1. Electronic States

Syllabus

Quantum free electron theory - Fermi distribution energy - Density of energy states - Electron in a periodic potential - Energy bands in solids -Conductors - Semiconductors - Insulators - Electron effective mass – the concept of hole - properties of conduction and valence bands.

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 Quantum free electron theory, Energy bands in solids, electron effective mass and concept of the hole.

1.2 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.

1.3 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

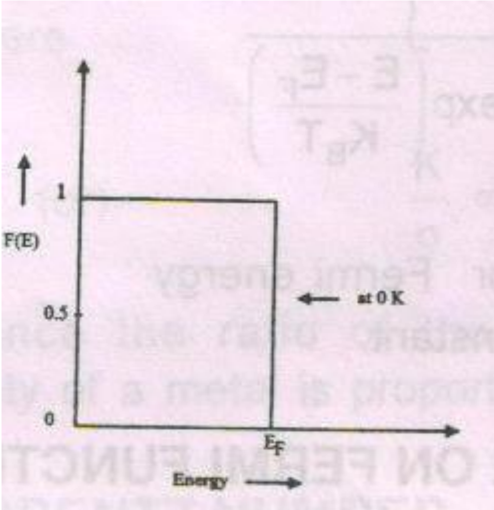
The dependence of Fermi distribution function on temperature and its effect on the occupancy of energy level is shown in fig. (5) and (6)

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

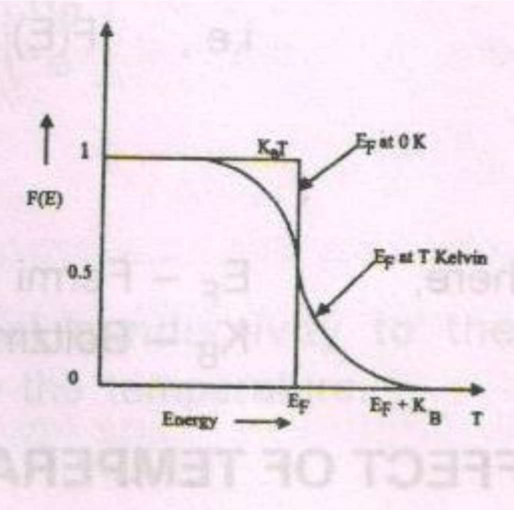
∴ F(E) = 1Thus, there is a 100% chance of electron occupy below the Fermi energy of the energy level

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

∴ 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

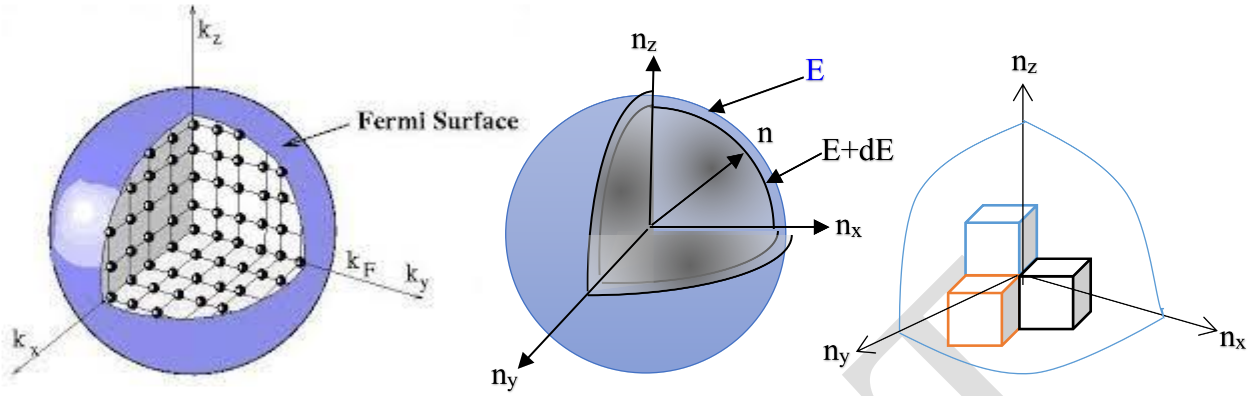
(iii) It is used to calculate the Fermi energy of the metal.

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.

