

UNIT I

ELECTRONIC MATERIALS

INTRODUCTION

Materials can be broadly classified into three types based on conductivity. They are,

1. Conductors (Example: metals),
2. Semi – conductors (Example: germanium, silicon) and
3. Insulators (Example: wood, mica, glass).

CONDUCTORS:

- Conductivity is the ability or power to conduct or transmit heat, electricity, or sound.
- Conductors are materials that electricity easily passes through, that do not resist the flow of electricity.
- Examples are copper, aluminum, steel, silver, gold, electrolytes. Not all materials conduct electricity equally well.

CLASSIFICATION OF CONDUCTORS:

Conducting materials are classified into three categories

1. Zero Resistivity materials:

These materials conduct electricity with zero resistance below transition temperature.

2. Low Resistivity materials:

These materials have very high electrical conductivity.

3. High Resistivity materials:

These materials have high resistivity and low temperature co-efficient of resistance.

Basic Terminologies

1. Bound Electrons:

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

2. Free electrons:

Electrons which moves freely or randomly in all directions in the absence of external field.

3. Drift Velocity

If no electric field is applied on a conductor, the free electrons move in random directions. They collide with each other and also with the positive ions. Since the motion is completely random, average velocity in any direction is zero. If a constant electric field is established inside a conductor, the electrons experience a force $F = -eE$ due to which they move in the direction opposite to direction of the field. These electrons undergo frequent collisions with positive ions. In each such collision, direction of motion of electrons undergoes random changes. As a result, in addition to the random motion, the electrons are subjected to a very slow directional motion. This motion is called drift and the average velocity of this motion is called **drift velocity v_d** .

4. 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).

$$\text{i.e., } E = V/l \quad \text{V/m}$$

5. Current density (J):

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

$$J = I/A \quad \text{A m}^{-2}$$

6. Fermi level

Fermi level is the highest filled energy level at 0 K.

7. Fermi energy

Energy corresponding to Fermi level is known as Fermi energy.

Electron Theory of metals:

The electron theory of metals explain the following concepts

- ➔ Structural, electrical and thermal properties of materials.
- ➔ Elasticity, cohesive force and binding in solids.
- ➔ Behaviour of conductors, semi conductors, insulators etc.

So far **three electron theories** have been proposed.

1. Classical Free electron theory:

- It is a macroscopic theory.
- Proposed by Drude and Loretz in 1900.
- It explains the free electrons in lattice

- It obeys the laws of classical mechanics.

2. Quantum Free electron theory:

- It is a microscopic theory.
- Proposed by Sommerfield in 1928.
- It explains that the electrons moves in a constant potential.
- It obeys the Quantum laws.

3. Brillouin Zone theory or Band theory:

- Proposed by Bloch in 1928.
- It explains that the electrons moves in a periodic potential.
- It also explains the mechanism of semiconductivity , based on bands and hence called band theory.

CLASSICAL FREE ELECTRON THEORY OF METALS:

This theory was developed by Drude and Lorentz during 1900 All the atoms are composed of and hence is also known as Drude-Lorentz theory. According to this theory, a metal consists of electrons which are free to move about in the crystal like molecules of a gas in a container. 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.

Postulates of Classical free electron theory:

1. All the atoms are composed of atoms. Each atom have central nucleus around which there are revolving electrons.
2. The electrons are free to move in all possible directions about the whole volume of metals.
3. In the absence of an electric field the electrons move in random directions making collisions from time to time with positive ions which are fixed in the lattice or other free electrons. All the collisions are elastic i.e.; no loss of energy.
4. When an external field is applied the free electrons are slowly drifting towards the positive potential.
5. Since the electrons are assumed to be a perfect gas they obey classical kinetic theory of gasses.
6. Classical free electrons in the metal obey Maxwell-Boltzmann statistics.

Drawbacks of Classical free electron theory:

- 1) According to this theory, r is proportional to $\frac{1}{T}$. But experimentally it was found that r is proportional to T .
- 2) According to this theory, $\frac{K}{sT} = L$, a constant (Wiedemann-Franz law) for all temperatures. But this is not true at low temperatures.
- 3) The theoretically predicted value of specific heat of a metal does not agree with the experimentally obtained value.

