
UNIT – 1 (Electronic Materials)

1.1 Introduction

Conducting materials are low resistivity materials, which conduct heat as well as electricity. Electrical conduction is due to free electrons, whereas normal conduction is due to free electrons as well as phonons.

1.1.1 Basic Terminology

Conductors:

Experimental measurements showed that the metals and their alloys exhibit large electrical conductivity in the order of $10^8 \Omega^{-1} \text{ m}^{-1}$. Hence they are known as conductors. Conducting materials are the materials having high electrical and thermal conductivities. Low resistive materials are also generally known as conducting materials.

Bound electrons:

All the valence electrons in an isolated atom are bound to their parent nuclei which are called as 'bound electrons'.

Free electrons:

In a solid, due to the boundaries of neighbouring atoms overlap each other, the valence electrons find continuity from atom to atom. Therefore, they can move easily throughout the solid. All such valence electrons of its constituent atoms in a solid are called free electrons.

Difference between ordinary gas and free electron gas:

The molecules of ordinary gas are neutral. But, the free electron gas is charged. The density of molecules is smaller than the density of free electrons.

Electric field (E):

The electric field (E) of a conductor having uniform cross section is defined as the potential drop (V) per unit length (l).

$$E = V/l \text{ Vm}^{-1}$$

Current density (j):

Current density (j) is defined as the current per unit area of cross section of an imaginary plane hold normal to the direction of flow of current in a current carrying conductor. If 'I' is the current, and 'A' is the area of cross section, then current density is given by,

$$\mathbf{J} = \mathbf{I} / \mathbf{A} \text{ Am}^{-2}$$

1.2 Conducting Materials

Conducting materials are classified into three major categories based on the conductivity.

- (i) Zero resistive materials
- (ii) Low resistive materials
- (iii) High resistive materials

(i) Zero resistive materials

The super conductors like alloys of aluminium, zinc, gallium, niobium, etc., are a special class of materials. These materials conduct electricity almost with zero resistance below transition temperature. Thus, they are called zero resistive materials. These materials are used for saving energy in the power systems, super conducting magnets, memory storage elements etc.,

(ii) Low resistive materials

The metals like silver, aluminium and alloys have high electrical conductivity. These materials are called low resistive materials. They are used as conductors, electrical conduct etc., in electrical devices and electrical power transmission and distribution, winding wires in motors and transformers.

(iii) High resistive materials

The materials like tungsten, platinum, nichrome etc., have high resistive and low temperature co-efficient of resistance. These materials are called high resistive materials. Such a metals and alloys are used in the manufacturing of resistors, heating elements, resistance thermometers.

The conducting properties of solid do not depend on the total number of the electrons available because only the valance electrons of the atoms take part in the conduction. When these valance electrons detached from the orbit they are called free electrons or conduction electrons.

In a metal, the number of free electrons available is proportional to its electrical conductivity. Hence, electronic structure of a metal determines its electrical conductivity.

1.3 Electron theory of solids

We know that the electrons in the outermost orbit of the atom determine the electrical properties in the 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

- (a) The behavior of conductors, semiconductors, and insulators.
- (b) The electrical, thermal and magnetic properties of solids.

So far three electron theories have been proposed.

(i) Classical free electron theory

This theory was developed by Drude and Lorentz. According to this theory, a metal consists of electrons which are free to move about in the crystal molecules of a gas it contains mutual repulsion between electrons is ignored and hence potential energy is taken as zero. Therefore the total energy of the electron is equal to its kinetic energy.

(ii) Quantum free electron theory

Classical free electron theory could not explain many physical properties. In classical free electron theory, we use Maxwell-Boltzmann statistics which permits all free electrons to gain energy. In Sommerfeld developed a new theory, in which he retained some of the features of classical free electron theory included quantum mechanical concepts and Fermi-Dirac statistics to the free electrons in the metals. This theory is called quantum free electron theory. Quantum free electron theory permits only a few electrons to gain energy.

(iii) Zone theory or band theory of solids

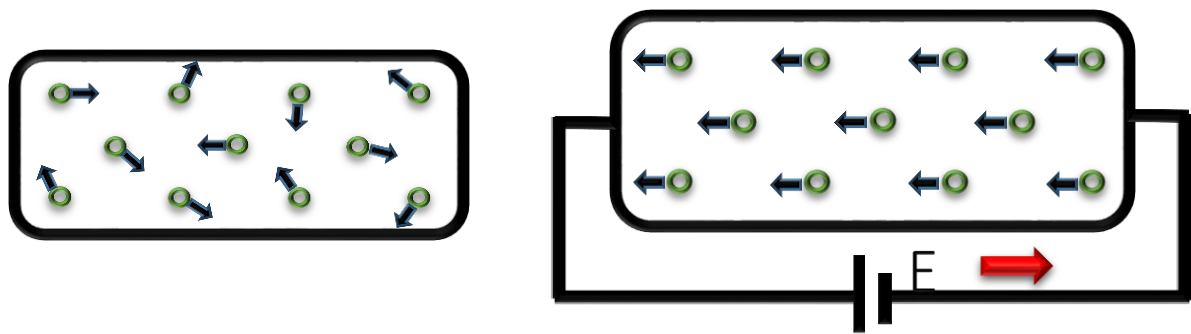
Bloch developed the theory in which the electrons move in a periodic field provided by the Lattice concept of holes, origin of Band gap and effective mass of electrons are the special features of this theory of solids. This theory also explains the mechanism of super conductivity based on band theory.

1.4 Classical free electron theory

Free electron theory of metals was proposed by P. Drude in the year 1900 to explain electrical conduction in metal. This theory was further extended by H.A. Lorentz in the year 1909.

1.4.1 Postulated of free electron theory

- ✓ Metal structure consists positive ion core, with valence electrons moves freely among these ion cores.
- ✓ These valence electrons moves inside metal just like molecules in gas.
- ✓ In the absence of electric field ($E=0$), free electrons move in random directions and collide with each other.
- ✓ In the collisions, no loss of energy will be observed because collisions are elastic.
- ✓ When electric field is applied ($E \neq 0$), the free electrons are accelerated in direction opposite to field.
- ✓ Free electrons obey Maxwell-Boltzmann statistics.



1.4.2 Postulates of free electron theory

Drift Velocity (V_d):

The drift velocity is defined as the average velocity acquired by the free electron in particular direction, due to the applied electric field.

$$\text{Drift Velocity} = \frac{\text{Average distance travelled by the electron}}{\text{Time taken}}$$

$$V_d = \lambda / t \text{ ms}^{-1}$$

Mobility (μ):

The mobility is defined as the drift velocity (V_d) acquired by the electron per unit electric field (E).

$$\mu = V_d/E \text{ m}^2\text{V}^{-1}\text{s}^{-1}$$

Mean free path (λ):

The average distance travelled by an electron between two successive collisions is called mean free path.

Mean collision time (τ_c) (or) Collision time

It is the time taken by the free electron between two successive collisions.

$$\tau_c = \lambda/V_d \text{ sec}$$

Relaxation time (τ):

It is the time taken by the electron to reach equilibrium position from disturbed position in the presence of electric field.

$$\tau = l/V_d \text{ sec}$$

Where l is the distance travelled by the electron. The value of relaxation time is of the order of 10^{-14} sec.

Band gap (E_g):

Band gap is the energy difference between the minimum energy of conduction band and the maximum energy of valence band.

Current density (J)

It is defined as the current per unit area of cross section of an imaginary plane held normal to the direction of the flow of current in a current carrying conductor.

$$\mathbf{J} = I/A \text{ Am}^{-2}$$

1.4.3 Expression for electrical conductivity

- ✓ Electrical conductivity of a semiconductor is different from that of a conductor. The charge carriers in a conductor are electrons. In the case of a semiconductor, both electron and holes are charge carriers.
- ✓ In the absence of an electric field, the motion of these free electrons is completely random like those of molecules in a gas.
- ✓ But when an electric field is applied, the electrons drift in opposite direction to that of applied field with an average velocity called the “drift velocity” (V_d).
- ✓ When electric field is applied, electrons experience a force eE , due to which they are accelerated.

$$\mathbf{F} = e\mathbf{E} \quad \text{But } \mathbf{F} = m\mathbf{a}$$

$$\therefore m\mathbf{a} = e\mathbf{E}$$

$$\therefore \mathbf{a} = (e\mathbf{E})/m \dots \dots (1)$$

As, electrons collision occurs during motion, the electrons will get accelerated momentarily so, the drift velocity will be

$$\therefore V_d = a \tau$$

$$\therefore V_d = \frac{eE}{m} \tau \dots \dots (2)$$

$$\text{Current density } J = \frac{I}{A} = neV_d \dots \dots (3)$$

$$\therefore J = ne \frac{eE}{m} \tau = \frac{ne^2 E \tau}{m} \dots \dots (4)$$

$$\text{From electrical conductivity } J = \sigma E \dots \dots (5)$$

$$\therefore \sigma E = \frac{ne^2 E \tau}{m}$$

$$\therefore \sigma = \frac{ne^2 \tau}{m} \dots \dots (6) \gg \gg \text{Expression for electrical conductivity}$$

Conductivity in terms of $k_B T$.

The relaxation time (τ) in terms of mean free path (λ) and average thermal velocity is given by:

$$\therefore \tau = \frac{\lambda}{v} \quad \dots \dots \dots (7)$$

Now, based on kinetic theory of gases,

$$\therefore \frac{1}{2} m v^2 = \frac{3}{2} k_B T$$

$$\therefore m = \frac{3 k_B T}{v^2} \quad \dots \dots \dots (8)$$

Using equation (8) & (7) in (6)

$$\therefore \sigma = \frac{n e^2 \lambda}{\frac{3 k_B T}{v^2}} = \frac{n e^2 \lambda v^2}{3 k_B T}$$

$$\therefore \sigma = \frac{n e^2 \lambda v}{3 k_B T} \quad \dots \dots \dots (9) \quad (\text{This equation says that electrical conductivity decreases}$$

with temperature)

| | |
|------|--|
| Q.1 | A current of 5 A is passing through a metallic wire of cross sectional area $4 \times 10^{-6} \text{ m}^2$. If the density of the charge carriers in the wire is $5 \times 10^{26} / \text{m}^3$, find the drift speed of the electrons. ($e = 1.6 \times 10^{-19}$) |
| Ans. | <p>$I = 5 \text{ A}$, $A = 4 \times 10^{-6} \text{ m}^2$, $n = 5 \times 10^{26} / \text{m}^3$, $V_d = ?$</p> <p>The relation between current (I) and drift velocity (V_d) of electron in wire of area (A) is</p> <p>$\therefore I = n e A V_d$</p> |

| | |
|------|---|
| | $\therefore V_d = \frac{I}{neA}$ $\therefore V_d = \frac{5}{(5 \times 10^{26})(1.6 \times 10^{-19})(4 \times 10^{-6})}$ $\therefore V_d = 1.5 \times 10^{-2} \text{ m/s}$ |
| Q.2 | <p>A conductor has an electron concentration of $5.9 \times 10^{28} / \text{m}^3$. What density in the conductor corresponds to a drift velocity of 0.625 m/sec. Calculate the mobility of charge carriers.</p> <p>Given $\sigma = 6.22 \times 10^7 \text{ } \Omega \text{m}^{-1}$.</p> |
| Ans. | <p>$n = 5.9 \times 10^{28} / \text{m}^3$, $V_d = 0.625 \text{ m/sec}$, $e = 1.6 \times 10^{-19}$, $J = ?$ & $\mu = ?$</p> $\therefore J = neV_d$ $\therefore J = (5.9 \times 10^{28})(1.6 \times 10^{-19})(0.625)$ $\therefore J = 5.9 \times 10^9 \text{ A/m}^2$ $\therefore \sigma = ne\mu$ $\therefore \mu = \frac{\sigma}{ne}$ $\therefore \mu = \frac{(6.22 \times 10^7)}{(5.9 \times 10^{28})(1.6 \times 10^{-19})}$ $\therefore \mu = 6.588 \times 10^{-3} \text{ m}^2/\text{V}\cdot\text{sec}$ |
| Q. 3 | <p>Calculate drift velocity of free electrons with a mobility of $3.5 \times 10^{-3} \text{ m}^2 / \text{V}\cdot\text{sec}$ in copper for an electric field strength of 0.5 V/m.</p> |
| Ans. | <p>$\mu = 3.5 \times 10^{-3} \text{ m}^2 / \text{V}\cdot\text{sec}$, $E = 0.5 \text{ V/m}$, $V_d = ?$</p> |

| | |
|------|---|
| | $\therefore \mu = \frac{V_d}{E}$ $\therefore V_d = \mu E$ $\therefore V_d = (3.5 \times 10^{-3}) (0.5)$ $\therefore V_d = 1.75 \times 10^{-3} \text{ m/sec}$ |
| Q. 4 | The density of silver $10.5 \times 10^3 \text{ kg m}^{-3}$ assuming that each silver atom provides one conduction electron. The conductivity of silver at 20°C is $6.8 \times 10^7 \Omega^{-1} \text{ m}^{-1}$. Calculate the density and mobility of electron in silver with atomic weight 107.9. |
| Ans. | <p>Density of silver $d = 10.5 \times 10^3 \text{ kg m}^{-3}$ Conductivity of silver at $20^\circ\text{C} = 6.8 \times 10^7 \Omega^{-1} \text{ m}^{-1}$ Atomic weight $A = 107.9$</p> <p>We know the carrier concentration (n) = $\frac{\text{Avagadro Number} \times \text{Density}}{\text{Atomic weight}}$</p> $\therefore n = \frac{6.023 \times 10^{23} \times 10.5 \times 10^3}{107.9}$ $\therefore n = 5.86 \times 10^{25} \text{ m}^{-3}$ <p>We know, the conductivity is given by $\sigma = ne\mu$</p> $\therefore \mu = \frac{\sigma}{ne}$ $\therefore \mu = \frac{6.8 \times 10^7}{5.86 \times 10^{25} \times 1.6 \times 10^{-19}}$ $\therefore \mu = 7.25 \times 10^{-3} \text{ m}^2 \text{V}^{-1} \text{s}^{-1}$ |

1.4.4 Expression for Thermal conductivity

The thermal conductivity is defined as the amount of heat flowing through a unit area per unit temperature gradient.