1.4. 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 $\left(\frac{1}{8}\right)$

$\therefore$ 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)

Ill^{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'

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

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

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

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

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

$$E=\frac{n^2h^2}{8ma^2} \quad (5)$$

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

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

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

(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'

$\therefore$ N (E) dE = $2\times\frac{\pi}{4}\times\left[\frac{8ma^2}{h^2}\right]^{\frac{3}{2}}\times E^{\frac{1}{2}}dE = \frac{\pi}{2}\times\left[\frac{2\times2^2m}{h^2}\right]^{\frac{3}{2}}\times a^3\times E^{\frac{1}{2}}dE$

$\therefore$ 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

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

$\therefore$ 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

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

$$n_c = \int_0^{E_{f_0}} \frac{4\pi}{h^3} \times (2m)^{\frac{3}{2}} \times E^{\frac{1}{2}} dE. \quad = \quad \frac{4\pi}{h^3} \times (2m)^{\frac{3}{2}} \times \int_0^{E_{f_0}} E^{\frac{1}{2}} dE.$$

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

$$E_T = \int_0^{E_{f_0}} Z(E) dE.E$$

$$\therefore E_T = \frac{4\pi}{h^3} \times (2m)^{\frac{3}{2}} \int_0^{E_{f_0}} E^{\frac{1}{2}}.E.dE$$

(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

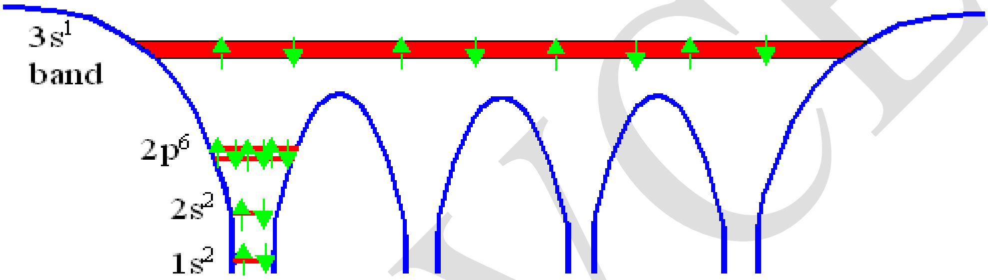
$$E_{Avg} = \frac{\frac{8\pi}{5h^3} \times (2m)^{\frac{3}{2}} \times E_{F_0}^{\frac{5}{2}}}{\frac{8\pi}{3h^3} (2m)^{\frac{3}{2}} \times E_{F_0}^{\frac{3}{2}}} = \frac{3}{5} E_{F_0}^{\frac{5}{2}} - E_{0F}^{\frac{3}{2}}$$

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

1.5. 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)

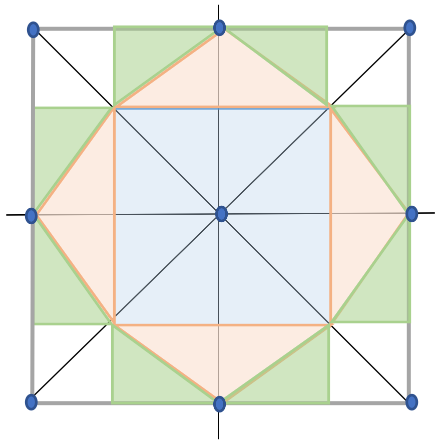
Substituting equation (2) in (1) we get $E = \frac{k^2h^2}{8m\pi^2}$ (3)

a plot is made between the total energy *'E'* and the wave vector *k*, for different values of *k* with *n = ±1, k = ±π/a. n = ±2, k = ±2π/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 *±π/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*π/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 (-*π /a* to *π/a*)

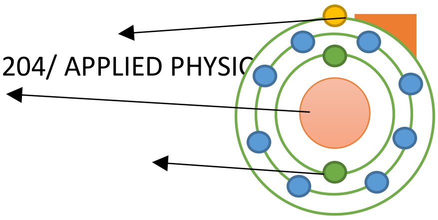
🟧 Second Brillouin Zone (-*2 π /a* to - *π/a* & *2 π /a* to *π/a*)

🟩 Third Brillouin Zone (-*3 π /a* to - *2π/a* & *3 π /a* to *2π/a*)

1.6 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*.