- 4) This theory fails to explain ferromagnetism, superconductivity, photoelectric effect, Compton Effect and black body radiation.
- 5) It is a macroscopic theory.
- 6) Dual nature is not explained.
- 7) Atomic fine spectra could not be accounted.

Merits of Classical Free Electron Theory:

1. It is used to verify Ohm's law.
2. The electrical and thermal conductivities of metals can be explained.
3. It is used to derive Wiedemann- Franz law
4. It is used to explain the optical properties of metals.

Drawbacks of Classical Free Electron Theory:

1. It is a macroscopic theory.
2. It cannot explain the electrical conductivity of semiconductors and insulators properly.
3. Dual nature is not explained.
4. It cannot explain the Compton effect, Photo-electric effect.
5. The theoretical and experimental values of specific heat are not matched.
6. Atomic fine spectra could not be accounted.

7. Different types of magnetisms could not be explained satisfactorily by this theory.

Wiedmann-Franz law:

The ratio of thermal conductivity to electrical conductivity of a metal is directly proportional to absolute temperature.

K/s is proportional to T

Or, $K/sT = L$, a constant called Lorentz number.

Quantum free electron theory:



Classical free electron theory could not explain many physical properties.



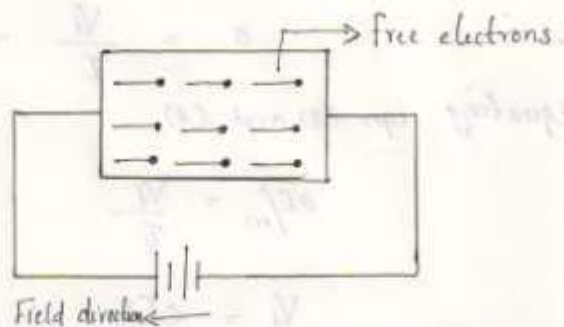
In 1928, Sommerfeld developed a new theory applying quantum mechanical concepts and Fermi-Dirac statistics to the free electrons in the metal. This theory is called quantum free electron theory.



Classical free electron theory permits all electrons to gain energy. But quantum free electron theory permits only a fraction of electrons to gain energy.

Determination of Electrical Conductivity of a metal based on Druide & Lorentz theory.

Consider a metal piece of length 'L' and area of cross-section 'A'. An electric field 'E' is applied to the metal piece.



The electrons are accelerated with a drift velocity v_d in a direction opposite to that of the applied field. Due to this field, the force experienced by the electrons can

$$\text{be given as, } F = eE \quad \text{--- (1)}$$

where, $e \rightarrow$ charge of an electron

$E \rightarrow$ applied electric field

From Newton's Second law of motion,

$$F = ma \quad \text{--- (2)}$$

$\therefore a \rightarrow$ acceleration

$m \rightarrow$ mass of the electron.

Equating (1) & (2),

$$eE = ma$$

$$\therefore a = \frac{eE}{m} \quad \text{--- (3)}$$

We know, acceleration in terms of drift velocity and relaxation time is given as,

$$\text{acceleration} = \frac{\text{drift velocity } V_d}{\text{relaxation time } \tau}$$

$$a = \frac{V_d}{\tau} \quad \dots \dots \dots (4)$$

equating eqn (3) and (4),

$$eE/m = \frac{V_d}{\tau}$$

$$V_d = \frac{eE\tau}{m} \quad \dots \dots \dots (5)$$

We know, Current density,

$$J = \sigma E \quad \dots \dots \dots (6)$$

Current density in terms of drift velocity is given as,

$$J = neV_d \quad \dots \dots \dots (7)$$

Substituting eqn (5) in eqn (7),

$$J = ne \frac{eE\tau}{m}$$

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

$$J/E = \frac{ne^2 \tau}{m} \quad \dots \dots \dots (8)$$

We know the expression for electrical conductivity.

$$\sigma = \frac{J}{E}$$

\therefore Eqn (8) is the equation for electrical conductivity

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

from this equation, we can find that with increase of electron concentration 'n', the conductivity ' σ ' increases. As 'm' increases, the motion of electron becomes slow and hence the conductivity ' σ ' decreases.

