*$is also positive

(ii) If $\frac{d^2E}{dk^2}$ is -ve, then effective mass $m^*$is also negative

(iii) If $\frac{d^2E}{dk^2}$ is zero, then effective mass m^* becomes infinity

Negative effective mass (or) concept of hole

To show that the effective mass has negative value. Let us take the Energy - wave vector (E-k) of a single electron in a periodic potential. i.e., consider the 1st Brillouin zone (allowed energy band) alone as shown in figure.

In the $E - k$ curve, the band can be divided in to two bands *viz.* upper band and lower band with respect to a point (P) called a **Point of inflection**.

(i) In the **lower band** the value of $\frac{d^2E}{dk^2}$ is a decreasing function from the point of inflection

$\therefore \frac{d^2E}{dk^2}$ is $+ve$ and hence m^* should be $+ve$ in the lower band. If a plot is made between $m^*$and k for different values of $\frac{d^2E}{dk^2}$, we get the curve as shown in figure

(ii) In the **Upper band** of E - k the value of $\frac{d^2E}{dk^2}$ is a increasing function from the point of inflection

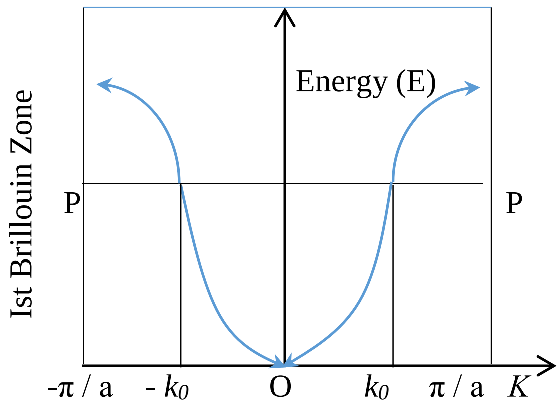
$\therefore \frac{d^2E}{dk^2}$ is $-ve$ and hence m^* should be $-ve$ in the upper band. If a plot is made between $m^*$and k for different values of $\frac{d^2E}{dk^2}$, we get the curve as shown in figure

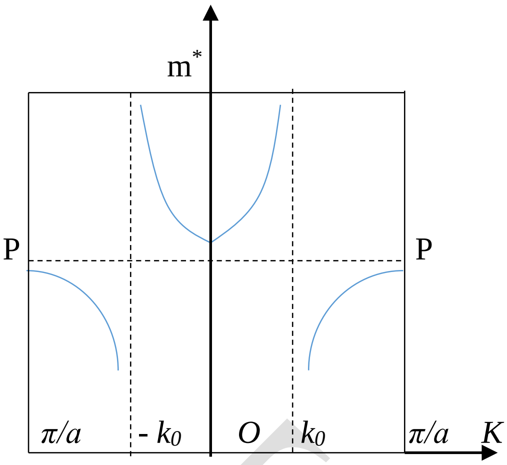
(iii) **At the point of inflection,** the value of $\frac{d^2E}{dk^2} = 0$ and hence in m^* - k plot, effective mass goes to infinity.

The electron with the negative effective mass is called **Hole**, in other words the electron in the upper band which behaves as a positively charged particle is called hole. It has the same mass as that of an electron but with positive charge.

Therefore, the advantage of the concept of hole is, for a nearly filled band with n number of empty states as shown in figure n number of holes arises

In other words, we can say that the presence of hole is attributed to an empty state, for an electron to be filled. Thus, based on the hole concept several phenomena like Thompson effect, Hall effect, etc., are well explained.


Ist Brillouin Zone
Energy (E)
P
P
-π / a
- k0
O
k0
π / a
K


m*
P
P
π/a
- k0
O
k0
π/a
K