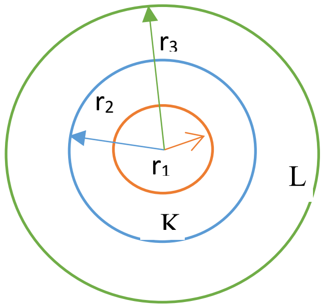
Valence electrons

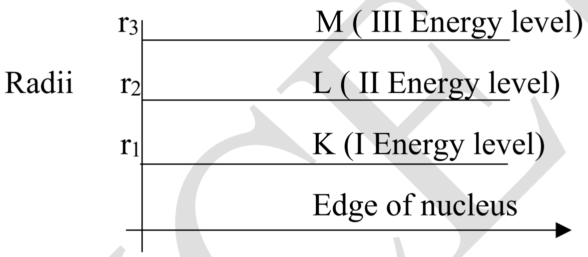
Nucleus

Bounded 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.



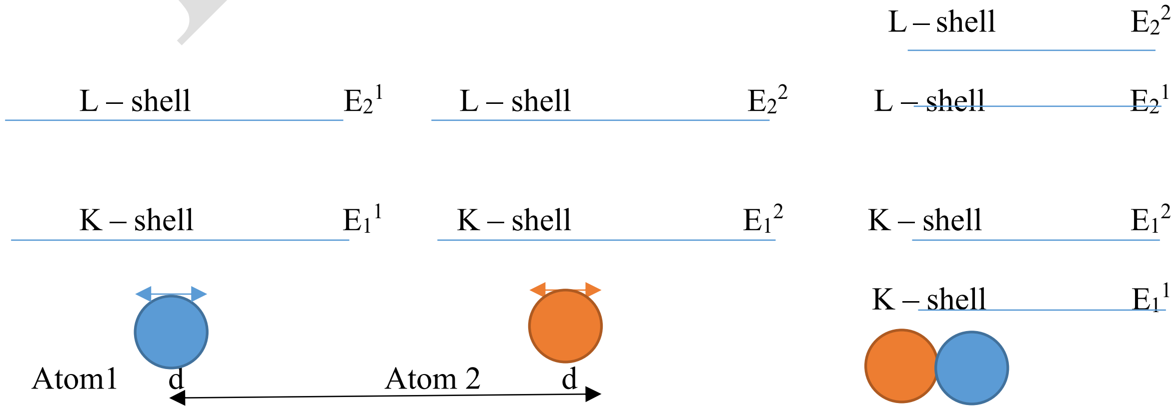


From the figure it is clear that the electrons can revolve only in certain permitted orbits of radii r_1, r_2 *and* r_3 *etc.,* and not in any arbitrary orbit. Since the electrons are not allowed in between the radii r_1 *and* r_2 or between the radii r_2 *and* r_3 etc., there won't be any electronic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



r>>d r = d

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.

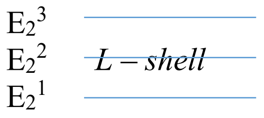
Inner Filled Bands, Valence band and Conduction band

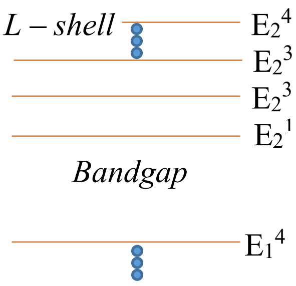
During the formation of energy bands, the inner filled energy levels forms a energy band called *Inner filled bands.* Similarly the electrons in the outermost shells of atoms forms an energy band called *valence band*. The valence band will be of completely filled (or) partially filled with electrons, based on the type of materials.

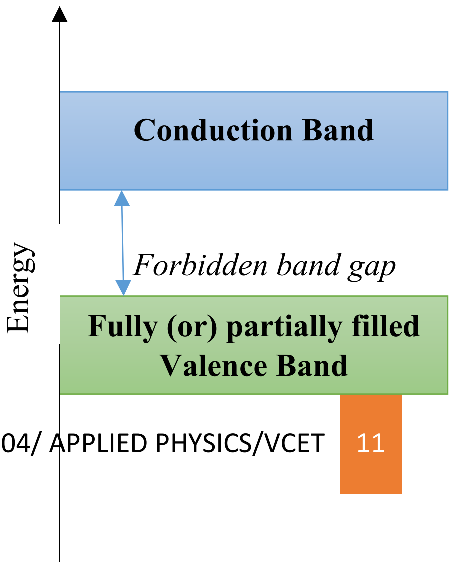
If an electron comes out from valence band for conduction, then they form an energy level corresponding to the energy band called *conduction band*