Verification of Ohm's law:

We know that, the Current density, $J = \frac{I}{A}$.

$$\therefore I = JA$$

$$= \sigma EA \quad [\because J = \sigma E]$$

$$= \sigma \left(\frac{V}{l} \right) A \quad [\because E = \frac{V}{l}]$$

$$= \left(\frac{\sigma A}{l} \right) V$$

$$= \left(\frac{A}{\rho l} \right) V \quad [\because R = \frac{\rho l}{A}]$$

$$I = \frac{V}{R}$$

$$\therefore V = IR$$

\therefore Ohm's law is Verified.

Derivation of Thermal conductivity:

Derivation of Thermal Conductivity (k):

Thermal conductivity of a metal is defined as the amount of heat (Q) conducted per unit time (t) through the material having unit area of cross section (A) maintaining at unit temperature gradient ($d\theta/dx$).

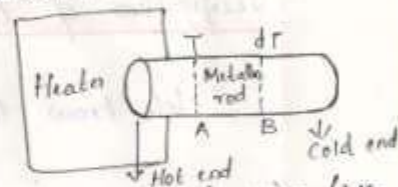
$$k = \frac{-Q}{d\theta/dx}$$

$$\therefore Q = -K \cdot d\theta/dx \cdot \text{Wm}^{-1}\text{K}^{-1}$$

$k \rightarrow$ Thermal conductivity of material.

$Q \rightarrow$ Amount of heat energy.

$d\theta/dx \rightarrow$ temperature gradient.



Consider a uniform metallic rod containing free electrons. One end of the rod is heated using a heater. Let A and B be the two cross-sections of temperature T and $(T - dT)$ separated by a distance of mean free path (λ). Heat flows from hot end 'A' to the cold end 'B'.

During the collision, the electrons near A lose their kinetic energy and the electrons near B gain the energy.

At point A:

$$\text{Average kinetic energy of electron} = \frac{1}{2}mv^2 = \frac{3}{2}kT$$

Where, $k \rightarrow$ Boltzmann's Constant

$T \rightarrow$ Temperature at A

At Point B:

$$\text{Average kinetic energy of an electron} = \frac{3}{2} k (T - dT) \quad \dots \dots \dots (2)$$

Hence the Excess kinetic energy carried out by electron from A to B,

$$\begin{aligned} &= \frac{3}{2} k T - \frac{3}{2} k (T - dT) \\ &= \frac{3}{2} k T - \frac{3}{2} k T + \frac{3}{2} k dT \\ &= \frac{3}{2} k dT \quad \dots \dots \dots (3) \end{aligned}$$

Let us assume that the electrons will flow in all 6 directions with equal probability. If 'n' is the free electron density and v is the thermal velocity, number of electrons carrying unit area per unit time from A to B = $\frac{1}{6} nv \quad \dots \dots \dots (4)$

Excess of energy caused from A to B for unit area in

$$\begin{aligned} \text{unit time} &= \frac{1}{6} nv \times \frac{3}{2} k dT \\ &= \frac{1}{4} nv k dT \quad \dots \dots \dots (5) \end{aligned}$$

Similarly, the deficiency of energy caused from B to A for unit area in unit time = $-\frac{1}{4} nv k dT \quad \dots \dots (6)$

Hence, the net energy transferred from A to B per unit area per unit time, $Q = \frac{1}{4} nv k dT - \left[-\frac{1}{4} nv k dT \right]$

$$\therefore Q = \frac{1}{2} n v k d \tau \quad \dots \dots \dots (7)$$

We know, Thermal Conductivity, $Q = k \left[\frac{dT}{dx} \right] \quad [\because dx = d]$
 $\dots \dots \dots (8)$