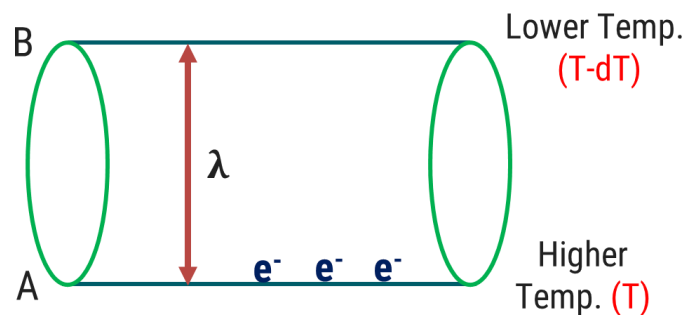
$$\therefore K = - \frac{\Delta Q}{\left(\frac{dT}{dx}\right) A} \frac{\text{Watt meter}}{\text{Kelvin}}$$

The negative sign indicates that heat flows hot end to cold end.

ΔQ = rate of heat flow (thermal energy) A =

Cross-sectional area of conductor

(dT/dx) = temperature gradient



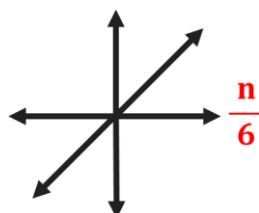
Average kinetic energy at A = $\frac{3}{2} K_B (T)$

Average kinetic energy at B = $\frac{3}{2} K_B (T - dT)$

The excess energy carried by electrons in traveling from point A to B

$$\begin{aligned} \frac{3}{2} K_B T &= \frac{3}{2} K_B (T - dT) \\ &= \frac{3}{2} K_B dT \end{aligned}$$

The electrons travel in all directions crossing unit area from A to B



$$\therefore e = \frac{1}{6} nv$$

So, excess energy transferred from A to B per unit area in unit time is:

$$\begin{aligned} & \frac{1}{6} nv \times \frac{3}{2} K_B dT \\ &= \frac{1}{4} nv K_B dT \end{aligned}$$

Similarly, deficiency of energy from B to A per unit time is:

$$= -\frac{1}{4} nv K_B dT$$

The rate of heat flow can be defined as the net energy transferred from A to B per unit area per unit time:

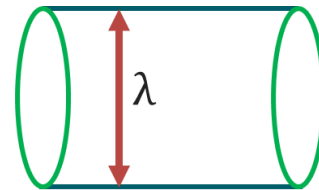
$$\begin{aligned} \therefore \Delta Q &= \frac{1}{4} nv K_B dT - \left(-\frac{1}{4} nv K_B dT \right) \\ \therefore \Delta Q &= nv K_B dT \left(\frac{1}{4} + \frac{1}{4} \right) \\ \therefore \Delta Q &= \frac{1}{2} nv K_B dT \end{aligned}$$

We know thermal conductivity k is defined as:

$$\therefore K = \frac{\Delta Q}{\left(\frac{dT}{dx} \right)}$$

Here, dx can be written as mean free path (λ)

$$\therefore K = \frac{\frac{1}{2} nv K_B dT}{\left(\frac{dT}{\lambda} \right)}$$



$$\text{Thermal conductivity, } K = \frac{1}{2} nv K_B \lambda$$

1.4.5 Wiedemann – Franz law

This law states that the ratio of thermal conductivity to electrical conductivity is directly proportional to the absolute temperature.

$$\text{i.e. } \frac{K}{\sigma} \propto T$$

$$\therefore \frac{K}{\sigma} = L T$$

L = Lorentz number

$$\therefore K = \frac{1}{2} n V K_B \lambda$$

$$\therefore \sigma = \frac{ne^2 \lambda V}{3 K_B T}$$

By, taking ratio

$$\therefore \frac{K}{\sigma} = \frac{\frac{1}{2} n V K_B \lambda_B}{\frac{ne^2 \lambda V}{3 K_B T}}$$

$$\therefore \frac{K}{\sigma} = \frac{3}{2} \left(\frac{K_B}{e} \right)^2 T$$

$$\therefore \frac{K}{\sigma} = L T$$

Theoretical value of L: $1.12 \times 10^{-8} \text{ W}\Omega/\text{K}^2$

Experimental value of L: $2.44 \times 10^{-8} \text{ W}\Omega/\text{K}^2$

Theoretical and experimental values of L doesn't match with each other.

So, Assumption is wrong that all electrons contribute in thermal conductivity.

1.4.6 Success of free electron theory

- ✓ It verifies ohm's law.
- ✓ It explains the thermal and electrical conductivities of a metal.
- ✓ It helps to deduce Wiedemann – Franz law.
- ✓ It explains optical properties of metals.

1.4.7 Drawbacks of classical free electron theory

- ✓ Theoretical value of specific heat and electronic specific heat of metal based is $\left(\frac{3R}{2}\right)$ is not in agreement with the experimental value $(10^{-4} RT)$.
- ✓ The classical free electron theory can't explain electrical conductivity of insulators and semiconductors.
- ✓ According to classical theory, $\frac{K}{\sigma} = T$ is constant at all temperature. But, this is not constant at low temperature.
- ✓ It failed to explain the superconductivity and magnetic susceptibility (χ).
- ✓ The phenomena such as photoelectric effect, Compton Effect and black body radiation can't be explained.
- ✓ According to classical free electron theory, the electrical conductivity (σ) proportional to the free electron density (n). But it failed to explain for different metals.

| | |
|------|--|
| Q.1 | Find the thermal conductivity of copper 20°C with a free electron density of $8.48 \times 10^{28}/\text{m}^3$ The thermal velocity of copper is $1.1536 \times 10^5 \text{ m/sec}$ at 20°C , with a mean free path of 2.813 nm . |
| Ans. | $n = 8.48 \times 10^{28}/\text{m}^3$, $\lambda = 2.813 \text{ nm} = 2.183 \times 10^{-9} \text{ m}$ $v = 1.1536 \times 10^5 \text{ m/sec}$ $K = ?$ We know, $\therefore K = \frac{1}{2} n V K_B \lambda$ $\therefore K = \frac{1}{2} (8.48 \times 10^{28}) \times (1.1536 \times 10^5) \times (1.38 \times 10^{-23}) \times (2.183 \times 10^{-9})$ $\therefore K = 18992 \text{ W/m} \cdot \text{K}$ |

1.5 Quantum free electron theory

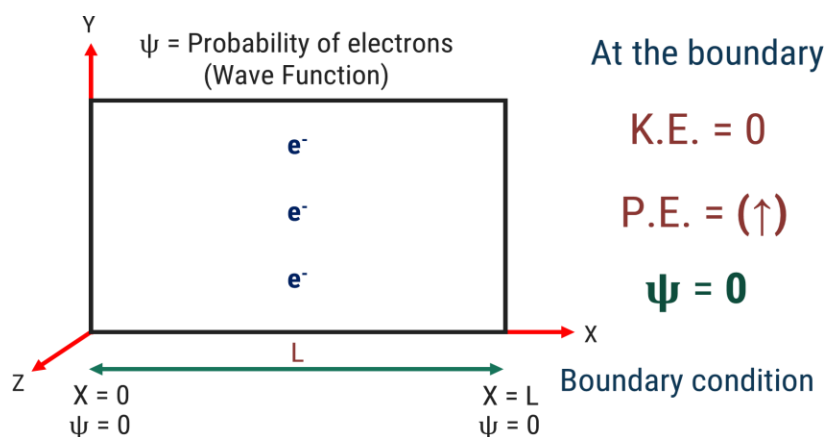
The failure of classical free electron theory paved this way for Quantum free electron theory. It was introduced by Sommerfield in 1928. This theory is based on making small concepts. This theory was proposed by making small changes in the classical free electron theory and by retaining most of the postulates of the classical free electron theory.

1.5.1 Assumptions (Postulates) of Quantum free electron

1. In a metal the available free electrons are fully responsible for electrical conduction.
2. The electrons move in a constant potential inside the metal. They cannot come out from the metal surface have very high potential barrier.
3. Electrons have wave nature, the velocity and energy distribution of the electron is given by Fermi – Dirac distribution function.
4. The loss of energy due to interaction of the free electron with the other free electron.
5. Electron's distributed in various energy levels according to Pauli Exclusion Principle.

Quantum free electron theory

- ✓ Each metal contains a very large number of electrons and these electrons can move freely inside the metal.
- ✓ Inside of the metal material uniform potential is applied:
 - Constantly moving electrons have only kinetic energy (K.E.) inside the metal while the potential energy (P.E.) is zero.
- ✓ P.E. = 0 can be only possible when,
 - Interaction of free electron with other electron and metallic core of the metal is negligible.



K.E. inside the material is not sufficient to overcome metal boundary.

- ✓ In quantum approach electrons move in wave form and wave nature of particle is given by Schrodinger.

- ✓ Schrodinger wave equation for 3-dimension:

$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{2m}{\hbar^2}[E - V]\psi = 0$$

- ✓ Schrodinger wave equation for 1-dimension:

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}[E - V]\psi = 0 \dots \dots (1)$$

E = total energy, V = potential energy, m = mass of electron

\hbar = modified Planck's constant ($\hbar = \frac{h}{2\pi}$)

In our case P.E. = 0, so, total energy (E) of the system is because of only K.E.

$$\therefore \frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}E\psi = 0$$

Consider, $\frac{2m}{\hbar^2}E = k^2$

$$\therefore \frac{d^2\psi}{dx^2} + k^2\psi = 0 \dots \dots (2)$$

- ✓ To identify complementary function of ψ :

$$\therefore \psi = [A \cos kx + B \sin kx] \dots \dots (3) \text{ (remember)}$$

Where, k = wave vector, A & B are constants

In order to find the values of A & B we can use two boundary conditions at X=0 and X=L.

For, (1) $X = 0 \rightarrow \psi = 0$ condition

$$\therefore 0 = [A \cos k0 + B \sin k0]$$

$$\therefore 0 = [A (1) + 0]$$

$$\therefore A = 0$$

Putting this value in equation (3)

$$\therefore \psi = B \sin kx \dots \dots \dots (4)$$

For, (2) $X = L \rightarrow \psi = 0$ condition

$$\therefore \psi = B \sin kL$$

Here, B can't be zero because then whole equation will be zero.

$$\therefore \psi = [A \cos kx + B \sin kx] \dots \dots \dots (3)$$

If ψ becomes zero then probability of having electron inside the metal becomes zero, which is not possible.

This problem can be satisfied by taking $\sin kL$ zero instead of B.