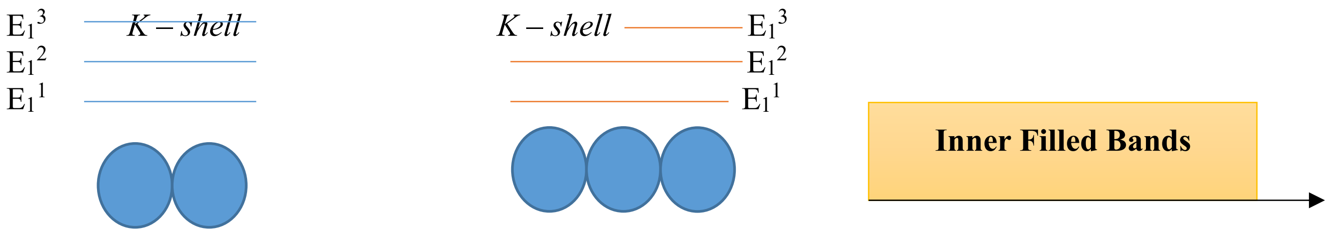
Forbidden gap

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,

1.7 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

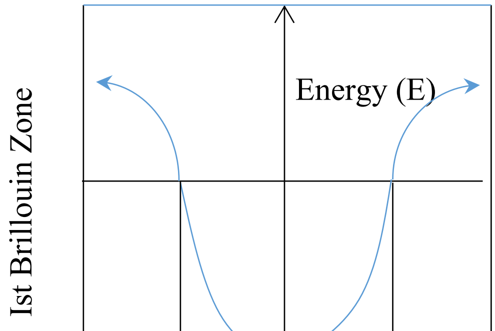
$\therefore$ $\frac{d^2E}{dk^2}$ is $-ve$ and hence m^* should be $-ve$ in the upper band. If a plot is made between $m^*$and k for different values of $\frac{d^2E}{dk^2}$, we get the curve as shown in figure

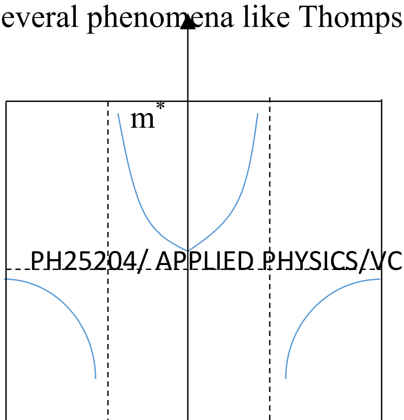
(iii) **At the point of inflection,** the value of $\frac{d^2E}{dk^2} = 0$ and hence in m^* - k plot, effective mass goes to infinity.

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.





P P P P

-π / a - k_0 O k_0 π / a K π/a - k_0 O k_0 π/a K

The valence band is the highest, lower-energy electron-occupied band (often filled or partially filled) where electrons are bound to atoms, while the conduction band is the lowest, higher-energy unoccupied band that allows free, mobile electrons for electrical conductivity. Separated by a forbidden band gap, they dictate a material's electrical behavior as conductors (overlap), semiconductors (small gap), or insulators (large gap).

Properties of the Valence Band

- Energy Level: Lower energy level compared to the conduction band.
- Occupancy: Generally, fully occupied or partially filled with valence electrons at absolute zero.
- Electron Behavior: Electrons are bound to the nucleus and do not contribute directly to electrical conduction.
- Location: Situated below the Fermi level.
- Holes: When electrons gain energy and jump to the conduction band, they leave behind vacancies known as "holes," which behave as positive charge carriers.

Properties of the Conduction Band

- Energy Level: Higher energy level than the valence band.
- Occupancy: Typically, empty at absolute zero, or partially filled.
- Electron Behavior: Contains "free electrons" that are not bound to any specific atom, enabling electrical conductivity.
- Location: Situated above the Fermi level.
- Mobility: Electrons in this band have high mobility, facilitating current flow.