By comparing eqn (7) and eqn (8),

$$k \left[\frac{dT}{dx} \right] = \frac{1}{2} n v k d \tau$$

$$k = \frac{1}{2} n v k \lambda \quad \dots \dots \dots (9)$$

For metals, relaxation time (τ) = Collision time (τ_c)

$$\therefore \tau = \tau_c = \lambda / v$$

$$\tau v = \lambda \quad \dots \dots \dots (10)$$

Substituting eqn. (10) in (9),

$$\therefore k = \frac{1}{2} n v k \tau v$$

$$k = \frac{1}{2} n v^2 k \tau \quad \dots \dots \dots (11)$$

Eqn (11) is the classical expression for thermal conductivity.

Wiedemann-Franz Law :

The ratio between the thermal conductivity and the electrical conductivity of a metal is directly proportional to the absolute temperature of the metal.

The ratio is constant for all metals in a given temp.

$$4; \quad k/\sigma \propto T$$

$$01) \quad k/\sigma = L T \quad \dots \dots \dots (1)$$

When,

$L \rightarrow$ Lorentz Number ($2.44 \times 10^{-8} \text{ W}\Omega/\text{K}^2$ at 293K)

$T \rightarrow$ absolute temperature

$k \rightarrow$ Thermal conductivity

$\sigma \rightarrow$ electrical conductivity.

Derivation:

From classical theory, the electrical conductivity,

$$\sigma = \frac{ne^2\tau}{m} \quad \dots \dots \dots (2)$$

iii) thermal conductivity,

$$k = \frac{1}{2} n \bar{v}^2 k \tau \quad \dots \dots \dots (3)$$

According to Wiedemann's Frang law,

$$\frac{\text{Thermal Conductivity}}{\text{Electrical conductivity}} = \frac{\frac{1}{2} n \bar{v}^2 k \tau}{ne^2\tau/m}$$

$$k/\sigma = \frac{1}{2} \frac{m \bar{v}^2 k}{e^2} \quad \dots \dots \dots (4)$$

Kinetic energy of an electron,

$$\frac{1}{2} m \bar{v}^2 = \frac{3}{2} k T \quad \dots \dots \dots (5)$$

Substituting eqn (5) in eqn (4),

$$\begin{aligned}\frac{k}{\sigma} &= \frac{3}{2} k T \frac{k}{e^2} \\ &= \frac{3}{2} \frac{k^2 T}{e^2} \\ &= \frac{3}{2} (k/e)^2 T \quad \dots \dots \dots (6)\end{aligned}$$

$$\frac{k}{\sigma} = L T \quad \dots \dots \dots (7)$$

Where, $L = \frac{3}{2} (k/e)^2$ is a constant and it is known as Lorentz Number.

Lorentz - Number :

The ratio between the thermal conductivity (k) to the product of electrical conductivity (σ) and absolute temperature (T) of the metal is a constant. The constant value is known as Lorentz number.

$$\text{Lorentz Number (L)} = \frac{k}{\sigma T}$$

According to classical theory,

$$L = \frac{3}{2} (k/e)^2$$

Substituting, $k = 1.38 \times 10^{-23} \text{ J K}^{-1}$, $e = 1.6021 \times 10^{-19} \text{ Coulomb}$

$$L = \frac{3}{2} \left[\frac{1.38 \times 10^{23}}{1.6021 \times 10^{19}} \right]^2$$

$$L = 1.112 \times 10^{-8} \text{ } \Omega \cdot \text{cm}^2$$

Hence it was found that the classical value of Lorentz number is only half of the experimental value i.e. $L = 2.24 \times 10^{-8} \text{ } \Omega \cdot \text{cm}^2$. This discrepancy in the experimental and theoretical value of Lorentz number is the failure of classical theory.

Fermi-Dirac Statistics:

There are three statistics

1. Maxwell- Boltzmann statistics

- Deals with particles which has no spin
 - Eg: Gaseous particles

2. Bose-Einstein statistics

- Deals with particles which has integral spin
 - Eg: Photons

3. Fermi-Dirac statistics

- Deals with particles which has half integral spin
- Also known as Fermions
 - Eg: Electrons

Fermi-Dirac Statistics Distribution function:

§ * Fermi distribution function ' $F(E)$ ' is used to calculate the probability of an electron occupying a certain energy level.