$\sin kL = 0$ only possible at $(\sin n\pi)$ Where, $n = 0, 1, 2, 3, \dots$

So, if we compare $kL = n\pi$ then:

$$\therefore k = \frac{n\pi}{L}$$

Therefore, the wave function will be valid only if:

$$\therefore \psi(x) = B \sin \left(\frac{n\pi}{L} x \right) \dots \dots \dots (5)$$

$$\therefore k^2 = \frac{n^2 \pi^2}{L^2}$$

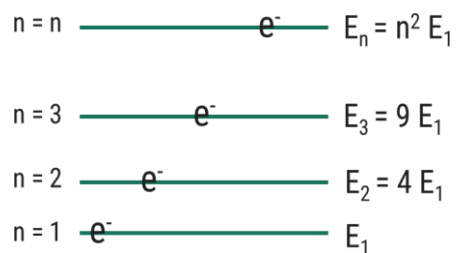
By, comparing the values of k^2

$$\frac{2m}{\hbar^2} E = \frac{n^2 \pi^2}{L^2}$$

$$\therefore E_n = \frac{n^2 \pi^2 \hbar^2}{L^2 2m}$$

$$\therefore E_n = \frac{n^2 \pi^2 \hbar^2}{L^2 2m 4\pi^2}$$

$$\therefore E_n = \frac{n^2 \hbar^2}{8 m L^2} \dots \dots \dots (6)$$



According to this equation, electrons will have the level of energy (E_n) inside the metal.

Value of constant B in equ. 5 obtained by applying the normalization condition to get the value of wave function ψ .

- ✓ Normalizing the wave function means you find the exact form of probability (ψ) of the particle which found somewhere in space is 1.

$$\therefore \int_{-\infty}^{\infty} \Psi^2 dx = 1$$

$$\therefore \int_0^L B^2 \sin^2 \left(\frac{n\pi x}{L} \right) dx = 1$$

$$\therefore \frac{B^2}{2} \int_0^L 1 - \cos \left(\frac{2\pi n x}{L} \right) dx = 1$$

$$\therefore \frac{B^2}{2} \int_0^L 1 dx - \int_0^L \cos \left(\frac{2\pi n x}{L} \right) dx = 1$$

$$\therefore \psi(x) = B \sin \left(\frac{n\pi}{L} x \right) \dots \dots \dots (5)$$

$$\therefore \frac{B^2}{2} \int_0^L \left[\sin^2 \left(\frac{2\pi n x}{L} \right) \right] dx = 1$$

$$\therefore \frac{B^2}{2} \int_0^L \left[\sin^2 \left(\frac{2\pi n x}{L} \right) \right] dx = 1$$

$$\therefore \frac{B^2}{2} \left[L - \frac{L}{2\pi n} \left[\sin \left(\frac{2\pi n L}{L} \right) - \sin \left(\frac{2\pi n 0}{L} \right) \right] \right] = 1$$

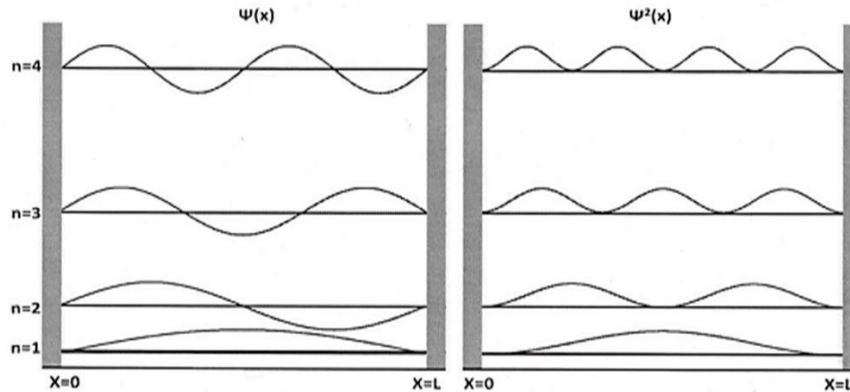
$$\therefore \frac{B^2}{2} [L] = 1$$

Putting this value in equation (5)

$$\therefore \psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L} x\right) \dots \dots \dots (7)$$

This equation gives the value of probability of electron in a confined system.

The wavefunctions corresponding to four lowest states for different values of n and probability of finding the particle are shown in fig.



1.5.2 Advantages of quantum free electron theory

- ✓ It explains the specific heat of materials.
- ✓ It explains Compton Effect, photoelectric effect, blackbody radiation, Zeeman Effect.
- ✓ It gives the correct mathematical expression for the thermal conductivity of metals.
- ✓ It explains the superconductivity.

1.5.3 Drawbacks of quantum free electron theory

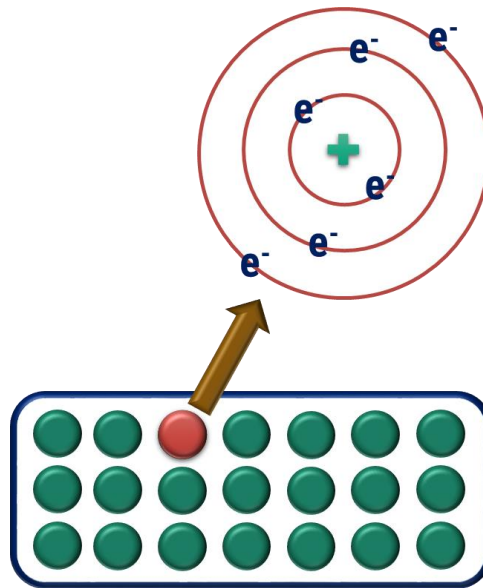
- ✓ This theory fails to explain the positive value of Hall coefficients.
- ✓ It failed to distinguish metal, semiconductor and insulator.
- ✓ It failed to explain lower conductivities of divalent metal than monovalent metals.

1.6 Band Theory or (Energy Band Diagrams)

(a) Formation of energy bands in solids:

- ✓ In a single isolated atom, the electrons in each orbit have definite energy associated with it.

- ✓ In case of solids, the atoms are close to each other, so the energy levels of outermost orbit electrons are affected by the neighbouring atom.
- ✓ When two single or isolated atoms are brought close to each other, the outermost orbit electrons of the two atoms interact with each other.
- ✓ I.e. The electrons in the outermost orbit of one atom experience an attractive force from the neighbouring atom nucleus.



- ✓ As a result of this, the energy of electrons is no more the same, the energy levels are changed to a value which is higher or lower than the original energy level.
- ✓ The Pauli's exclusive principle allows each energy level to contain only two electrons. [“This grouping of different energy levels is called energy bands”](#).
- ✓ The energy level of the inner orbit electrons are not much affected by presence of neighbouring atoms.

(b) Energy bands in solids:

Valence band:

- ✓ “The energy band formed by grouping the energy levels of valence electrons is called valence band”.
- ✓ Electrons in valence band have lower energy than electrons in conduction band.

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- ✓ The electrons in valence band are loosely bound to nucleus of atom, they can be moved to conduction band by applying energy.

Forbidden band:

- ✓ "The energy gap that is present between the valence band and conduction band by separating the two energy bands is called the forbidden band or forbidden gap."
- ✓ Electrons can't stay in this band as there is no allowed energy state in this gap.
- ✓ The energy associated with the forbidden gap is called the band gap energy.

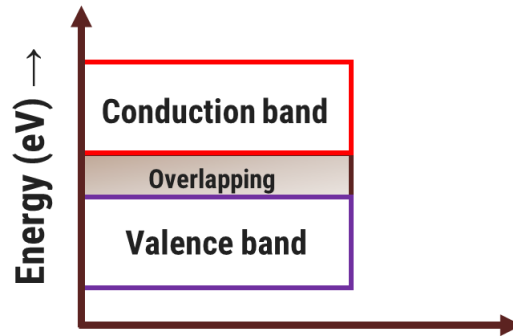
Conduction band:

- ✓ "The energy gap or band formed by grouping the energy levels of free electrons is called conduction band."
- ✓ It is the uppermost band with free electrons, electrons have higher energy than electron in valence band.
- ✓ The band is completely empty for insulators and partially filled for conductors.
- ✓ The conduction band electrons are not bound to the nucleus of atom.

1.6.1 Types of electronic materials: conductor, Insulators, and semiconductors

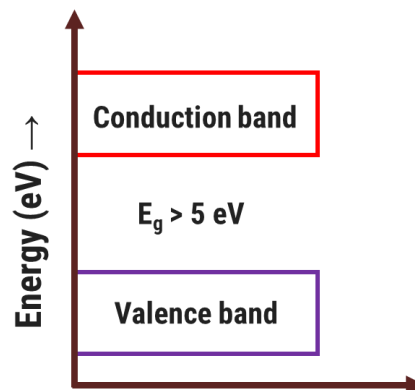
Conductors:

- ✓ "The materials which easily allow the flow of electric current are called conductors." e.g. copper, iron, silver, etc.
- ✓ The resistivity is of an order of $10^{-9} \Omega\text{m}$ at room temperature.
- ✓ In a conductor, the conduction and valence band overlap each other as shown in figure.
- ✓ A small amount of energy provides enough energy for valence band electrons to move in conduction band.



Insulators:

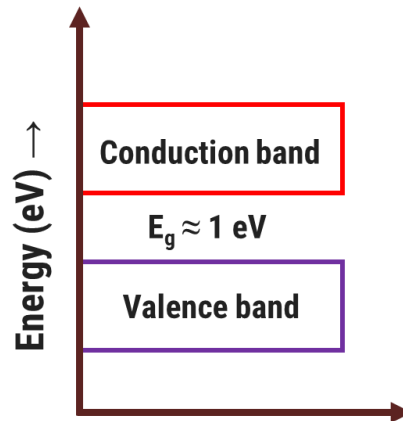
- ✓ “The materials which do not allow the flow of electric current through them are called insulators.”
- ✓ The valence band is completely filled with electrons. The forbidden energy gap is greater than 5 eV.
- ✓ The electrons in valence band can't move to conduction as they are locked up between the atoms.
- ✓ It requires large amount of external energy to move the electrons to conduction band.
- ✓ The resistivity is of approx. 10^3 to $10^{17} \Omega\text{m}$ at room temp.



Semi-conductors:

- ✓ “The materials which have electrical conductivity between that of conductors and insulators are called semiconductors.” e.g. Silicon, germanium.
- ✓ The forbidden gap in semiconductors is very small (approx. 1.1 eV).

- ✓ At low temp., valence band is completely filled with electrons and conduction band is completely empty as electrons don't have sufficient energy to move in conduction band.
- ✓ As temp. increases, electrons gain energy and move to conduction band. I.e. electrical conductivity increases with temperature.
- ✓ So, they have negative temperature coefficient of resistance.



1.6.2 Kronig Penney model

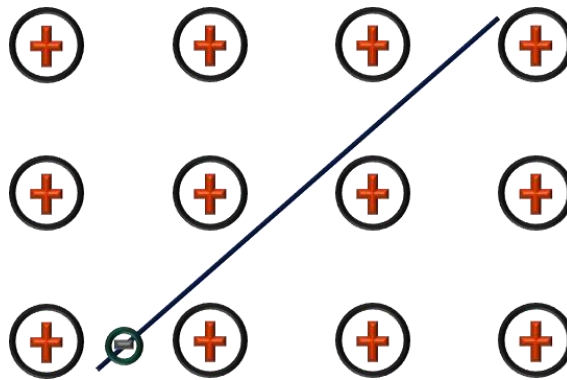
- ✓ It is a simplified model for an electron in one-dimensional periodic potential.
- ✓ It demonstrates that a simple one-dimensional periodic potential yields energy bands as well as energy bandgaps.
- ✓ It is an instructive tool to demonstrate how band structure can be calculated for periodic potential and how allowed and forbidden energies are obtained using Schrodinger's equation.
- ✓ It also helps in understanding the concept of Effective mass and E-K diagrams.

According to free electron theory:

- ✓ Homogeneous distribution of potential (voltage) electrons in metal. But it doesn't explain it for semiconductor and insulators.

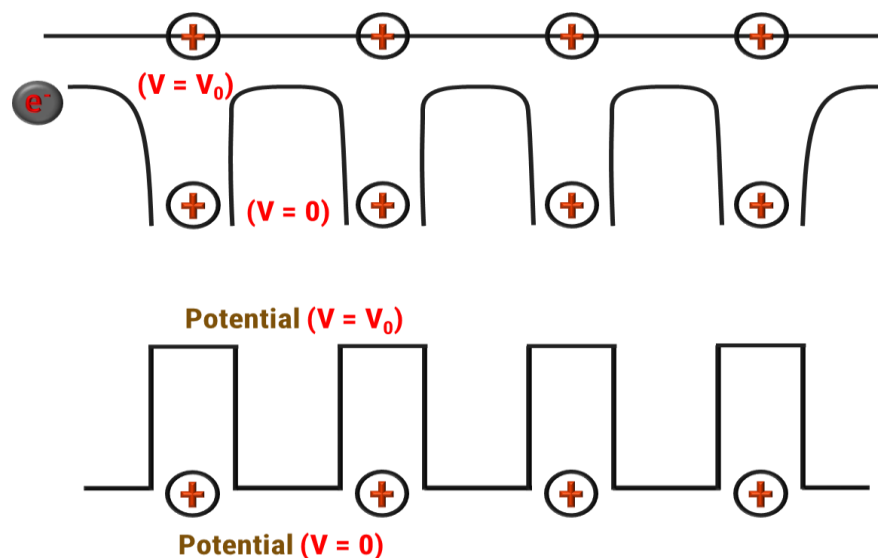
From Band theory:

- ✓ Bloch suggested that: Potential of electrons varies periodically with lattice.
- ✓ Because inside the crystal, there is periodic arrangement positively charged ions, through which the electrons move.