* The distribution of electrons among the different energy levels as a function of temperature is known as Fermi-Dirac distribution function.

$$F(E) = \frac{1}{1 + \exp[(E - E_f)/kT]}$$

Where,

$E_f \rightarrow$ fermi energy

$k \rightarrow$ Boltzmann Constant

$T \rightarrow$ Temperature in K.

The probability value $F(E)$ lies between 0 and 1

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

\rightarrow If $F(E) = 0$, the energy level is vacant

\rightarrow If $F(E) = 0.5$ or $\frac{1}{2}$, then there is a 50% chance for finding the electron in the energy level.

Effect of Temperature on Fermi function:

(i) At $T = 0K$

At $0K$, the electrons are filled upto a maximum

energy level called Fermi Energy level E_f . All the energy levels above the Fermi Energy level are empty.

Case (i): At $T = 0\text{ K}$ and $E < E_f$

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

\therefore The probability of electrons to occupy the energy level below Fermi energy level is 100%.

Case (ii): At $T = 0\text{ K}$ and $E > E_f$

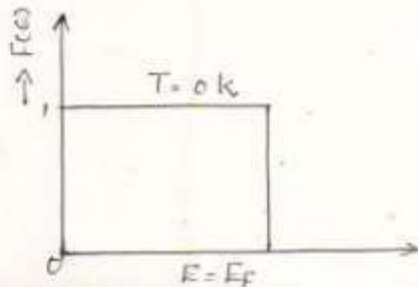
$$F(E) = \frac{1}{1 + e^{\infty}} = \frac{1}{1 + \infty} = 0$$

This means that at 0 K , electrons are completely occupied below ' E_f ' and above ' E_f ' electrons are unoccupied.

Case (iii): At $T = 0\text{ K}$ and $E = E_f$

$$F(E) = \frac{1}{1 + 1} = \frac{1}{2} = 0.5$$

The Fermi-function at 0 K can also be graphically represented as,



Electrons with fermi energy move with fermi velocity and the same is related to the fermi temperature by the relation,

$$\frac{1}{2} m v_f^2 = k T_f$$

Effect of temperature on Fermi-Dirac distribution function:

Fermi-Dirac distribution function is given by,

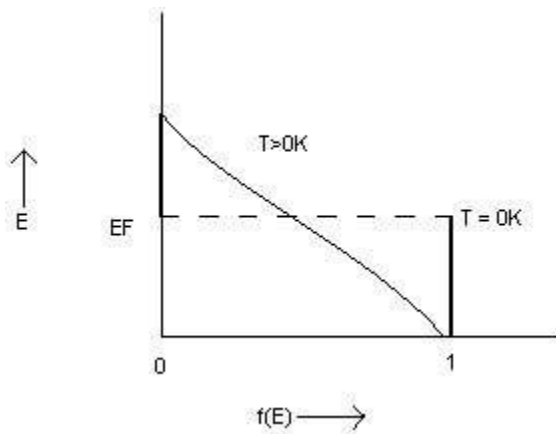
$$f(E) = 1 / [1 + e^{(E - E_F)/KT}]$$

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

At $T=0K$, for $E = E_F$, $f(E)=\text{indeterminate}$

At $T>0K$, for $E = E_F$, $f(E)=1/2$

All these results are depicted in the figure.



Importance of Fermi Energy:

- ◆ Fermi energy is used to separate the vacant and filled states at 0 K
- ◆ It is used to know the status of the electrons.

- ◆ Electrons are completely filled below fermi energy level and completely empty above the fermi level at 0 K
- ◆ Above 0 K some electrons absorb thermal energy and they jumps to the higher energy levels.