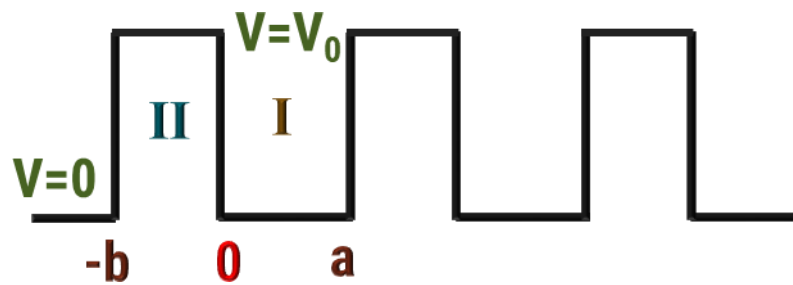


Kroning and Penney suggested:

- ✓ The potential of electron at the positive ion site is zero and is maximum in between the two (i.e. middle of two ions).
- ✓ It was difficult to solve Schrodinger equation with varying potential.
- ✓ Kroning–Penney suggested that take potential as shape of rectangular steps.
- ✓ This model is called Kroning–Penney model.



- ✓ The wave functions associated with this model can be calculated by solving Schrodinger equations for the two regions I and II. (I=Potential well & II=Potential barrier).
- ✓ Two consecutive potential wells are separated by a distance "b" (regions II) and the value of the potential in each of these regions is "V₀".
- ✓ Therefore, potential of electron for the two regions can be expressed as v(x) = 0 for region-I and v(x) = v₀ for region-II.



The Schrodinger's equations are:

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} E \psi = 0 \dots \text{(for region - I)} \quad 0 < x < a \dots \dots (1)$$

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} [E - V_0] \psi = 0 \dots \text{(for region - II)} \quad -b < x < 0 \dots \dots (2)$$

- ✓ Now let us assume that the system is at room temperature and electrons do not acquire sufficient thermal energy to escape from the crystal. Let us define two real quantities α and β such that:

$$\alpha^2 = \frac{2mE}{\hbar^2} \quad \text{and} \quad \beta^2 = - \frac{2m(E - V_0)}{\hbar^2} \dots \dots (3)$$

$$\therefore \frac{d^2\psi}{dx^2} + \alpha^2 \psi = 0 \dots \text{(for region - I)} \quad 0 < x < a \dots \dots (4)$$

$$\therefore \frac{d^2\psi}{dx^2} - \beta^2 \psi = 0 \dots \text{(for region - II)} \quad -b < x < 0 \dots \dots (5)$$

- ✓ The solution (according to Bloch theorem) that will be appropriate for both the regions (I & II) will be of the form of a plane wave e^{ikx} modulated with a periodic function $u_k(x)$:

$$\therefore \psi(x) = e^{ikx} u_k(x)$$

Where $k = \frac{2\pi}{\lambda}$ is propagation vector or wave vector

- ✓ Using Bloch theorem and applying all boundary conditions for region (I & II) for continuity of the wavefunction, solution of Schrodinger equation is obtained as:

$$\therefore P \frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos ka \dots \dots (6) \text{ where, } P = \frac{mV_0ab}{\hbar^2} \text{ (Scattering power)}$$

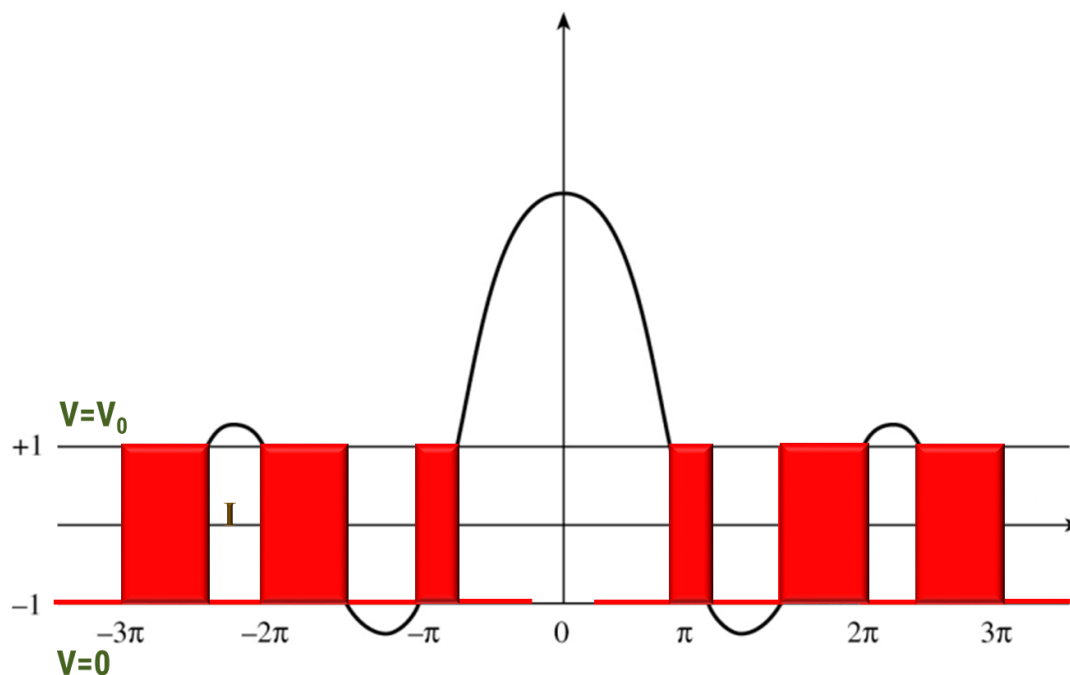
The term V_0b is called barrier strength

$$\therefore \cos ka = \pm 1$$

$$\therefore ka = \pm n\pi \quad (n = 1, 2, 3, \dots)$$

$$\therefore k = \frac{\pm n\pi}{a}$$

Graph of Kronig Penny Model:



Findings or conclusions from Kronig – Penny Model:

- ✓ The permissible limit of the term $P \frac{\sin \alpha a}{\alpha a} + \cos \alpha a$ lies between +1 and -1.
- ✓ The shaded portion of the wave shows the bands of allowed energy.
- ✓ By increasing αa , allowed energy state for electron increases, thereby increase in band- width.
- ✓ Increase in band-width lead to distance between electrons and total energy.

Case (I): $P \rightarrow 0$

$$\therefore \cos \alpha a = \cos ka$$

$$\therefore \alpha a = ka$$

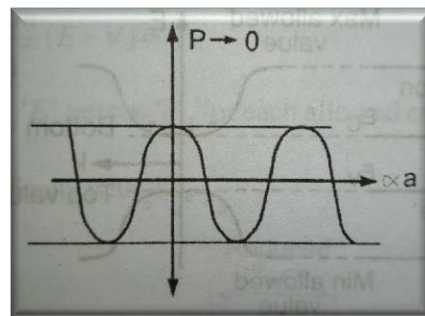
$$\therefore \alpha = k$$

$$\therefore \alpha^2 = k^2 \quad \text{By using equation (3)}$$

$$\therefore k^2 = \frac{2mE}{\hbar^2}$$

$$\therefore E = \frac{k^2 \hbar^2}{2m} \dots \dots (7)$$

$$\therefore E = \frac{p^2}{2m} \dots \dots (8)$$



- ✓ Above equation shows the energy of free electron in conduction band.
- ✓ Energy band is broadened and it is continuous.

Case (I): $P \rightarrow \infty$

$$\therefore P \frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos ka \dots \dots (6)$$

$$\therefore \sin \alpha a = \frac{\alpha a (\cos ka - \cos \alpha a) P}{\alpha a}$$

$\therefore \sin \alpha a = 0$ sin becomes zero at $n\pi$

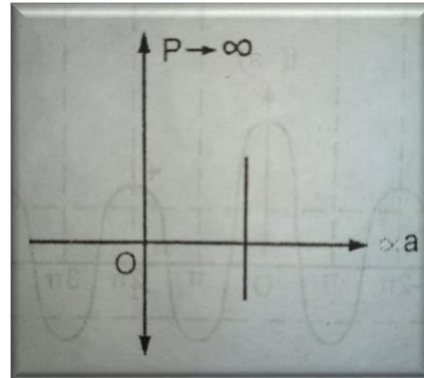
$\therefore \alpha a = n\pi$

$$\therefore \alpha^2 = \frac{n^2 \pi^2}{a^2}$$

$$\therefore \frac{2mE}{\hbar^2} = \frac{n^2 \pi^2}{a^2}$$

$$\therefore E = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$$

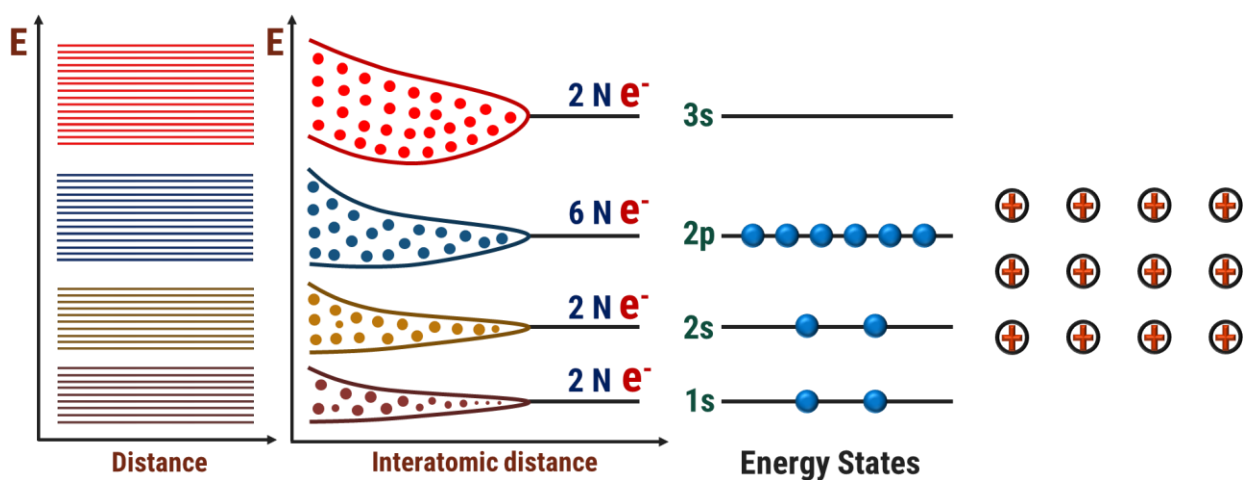
$$\therefore E = \frac{n^2 h^2}{8ma^2}$$



- ✓ If P is large, it results in decrease of allowed energy and increase in forbidden gap.
- ✓ The allowed states are compressed to a line spectrum.

1.6.3 Energy band structure of a solid

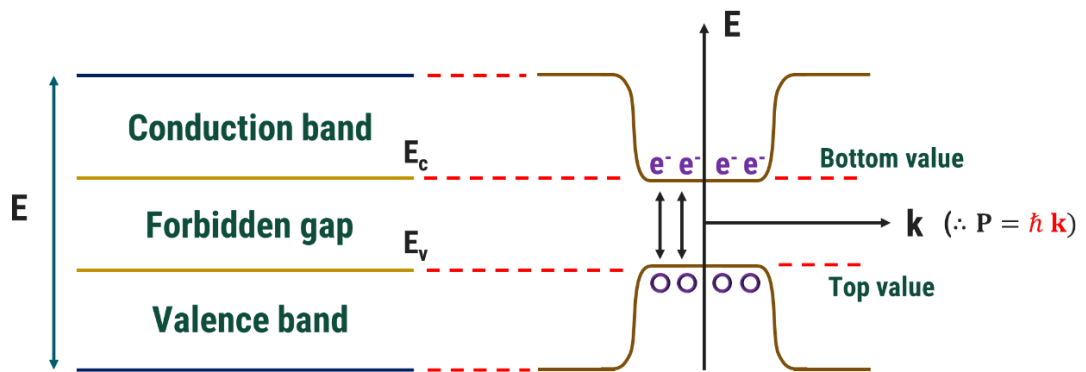
- ✓ A crystal consists of large number of atoms arranged in a regular periodic structure. The extent of energy levels splits in the solids depends on the nearness of atoms.
- ✓ Let us assume N identical atoms form a crystal.