Density of States:

Density of states $N(E)dE$ is defined as the number of energy states present per unit volume of a metal in an energy interval E and $E+dE$

No. of energy states available between E
and $E+dE$ in a metal piece

$$\text{Density of states } [N(E)dE] = \frac{\text{No. of energy states available between } E \text{ and } E+dE \text{ in a metal piece}}{\text{Volume of that metal piece}}$$

Derivation of Density of States ($N(E)dE$):

Figure shows a graph between number of states ($N(E)$) and energy (E). To fill the electrons in energy level, we must know the number of states present within the energy interval E and $E+dE$.

Let us calculate the density of states in a cubical metal piece with sides 'a'. Let n_x , n_y and n_z be the coordinate axes. Draw the sphere in these axes with radius $n = \sqrt{n_x^2 + n_y^2 + n_z^2}$ and energy E .

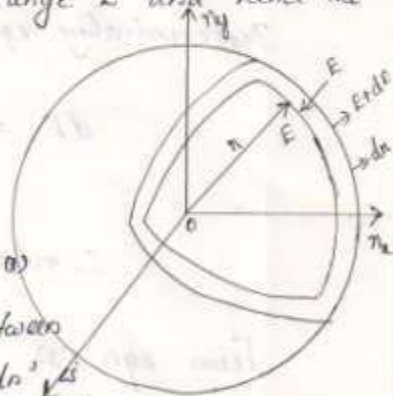
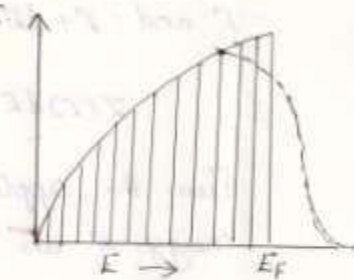
Any change in n_x, n_y, n_z will change E and hence the radius n .

The number of energy states within a sphere of radius 'n' is

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

\therefore Number of available energy state between the sphere of radius 'n' and 'n+dn' is

$$\begin{aligned} Z(E)dE &= \frac{1}{8} \left[\frac{4\pi}{3} \right] (n+dn)^3 - \frac{1}{8} \left[\frac{4\pi}{3} \right] n^3 \\ &= \frac{1}{8} \left[\frac{4\pi}{3} \right] ((n+dn)^3 - (n)^3) \\ &= \frac{1}{8} \left[\frac{4\pi}{3} \right] (n^3 + dn^3 + 3n^2 dn + 3n dn^2 - n^3) \\ &= \frac{1}{8} \left[\frac{4\pi}{3} \right] (dn^3 + 3n^2 dn + 3n dn^2) \end{aligned}$$



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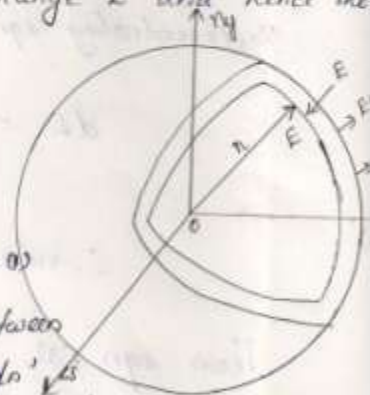
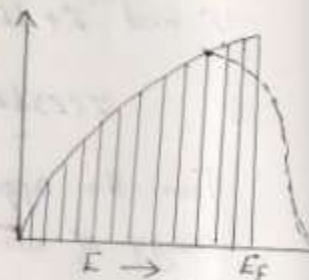
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$$\begin{aligned}
 &= \frac{\pi}{2} \cdot \frac{1}{2} \left(\frac{8ma^3}{h^2} \right)^{1/2} \left(\frac{8ma^3}{h^2} \right) E^{1/2} dE \\
 &= \frac{\pi}{4} \left(\frac{8ma^3}{h^2} \right)^{3/2} E^{1/2} dE \\
 &= \frac{\pi}{4} \left(\frac{8m}{h^2} \right)^{3/2} a^3 E^{1/2} dE \\
 Z(E) dE &= \frac{\pi}{4} \left(\frac{8m}{h^2} \right)^{3/2} V E^{1/2} dE \quad (\because V = a^3) \quad \dots \dots (6)
 \end{aligned}$$