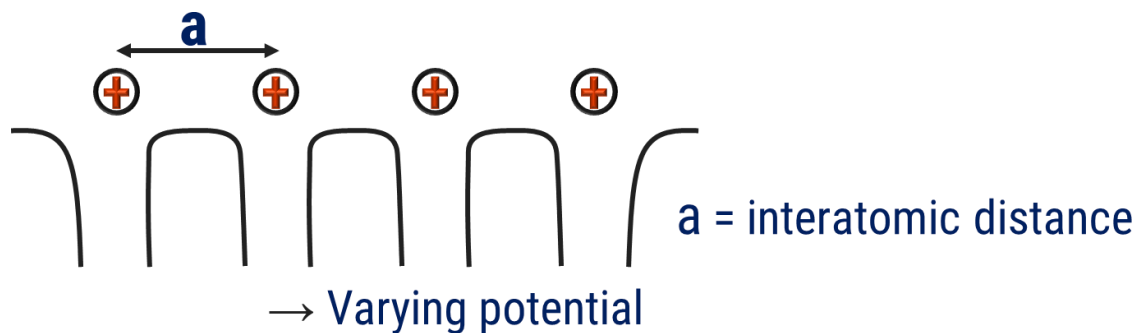
- ✓ The energy levels of the isolated atoms are shown in fig. All the N atoms have identical sets of energy levels.
- ✓ Electrons fill the energy levels in each atom independently.
- ✓ As the atoms approach, a continuous increasing interaction occurs between the atoms.
- ✓ Each of the energy levels splits into many distinct levels and forms energy bands, as shown in fig.
- ✓ While occupying energy band, electrons start from the lowest energy level in the band and fill the levels one after another.
- ✓ When $2N$ electrons occupy the N levels available in the band, the band is said to be completely filled.
- ✓ In case of non-availability of $2N$ electrons, the energy band gets **partially filled**.
- ✓ When there are no electrons to occupy the levels, the band remains **vacant**.
- ✓ At room temperature, the kinetic energy of the electron is of the order of $k_B T$ ($\approx 0.026 \text{ eV}$) which is very large compared to the energy level separation in an allowed band.
- ✓ Electrons can easily move into higher vacant levels within the allowed energy band either due to thermal energy or due to a small externally applied electric field.
- ✓ The following two conditions are to be fulfilled for electrical conduction to take place in a solid.
 1. There should be free electrons available in the solid.
 2. Vacant energy levels should be available above the levels occupied by free electrons.

1.6.4 E – K diagram

“An E-K diagram is a dispersion diagram that shows the relationship between energy and momentum of available states of electrons in a material.”



- ✓ From the above diagram, we see the bottom value of conduction band corresponding to 'E_c' and top value of valence band corresponds to 'E_v'.
- ✓ From the E-K diagram, it can be seen that the holes which are closed to the top valence band and electron which are close to the bottom of conduction band, participate in the transition processes.



- ✓ As all atoms are arranged periodically in lattice, we can say that semiconductors are crystalline in nature.
- ✓ As per Bloch's theorem, as the potential varies periodically, probability of finding an electron also varies periodically.

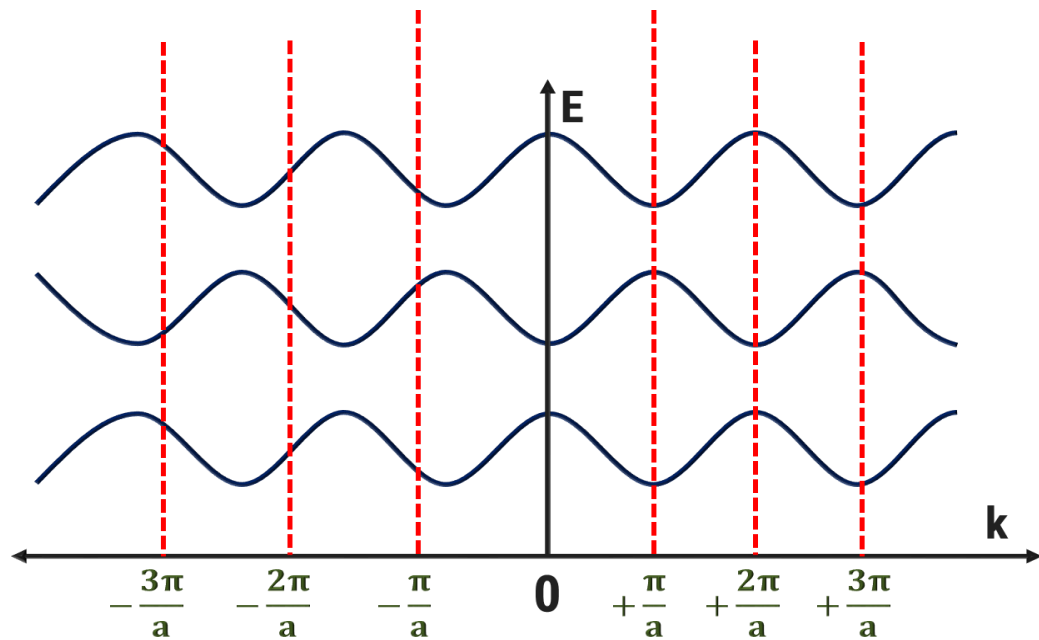
i.e. $\psi_k(r) = u_k(r) e^{ikx}$

e^{ikx} = plane function & $u_k(r)$ periodic function

Using this value in Schrodinger's equation:

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}[E - V]\psi = 0$$

- ✓ Here, Schrodinger's equation gives periodic graph of 'E' versus 'k' for each allowed energy value.

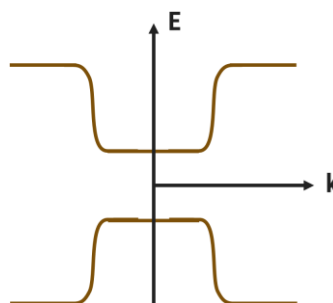


- ✓ The discrete energy value of k is in the form of $\pm \frac{\pi}{a}, \pm \frac{2\pi}{a}, \pm \frac{3\pi}{a}, \dots$
- ✓ The area between the $+\frac{\pi}{a}$ to $-\frac{\pi}{a}$ is known as **1st Brillouin zone**, and between $+\frac{2\pi}{a}$ to $-\frac{2\pi}{a}$ is known as **2nd Brillouin zone**.

Here this periodic arrangement can be understood by three zones.

1. Periodic Zone
2. Reduced Zone
3. Extended Zone

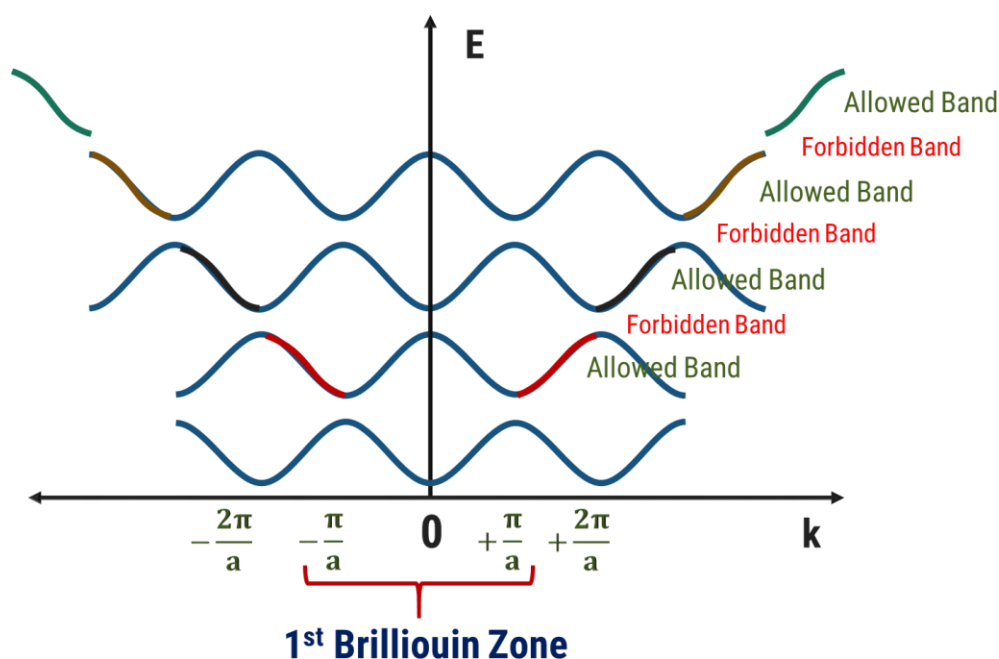
As the variation of E vs k is periodic, we can restrict ourself to only one period. I.e. $+\frac{\pi}{a}$ to $-\frac{\pi}{a}$. The final reduced zone diagram is as below.



(According to De – Broglie's theorem, $P = \hbar k$)

Energy of the particle is given by: $E = \frac{p^2}{2m}, E = \frac{\hbar^2 k^2}{2m}$

Extended Zone:



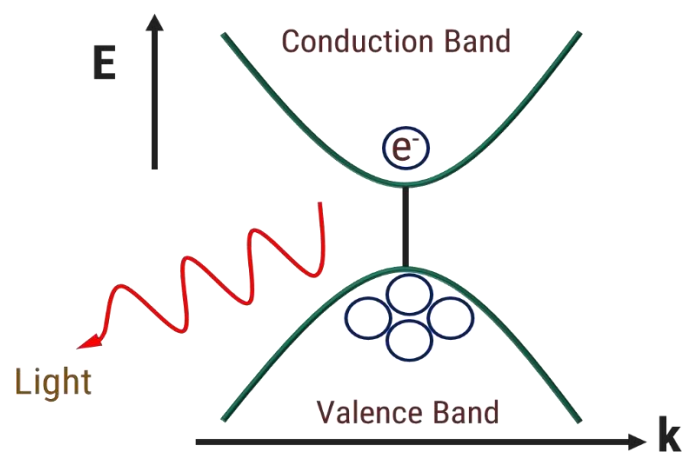
- ✓ From the graph, it is clear that electrons have allowed energy values in the region or zone extending from $k = -\pi/a$ to π/a . This is called first Brillouin zone. After a break in energy values, called forbidden band, the electrons have another allowed zone of energy values in the region extended from $k = -\pi/a$ to $-2\pi/a$ and from $k = \pi/a$ to $2\pi/a$. This zone is called the second Brillouin zone.
- ✓ Similarly, the higher order Brillouin zones can be defined.

| | |
|------|---|
| Q.1 | Consider two-dimensional square lattice of side 3.0 \AA . At what electron momentum values do the sides of first Brillouin zone appear? What is the energy of free electron with this momentum? |
| Ans. | <p>We know, $p = \hbar k$</p> <p>Here, \hbar = Reduced Plank constant k = wave number</p> |

| | |
|--|--|
| | <p>p = momentum</p> <p>a = Side of the lattice</p> <p>For 1st Brillouin zone</p> $k = \pm \frac{\pi}{a}$ $\therefore p = \hbar \frac{\pi}{a} = \frac{h}{2a}$ $\therefore p = \frac{66 \times 10^{-34}}{10^{-10}} = 11 \times 10^{-24} \text{ kg} \cdot \text{m/sec}$ <p>Therefore, Energy (E) = $\frac{p^2}{2m}$</p> $\therefore E = \frac{(11 \times 10^{-24})^2}{10^{-31}} = 66 \times 10^{-19} \text{ Joule}$ $\therefore E = \frac{66 \times 10^{-19}}{1.6 \times 10^{-19}} = 42 \text{ eV}$ |
|--|--|

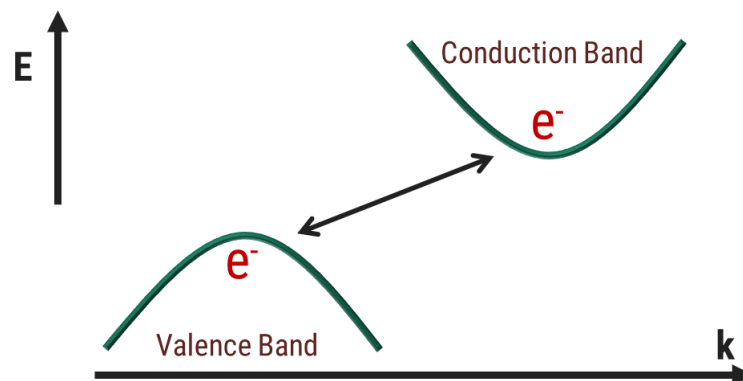
1.6.5 Direct and Indirect bandgap semiconductors as per E – K Diagram

Direct bandgap semiconductor:



- ✓ A direct band gap semi-conductor is the one in which maximum energy level of valence band aligns with the minimum energy level of conduction band with respect to momentum. e.g. GaAs
- ✓ In a semi-conductor, the minimum energy state in conduction band and maximum energy state in valence band is characterized by crystal momentum and wave vector ' k ' (propagation constant).
- ✓ In a direct bandgap semiconductor, the k -vectors are same for conduction band minima and valence band maxima.
- ✓ Whenever an electron from conduction band recombines with a hole from valence band, the energy and momentum, both should be conserved.
- ✓ The energy difference between conduction band and valence band is released in the form of a photon.
- ✓ The k -vectors of electron and hole are same. So, we say that momentum is also conserved.
- ✓ We say the energy is conserved by emitting a photon.

Indirect bandgap semiconductor:



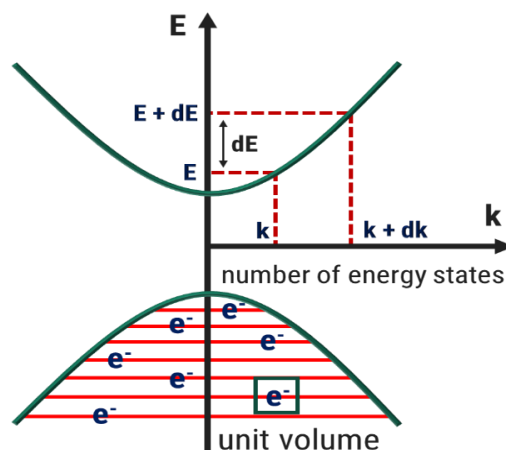
- ✓ An indirect bandgap semiconductor is the one in which maximum energy level of valence band and minimum energy level of conduction band are not aligned with respect to momentum. e.g., Si, Ge.
- ✓ In an indirect bandgap semiconductor, the k -vectors are different for conduction band minima and valence band maxima.
- ✓ In an indirect bandgap semiconductor, there is a difference in momentum. The recombination process can occur only after the momentum aligns.

- ✓ Due to crystal imperfections in certain semiconductors, the electron in the conduction band loses energy and momentum at the same time.
- ✓ The electron actually passes through an intermediate state and transfers its momentum to the crystal lattice.
- ✓ In this case, the energy is emitted in the form of heat. The transition is non-radiative in nature.

1.6.6 Difference between direct and Indirect bandgap semiconductors

| DBG semiconductor | IBG semiconductor |
|---|--|
| It is one in which maximum energy level of valence band aligns with the minimum energy level of conduction band with respect to momentum. | It is the one in which maximum energy level of valence band and minimum energy level of conduction band are not aligned with respect to momentum. |
| In this direct recombination takes place with energy equal to the difference between energy of recombining particles. | In this due to a difference in momentum, first momentum is conserved by release of energy and only when the two momenta are aligned, recombination occurs. |
| The probability of radiative recombination is very high. | The probability of radiative recombination is almost negligible. |
| Efficiency factor is high. | Efficiency factor is low. |
| They are preferred for making optical devices like LED's | Cannot be used to make optical device. |

1.6.7 Density of states



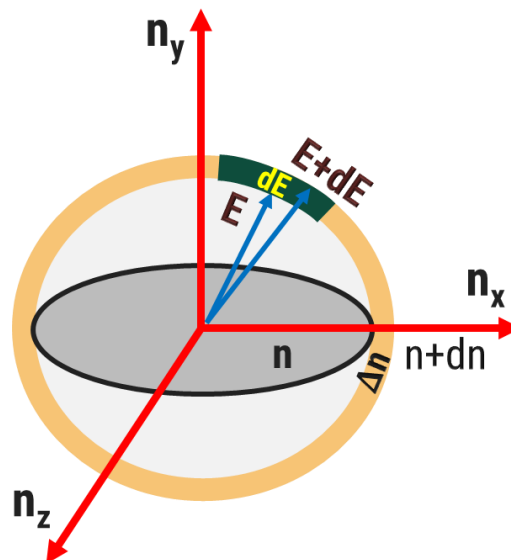
- ✓ Density of states: The number of energy states per unit volume of a metal.
- ✓ It is used to calculate the number of charge carriers per unit volume of any solid.

$$N(E)dE = \frac{\text{Number of energy states between } E \text{ and } E + dE}{\text{Volume of the metal}}$$

$$N(E)dE = \frac{D(E)dE}{V} \dots \dots (1)$$

Density of states $N(E)dE$ is defined as the number of available electron states per unit volume in an energy interval (dE).

Derivation:



- ✓ Let us consider a sphere of radius " n " in space with quantum numbers n_x, n_y, n_z .

$$n^2 = n_x^2 + n_y^2 + n_z^2$$
- ✓ The sphere is further divided into many shells represents a particular combination of quantum numbers and represents particular energy value.
- ✓ Let us consider two energy values E and $E + dE$ can be found by finding the number of energy states between the shells of radius n and $n + dn$ from the origin.
- ✓ Since the quantum numbers are positive integers, n values can be defined only in the positive octant of the n -space.

The number of energy states within a sphere: $n = \frac{4}{3}\pi n^3$

- ✓ The number of available energy states within the sphere of radius "n" due to one octant.

$$\therefore n = \frac{1}{8} \left[\frac{4}{3} \pi n^3 \right]$$

- ✓ Similarly the number of available energy states within the sphere of radius $n+dn$ corresponding energy.

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

The number of available energy states between the shells of radius n and $n+dn$ (or) between the energy levels E and $E + dE$.

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

$$\therefore D(E)dE = \frac{1}{8} \left[\frac{4}{3} \pi (n^3 + dn^3 + 3n^2dn + 3dn^2n - n^3) \right]$$

- ✓ Since the higher powers of dn is very small, dn^2 and dn^3 terms can be neglected.

$$\therefore D(E)dE = \frac{1}{8} \left[\frac{4}{3} \pi (3n^2dn) \right] \dots \dots (2)$$

$$\therefore D(E)dE = \frac{\pi n^2 dn}{2} \dots \dots (3)$$

- ✓ We know that allowed energy values is

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

$$\therefore n^2 = \frac{8ma^2 E}{h^2} \dots \dots (4)$$

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

Differentiating equation (4) w.r.t 'n'

$$\therefore n \, dn = \frac{8 m a^2 dE}{2h^2} \dots \dots (6)$$

Substituting (5) & (6) in equation (3)

$$\therefore D(E)dE = \frac{\pi}{2} n \cdot dn$$

$$\therefore D(E)dE = \frac{\pi}{2} \left(\frac{8 m a^2 E^{\frac{1}{2}}}{h^2} \right) \left(\frac{8 m a^2}{2h^2} \right) dE$$

$$\therefore D(E)dE = \frac{\pi}{4} \left(\frac{8 m a^2}{h^2} \right)^{\frac{1}{2}} \left(\frac{8 m a^2}{h^2} \right)^{\frac{1}{2}} E^{\frac{1}{2}} dE$$

$$\therefore D(E)dE = \frac{\pi (8 m a^2)^{\frac{3}{2}}}{4 (h^2)^{\frac{3}{2}}} E^{\frac{1}{2}} dE$$

$$\therefore D(E)dE = \frac{\pi}{4 h^3} \frac{(8 m)^{\frac{3}{2}} a^{\frac{3}{2}}}{(h^2)^{\frac{3}{2}}} E^{\frac{1}{2}} dE$$

✓ Volume of the metal, $V = a^3$

$$\therefore D(E)dE = \frac{\pi}{4 h^3} \frac{(8 m)^{\frac{3}{2}} V E^{\frac{1}{2}} dE}{(h^2)^{\frac{3}{2}}}$$

✓ For unit volume of metal $V = 1 \text{ m}^3$

$$\text{From equation (1)} \therefore N(E)dE = \frac{D(E)dE}{V}$$

$$\therefore N(E)dE = \frac{\frac{\pi}{4 h^3} \frac{(8 m)^{\frac{3}{2}} V E^{\frac{1}{2}} dE}{(h^2)^{\frac{3}{2}}}}{V}$$

$$\text{Density of states} \therefore N(E)dE = \frac{\pi}{4 h^3} \frac{(8 m)^{\frac{3}{2}} E^{\frac{1}{2}} dE}{(h^2)^{\frac{3}{2}}}$$

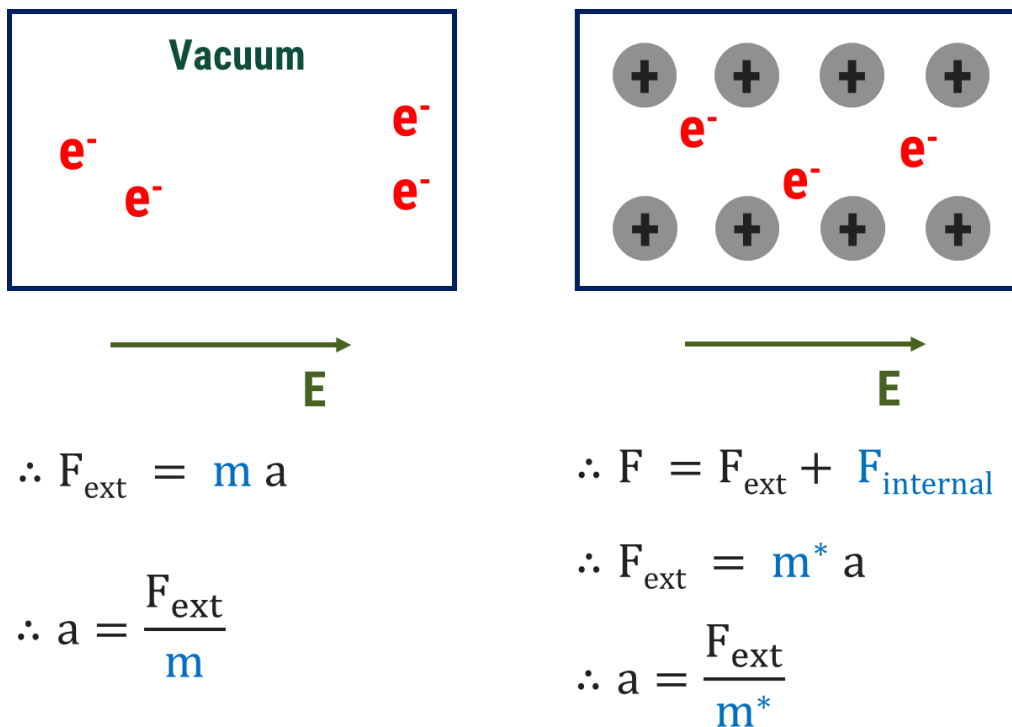
✓ Each electron energy level can accommodate two electrons as per Pauli's exclusion principle. (Spin up and Spin down = $2(e) \times \text{density of states}$).

$$\therefore N(E)dE = 2 \times N(E)dE$$

$$\therefore N(E)dE = \frac{\pi}{2h^3} \left(\frac{m}{m^*}\right)^2 E^2 dE$$

1.6.8 Effective mass of electron

- ✓ Experimentally measured values shows that for some solids the mass is larger, while in case of other solids it is slightly smaller than free electron mass.
- ✓ This experimentally determined electron mass is known as effective mass (m^*).



- ✓ Consider mass of electron as effective mass (m^*).
- ✓ Consider mass as per quantum mechanical approach.
- ✓ Then we can neglect internal force in the crystal system, where atoms have periodic arrangement.
- ✓ So, Periodic potential will be applied on each electron.
- ✓ We see that same magnitude of electric field (E) is applied to both electrons (In vacuum and inside the crystal), but the electron accelerates at a different rate inside the crystal, due to varying (periodic) potential inside the crystal.
- ✓ The electron mass is altered in this case due to the varying potential.
- ✓ "This altered mass is called effective mass of electron."