The density of states is equal to the number of states per unit volume in the range E and $E+dE$

$$\begin{aligned}
 \therefore N(E) dE &= \frac{Z(E) dE}{V} \\
 &= \frac{\pi}{4} \left(\frac{8m}{h^2} \right)^{3/2} E^{1/2} dE \quad \dots \dots (7)
 \end{aligned}$$

According to Pauli's exclusion principle, in each state two electrons can accommodate.

$$\begin{aligned}
 N(E) dE &= 2 \times N(E) dE \\
 &= 2 \times \frac{\pi}{4} \left(\frac{8m}{h^2} \right)^{3/2} E^{1/2} dE \\
 &= \frac{\pi}{2} \left(\frac{8m}{h^2} \right)^{3/2} E^{1/2} dE
 \end{aligned}$$

$$\text{Density of States } (N(E) dE) = \frac{\pi}{2h^3} (8m)^{3/2} E^{1/2} dE \quad \dots (8)$$

$$\begin{aligned}
 &= \frac{\pi}{2} \cdot \frac{1}{2} \left(\frac{8ma^3}{h^2} \right)^{1/2} \left(\frac{8ma^3}{h^2} \right) E^{1/2} dE \\
 &= \frac{\pi}{4} \left(\frac{8ma^3}{h^2} \right)^{3/2} E^{1/2} dE \\
 &= \frac{\pi}{4} \left(\frac{8m}{h^2} \right)^{3/2} a^3 E^{1/2} dE \\
 Z(E) dE &= \frac{\pi}{4} \left(\frac{8m}{h^2} \right)^{3/2} V E^{1/2} dE \quad (\because V=a^3) \quad \dots \dots (6)
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 \end{aligned}$$

$$\text{Density of States } (N(E) dE) = \frac{\pi}{2h^3} (8m)^{3/2} E^{1/2} dE \quad \dots (8)$$

$$E_f = \frac{h^2}{8m} \left(\frac{3N}{\pi} \right)^{2/3}$$

The above equation represents the Fermi energy of electrons in solids at absolute zero.

When temperature increases, Fermi energy E_f is related with temperature as

$$E_f = E_{f_0} \left[1 - \frac{\pi^2}{12} \left(\frac{kT}{E_{f_0}} \right)^2 \right]$$

where, E_{f_0} is Fermi energy at 0 K.

Average Energy (E_{ave}) of an Electron at 0 K:

$$\text{Average Energy, } E_{ave} = \frac{\text{Total Energy}}{\text{Carrier Concentration}}$$

$$\text{Total Energy, } E_{tot} = \int_0^{E_{f_0}} \text{Density of states} \times \text{Energy of an electron}$$

$$= \int_0^{E_{f_0}} N(E) dE \times E$$

$$= \int_0^{E_{f_0}} \frac{\pi}{2h^3} (8m)^{3/2} E^{1/2} E dE$$

$$= \frac{\pi}{2h^3} (8m)^{3/2} \int_0^{E_{f_0}} E^{3/2} dE$$

$$= \frac{\bar{n}}{2h^3} (8m)^{3/2} \frac{E_{F_0}^{5/2}}{5/2}$$

$$\text{Total Energy } (E_{\text{tot}}) = \frac{\bar{n}}{5h^3} (8m)^{3/2} E_{F_0}^{5/2}$$

From eqn (1),

$$N = \frac{\bar{n}}{3h^3} (8m)^{3/2} E_{F_0}^{3/2}$$

\therefore Average Energy,

$$(E_{\text{ave}}) = \frac{\frac{\bar{n}}{5h^3} (8m)^{3/2} E_{F_0}^{5/2}}{\frac{\bar{n}}{3h^3} (8m)^{3/2} E_{F_0}^{3/2}}$$

$$= \frac{3}{5} E_{F_0}^{5/2} E_{F_0}^{-3/2}$$

$$= \frac{3}{5} E_{F_0}$$

\therefore The average energy of an electron at 0 K

$$E_{\text{ave}} = \frac{3}{5} E_{F_0}$$