Derivation:

- ✓ Let E be the electric field applied to the electron inside the crystal. The force experienced by it is

$$\therefore F_{\text{ext}} = m^* a$$

- ✓ According to De-Broglie hypothesis electron behaves like wave. Here, velocity acquired by electron is known as group velocity (V_g):

$$\therefore V_g = \frac{d\omega}{dk} \quad \text{where, } \omega = \text{angular frequency}$$

$$\therefore V_g = \frac{d}{dk} \left(\frac{2\pi E}{h} \right) \dots \dots \dots (1)$$

- ✓ differentiating equ. (1) w.r.t (t)

$$\therefore \frac{dV_g}{dt} = \frac{2\pi}{h} \frac{d}{dt} \left(\frac{dE}{dk} \right)$$

$$\therefore a = \frac{1}{\hbar} \frac{d}{dt} \left(\frac{dE}{dk} \right)$$

$$\therefore a = \frac{1}{\hbar} \frac{d}{dk} \left(\frac{dE}{dt} \right) \quad (\text{Energy and Time are dependent term, that's why we exchange it})$$

$$\therefore a = \frac{1}{\hbar} \frac{d}{dk} \left(\frac{dE}{dk} \frac{dk}{dt} \right) \dots \dots \dots (2)$$

$$\therefore P = \hbar k$$

- ✓ differentiate above equ. w.r.t (t)

$$\therefore \frac{dP}{dt} = \frac{d}{dt} \hbar k$$

$$\therefore F = \hbar \frac{dk}{dt}$$

$$\therefore \frac{dk}{dt} = \frac{F}{\hbar} \dots \dots \dots (3)$$

- ✓ Substitute this value in equ. (2)

$$\therefore a = \frac{1}{\hbar} \frac{d}{dk} \left(\frac{dE}{dk} \frac{F}{\hbar} \right)$$

$$\therefore a = \frac{F}{\hbar^2} \frac{d^2E}{dk^2}$$

$$\therefore F = \left[\frac{\hbar^2}{d^2E}{a} \dots \dots (4) \right]$$

- ✓ Comparing equ (4) with $F = m a$

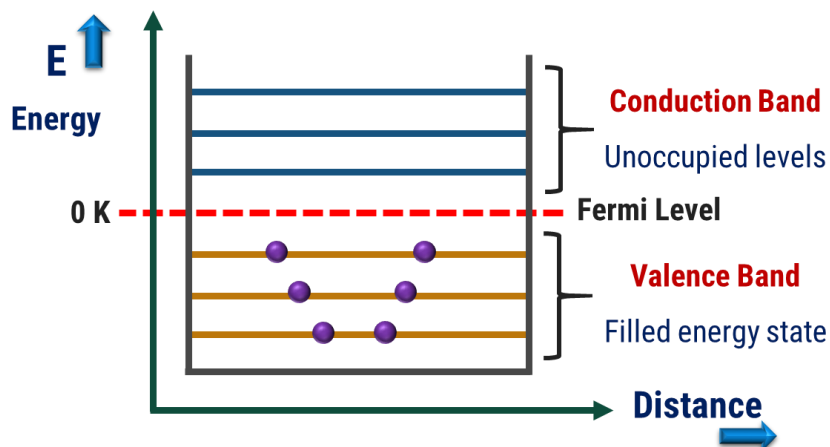
$$\therefore m^* = \frac{\hbar^2}{\frac{d^2E}{dk^2}} \quad \text{Expression of effective mass of an electron.}$$

- ✓ It is clear from the above equation that effective mass of an electron depends on E-K diagram.

1.6.9 Fermi level and fermi function

Fermi level: “The highest energy level which an electron can occupy at absolute zero (0 K) or (–273°C) temperature is called fermi level.”

Fermi energy: “The energy possessed by electrons in the fermi level at absolute zero temperature is called fermi energy.”



Fermi function:

Also known as **Fermi – Dirac distribution function**.

Fermi distribution function is used for half integer spin particles (fermions) like electrons, which obey Pauli's exclusive principle.

Statement: It is an expression for the distribution of electrons among the energy levels as a function of temperature, the probability of finding an electron in a particular energy state of energy E is given by:

$$f(E) = \frac{1}{1 + e^{\frac{E - E_f}{k_B T}}}$$

Where, $f(E)$ = Fermi function E_f =

Fermi energy

T = Absolute temperature (0 K) k_B =

Boltzmann constant

- ✓ From above equation, we can say that a system is characterized by its temperature and fermi energy (E_f).
- ✓ For a filled energy level $f(E) = 1$ and for unfilled level $f(E) = 0$.

Case I: At $T = 0$ K

- ✓ At $T = 0$ K, Electron occupy lowest energy first, followed by next higher levels as per Pauli's exclusive principle.

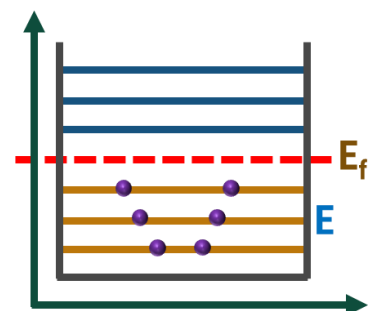
(a) At $T = 0$ K, $E < E_f$

For energy level E , lying below E_f , $(E - E_f)$ makes negative value.

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

$$\therefore f(E) = 1$$

- ✓ This implies that all energy levels below E_f are completely filled.



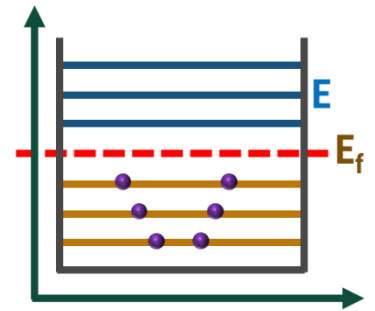
(b) At $T = 0\text{ K}$, $E > E_f$

For energy level E , lying above E_f , $(E - E_f)$ makes positive value.

$$\therefore f(E) = \frac{1}{1 + e^{\left(\frac{E - E_f}{k_B T}\right)}}$$

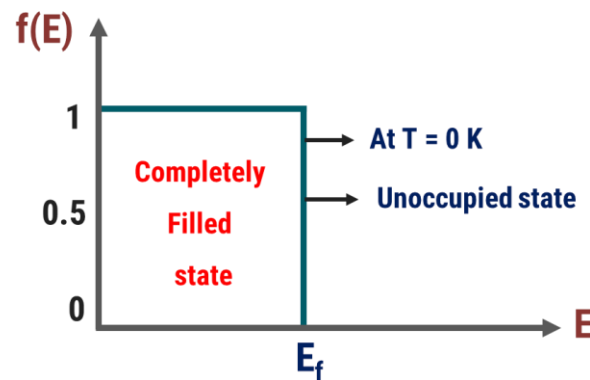
$$\therefore f(E) = \frac{1}{1 + e^\infty} = \frac{1}{1 + \infty} = 0$$

$$\therefore f(E) = 0$$



- ✓ This implies that all energy levels above E_f are completely Vacant.
- ✓ There is no possibility of electron occupying an energy level above E_f .

Variation of $f(E)$ at $T = 0\text{ K}$



Case II: At $T > 0\text{ K}$

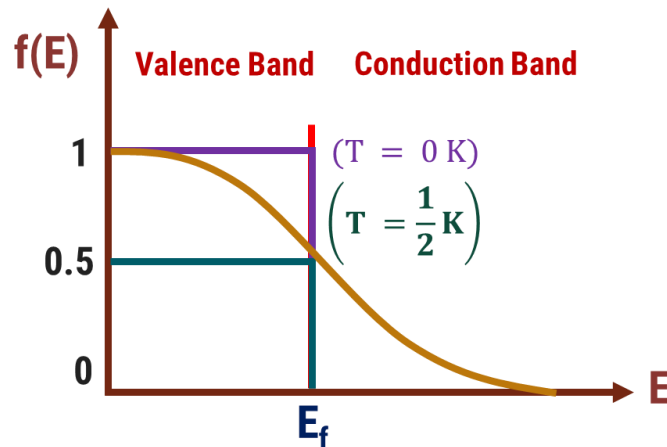
- ✓ At room temperature, the probability starts reducing from 1 for values of E close to E_f , but larger than E_f .
- ✓ At $T > 0\text{ K}$, for $E = E_f$, exponential function becomes zero.

$$\therefore f(E) = \frac{1}{1 + e^{\left(\frac{E - E_f}{k_B T}\right)}}$$

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

$$\therefore f(E) = 0.5$$

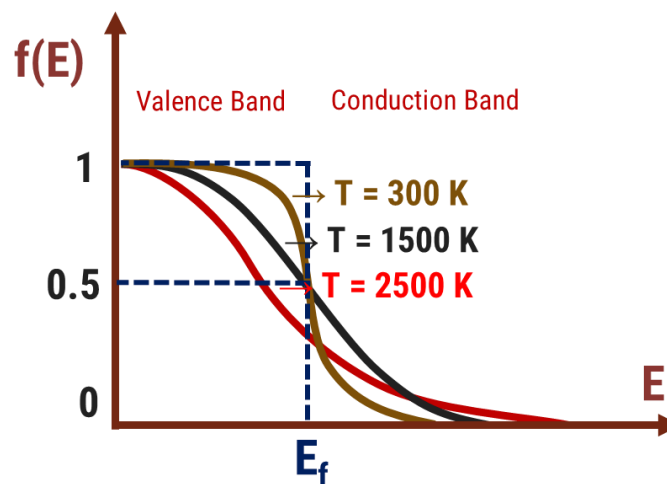
- ✓ $f(E) = 0.5$ implies that probability of occupancy of an electron is 50% at any temperature above 0 K .



- ✓ For $E = E_f$, the value of $f(E)$ falls off to zero rapidly as shown in the figure above.

Case III: At $T = \text{very high temperature}$

- ✓ At room temperature, it can be seen from the figure that the transition between completely filled states and completely empty states is rather gradual than abrupt.
- ✓ i.e. $f(E)$ changes from 1 to 0 more gradually.



- ✓ As temperature (T) increases, electron may get an energy of an order $k_B T$ and go to the higher vacant state.
- ✓ Relation between fermi energy E_f , fermi velocity V_f , temperature T_f and mean free path λ is given by:

$$\text{Fermi velocity: } V_f = \sqrt{\frac{2E_f}{m}}$$

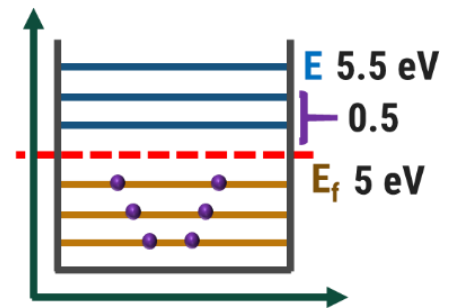
$$\text{Fermi temperature: } T_f = \frac{E_f}{k_B}$$

$$\text{The mean free path: } \lambda = \tau V_f$$

| | |
|------|--|
| Q.1 | Evaluate the Fermi function for energy $k_B T$ above the Fermi energy. |
| Ans. | $E - E_F = k_B T, \quad f(E) = ?$ We know Fermi Function $\therefore f(E) = \frac{1}{1 + e^{\left(\frac{E - E_f}{k_B T}\right)}}$ For an energy $K_B T$ above Fermi energy: $E - E_F = k_B T$ $\therefore f(E) = \frac{1}{1 + e^1} = \frac{1}{1 + 2.78}$ Fermi distribution function $f(E) = 0.269$ |
| Q.2 | Calculate the fermi velocity and mean free path for conduction electrons, given that its fermi energy is 11.63 eV and relaxation time for electrons is 7.3×10^{-15} sec. |
| Ans. | $E_f = 11.63 \text{ eV} = 11.63 \times 1.6 \times 10^{-19} \text{ Joule},$ $\tau = 7.3 \times 10^{-15} \text{ sec}, V_f =$ $?,$ $\lambda = ?$ $\therefore V_f = \sqrt{\frac{2 E_f}{m}}$ |

| | |
|------|--|
| | $\therefore V_f = \sqrt{\frac{2 \times (11.63 \times 1.6 \times 10^{-19})}{9.11 \times 10^{-31}}}$ $\therefore V_f = \sqrt{4085 \times 10^{12}}$ $\therefore V_f = 202 \times 10^6 \text{ m/sec}$ <p>The mean free path: $\lambda = \tau V_f$</p> $\therefore \lambda = \tau V_f$ $\therefore \lambda = (7.3 \times 10^{-15}) (202 \times 10^6)$ $\therefore \lambda = 1.47 \times 10^{-8} \text{ m}$ $\therefore \lambda = 14.75 \text{ nm}$ |
| Q.3 | Calculate the fermi energy and fermi temperature in a metal. The fermi velocity of electrons in the metal is $0.86 \times 10^6 \text{ m/sec}$. |
| Ans. | $V_f = 0.86 \times 10^6 \text{ m/sec}$ $E_f =$? $T_f = ?$ $E_f = \frac{1}{2} m V_f^2$ $\therefore E_f = \frac{1}{2} (9.11 \times 10^{-31}) (0.86 \times 10^6)^2$ $\therefore E_f = 336 \times 10^{-19} \text{ Joule}$ $\therefore E_f = \frac{336 \times 10^{-19}}{1.6 \times 10^{-19}}$ $\therefore E_f = 210 \text{ eV}$ |

| | |
|------|---|
| | <p>Fermi temperature: $T_f = \frac{E_f}{k_B}$</p> <p>$\therefore T_f = \frac{336 \times 10^{-19}}{138 \times 10^{-23}}$</p> <p>$\therefore T_f = 2441 \times 10^3 \text{ K}$</p> |
| Q.4 | Using fermi function, evaluate the temperature at which there is 1% probability that an electron in a solid will have an energy 0.5 eV above E_f of 5 eV. |
| Ans. | <p>$E = 5.5 \text{ eV}$</p> <p>$E_f = 5 \text{ eV}$</p> <p>$f(E) = 1\% = 0.01$</p> <p>$= ?$</p> <p>$\therefore E - E_f = 5.5 - 5 = 0.5 \text{ eV}$</p> <p>$\therefore E - E_f = 0.5 \times (1.6 \times 10^{-19}) \text{ J}$</p> <p>$\therefore f(E) = \frac{1}{1 + e^{\left(\frac{E - E_f}{k_B T}\right)}}$</p> <p>$\therefore f(E) \left(1 + e^{\left(\frac{E - E_f}{k_B T}\right)} \right) = 1$</p> <p>$\therefore f(E) + f(E) e^{\left(\frac{E - E_f}{k_B T}\right)} = 1$</p> <p>$\therefore f(E) e^{\left(\frac{E - E_f}{k_B T}\right)} = 1 - f(E)$</p> <p>$\therefore e^{\left(\frac{E - E_f}{k_B T}\right)} = \frac{1 - f(E)}{f(E)}$</p> <p>$\therefore e^{\left(\frac{E - E_f}{k_B T}\right)} = \frac{1 - f(E)}{f(E)}$</p> <p>Taking logarithm on both side</p> |



| | |
|------|---|
| | $\therefore \frac{E - E_f}{k_B T} = \ln \left[\frac{1 - f(E)}{f(E)} \right]$ $\therefore \frac{E - E_f}{k_B T} = \ln(1 - f(E)) - \ln(f(E))$ $\therefore \frac{1}{k_B T} = \frac{\ln(1 - f(E)) - \ln(f(E))}{E - E_f}$ $\therefore k_B T = \frac{E - E_f}{\ln(1 - f(E)) - \ln(f(E))}$ $\therefore T = \frac{E - E_f}{k_B [\ln(1 - f(E)) - \ln(f(E))]}$ $\therefore T = \frac{0.5 \times (1.6 \times 10^{-19})}{1.38 \times 10^{-23} [\ln(1 - 0.01) - \ln(0.01)]}$ $\therefore T = \frac{8 \times 10^{-20}}{(1.38 \times 10^{-23}) [-0.01005 - (-4.6051)]}$ $\therefore T = \frac{8 \times 10^{-20}}{6.341 \times 10^{-23}}$ $\therefore T = 1261597$ $\therefore T = 1261 \times 10^3 \text{ K}$ |
| Q.5 | Find the probability with which an energy level 0.02 eV above Fermi level will be occupied at room temperature of 300 K and at 1000 K. |
| Ans. | $E - E_f = 0.02 \text{ eV} = 0.02 \times 1.6 \times 10^{-19} \text{ J}$ Probability of occupancy at 300 K |

$$\therefore f(E) = \frac{1}{1 + e^{\left(\frac{E - E_f}{k_B T}\right)}}$$

$$\therefore f(E) = \frac{1}{1 + e^{\left(\frac{0.02 \times 1.6 \times 10^{-19}}{1.38 \times 10^{-23} \times 300}\right)}}$$

$$\therefore f(E) = \frac{1}{1 + e^{(0.7729)}}$$

$$\therefore f(E) = \frac{1}{1 + 2166}$$

$$\therefore f(E) = 0.315$$

Probability of occupancy at 1000 K

$$\therefore f(E) = \frac{1}{1 + e^{\left(\frac{E - E_f}{k_B T}\right)}}$$

$$\therefore f(E) = \frac{1}{1 + e^{\left(\frac{0.02 \times 1.6 \times 10^{-19}}{1.38 \times 10^{-23} \times 1000}\right)}}$$

$$\therefore f(E) = \frac{1}{1 + e^{(0.2318)}}$$

$$\therefore f(E) = \frac{1}{1 + 12609}$$

$$\therefore f(E) = 0.442$$

1.6.10 Carrier concentration in metals

- ✓ Number of electrons per unit volume can be obtained by multiplying density of states with probability function.

$$n_c = f(E) \times N(E) dE$$

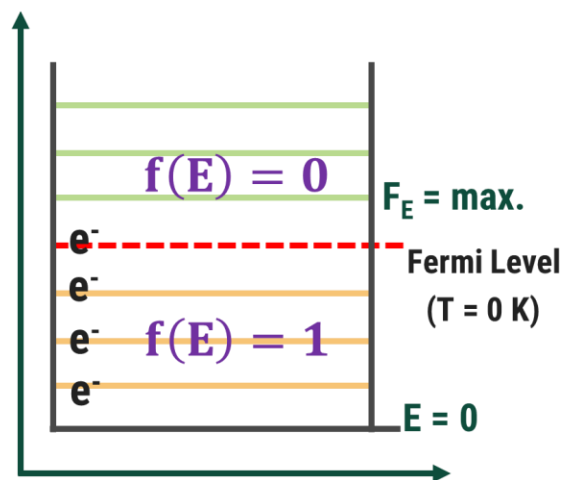
$N(E)dE$ = density of states $f(E)$ = fermi function

$$\therefore n_c = f(E) \times \frac{\pi}{2h^3} \left(\frac{2m}{h^2}\right)^{\frac{3}{2}} E^{\frac{1}{2}} dE$$

$$\therefore n_c = \frac{\pi}{2h^3} \left(\frac{2m}{h^2}\right)^{\frac{3}{2}} E^{\frac{1}{2}} dE \times f(E)$$

$$\therefore n_c = \frac{\pi}{2} \left(\frac{2m}{h^2}\right)^{\frac{3}{2}} E^{\frac{1}{2}} dE \times f(E)$$

Calculation of fermi energy at $T = 0$ K



- ✓ We will calculate the energy state in the order of increasing energy starting from $E=0$ to the highest filled state E_f , at $T=0$ K.

$$\therefore n_c = \frac{\pi}{2} \left(\frac{2m}{h^2}\right)^{\frac{3}{2}} E^{\frac{1}{2}} dE \times f(E)$$

$$\therefore n_c = \frac{\pi}{2} \left(\frac{8m}{h^2} \right)^{\frac{3}{2}} \int_0^{E_F} E^{\frac{1}{2}} dE \times f(E)$$

At $T = 0$ K, $f(E) = 1$

$$\therefore n_c = \frac{\pi}{2} \left(\frac{8m}{h^2} \right)^{\frac{3}{2}} \int_0^{E_F} E^{\frac{1}{2}} dE \times f(E)$$

$$\therefore n_c = \frac{\pi}{2} \left(\frac{8m}{h^2} \right)^{\frac{3}{2}} \int_0^{E_F} E^{\frac{1}{2}} dE \times f(E)$$

$$\therefore n_c = \frac{\pi}{2} \left(\frac{8m}{h^2} \right)^{\frac{3}{2}} \left[\frac{E^{\frac{3}{2}}}{\frac{3}{2}} \right]_0^{E_F}$$

$$\therefore n_c = \frac{\pi}{2} \left(\frac{8m}{h^2} \right)^{\frac{3}{2}} \frac{2}{3} E_F^{\frac{3}{2}}$$

$$\therefore n_c = \frac{\pi}{3} \left(\frac{8m}{h^2} \right)^{\frac{3}{2}} E_F^{\frac{3}{2}} \dots \dots \dots (1)$$

Re-arranging the equation 1, we can define fermi energy

$$\therefore \left(\frac{3n_c}{\pi} \right) = \left(\frac{8m}{h^2} \right)^{\frac{3}{2}} E_F^{\frac{3}{2}} \dots \dots \dots (2)$$

Multiply equ.2 with power $2/3$

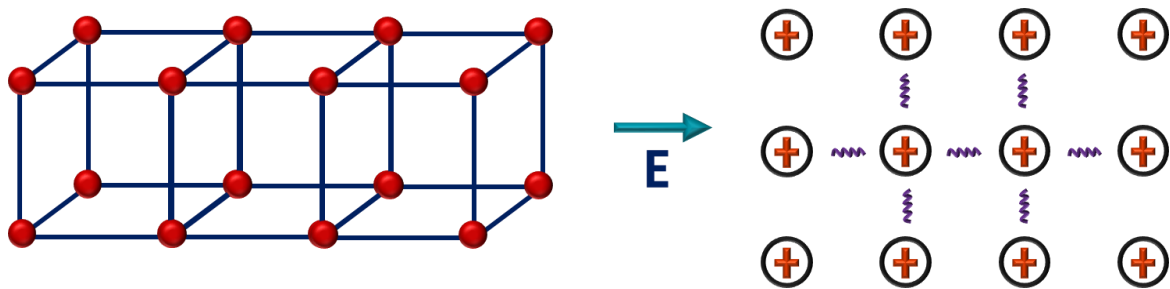
$$\therefore \left(\frac{3n_c}{\pi} \right)^{\frac{2}{3}} = \left(\frac{8m}{h^2} \right)^{\frac{3}{2} \times \frac{2}{3}} E_F^{\frac{3}{2} \times \frac{2}{3}}$$

$$\therefore E_F = \left(\frac{h^2}{8m} \right) \left(\frac{3n_c}{\pi} \right)^{\frac{2}{3}}$$

| | |
|------|--|
| Q.1 | Calculate the fermi energy for sodium. Given atomic weight 23 gm/mole and density of sodium 0.97 gm/cm ³ . |
| Ans. | <p>Atomic weight = 23 gm/mole = 0.023 Kg/mole = 23×10^{-3} Kg/mole</p> <p>Density of sodium = $0.971 \text{ gm/cm}^3 = 0.971 \times 10^3 \text{ Kg/m}^3$</p> <p>$E_f = ?$</p> <p>carrier concentration (n_c) = $\frac{\text{No. of atoms Charge}}{\text{Volume}}$</p> <p>$\therefore n_c = \frac{\text{Avegadro no.} \times \text{density}}{\text{Atomic weight}}$</p> <p>$\therefore n_c = \frac{(6023 \times 10^{23}) \times (0.971 \times 10^3)}{23 \times 10^{-3}}$</p> <p>$\therefore n_c = 2541 \times 10^{28} \text{ atoms/m}^3$</p> <p>$\therefore E_F = \left(\frac{h^2}{8m} \right) \left(\frac{3 n_c}{\pi} \right)^{\frac{2}{3}}$</p> <p>$\therefore E_F = \left(\frac{(6.62 \times 10^{-34})^2}{314} \right) \left(\frac{3 \times 2541 \times 10^{28}}{8 \times 9.11 \times 10^{-31}} \right)^{\frac{2}{3}}$</p> <p>$\therefore E_F = (6022 \times 10^{-38}) (2427 \times 10^{28})^{\frac{2}{3}}$</p> <p>$\therefore E_F = (6022 \times 10^{-38}) (838 \times 10^{28})$</p> <p>$\therefore E_F = 5049 \times 10^{-19} \text{ J}$</p> |

1.6.11 Phonon

- ✓ A solid crystal consists of atoms bound into a specific three-dimensional pattern called lattice.
- ✓ The atoms behave as if they are connected by tiny springs and so their own thermal energy (internal energy present in a system by virtue of temperature) or outside forces makes the lattice vibrate.
- ✓ This generates mechanical waves that carry heat and sound through the material.
- ✓ A packet of these waves can travel throughout the crystal with definite energy and momentum.
- ✓ These waves are treated as a particle called “phonons”.



- ✓ Phonons act like bosons, they can be created or destroyed in collisions.
- ✓ Phonons exist with discrete amount of energy, given by

$$E = \hbar \omega = h \nu$$

Where, $\omega/2\pi$ = frequency of vibrations, h = plank constant, ν = frequency

- ✓ Phonons can carry heat and sound and they play a major role in determine heat capacities of solid and liquids.