

Most of the properties of metal can be explained by assigning a free electron model to them. A classical model of electrical conduction in a metal was first proposed by Paul Drude.

Drude –Lorentz theory (Classical free electron theory) :

Free-electron and phonon concept:

All metal atom consists of valance electrons. These valance electrons are responsible for electrical conduction in a metal. Consider copper as an example for metals. A copper atom consists of 29 electrons, out of which 28 electrons are filled in the first 3 shells. And forms the core part. The remaining one electron will be present in the 4th shell and is the valance electron of the copper atom. It is very loosely bound in the atom.

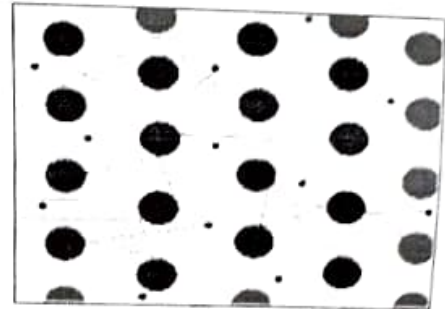
When large number of copper atoms join to form a metal, the boundaries of the neighbouring atoms slightly overlap on each other. Due to this the valance electron find continuity from atom to atom. Thus, it can move easily throughout the body of the metal. The free movement of electrons means none of them belongs to any atom, but each of them belongs to the metal to which they are confined to. Thus, such electrons are named free electrons. These free electrons are responsible for physical property of metal such as electrical and thermal conductivities, electron emission etc. Since free electrons are responsible for electrical conduction in a solid, they are also called conduction electrons.



However, the loss of electrons makes the atom to loose their electrical neutrality. They become positive ions fixed about in their mean position. The structure formation due to the array of such ions in 3 dimension is called lattice. Thermal vibrations of ions at lattice points cause elastic waves in crystal. The energy of these lattice vibrations is quantised and quantum of this energy is phonon.

Phonon: it is particle like entity which carries the unit energy of elastic field in a particular mode is called phonon. The energy of the phonon is given by $h\nu$.

The free electrons collide with ion core at lattice point. The collision results in a change in the direction of velocity of the electrons. In absence of electric field, the velocities of electrons are in random directions as in fig.2 due to which there is no net transfer of charge.



According to Drude –Lorentz theory all metals contain free electrons move through the positive ionic core of the metals. The metal is then pictured to be held together by electrostatic forces of attraction between the positively charged ions and negatively charged electron gas. Mutual repulsion between negative electrons is ignored in this theory.

Review of Classical Free Electron Theory.

This theory was proposed by Drude and Lorentz. According to this theory, the electrons are moving freely and randomly in the entire volume of the metal just like gas atoms in gas container. When an electric field is applied the free electrons gets accelerated.

The expression for electrical conductivity of metals based on this theory was given by,

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

where n is concentration of free electron.
 e is charge of the electron.

τ is the relaxation time of free electrons.
 m is mass of the free electron.

Failures of CFET:

1) Dependence of electrical conductivity (σ) on T :

According to CFET,

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

$$\Rightarrow v \propto \sqrt{T} \quad \text{--- (1)}$$

$$\text{But Relaxation time } \tau \propto \frac{1}{v}$$

$$\Rightarrow \tau \propto \frac{1}{\sqrt{T}} \quad \text{--- (2)}$$

$$\text{WKT, } \sigma = \frac{ne^2\tau}{m}$$

$$\Rightarrow \sigma \propto \tau \quad \text{--- (3)}$$

$$\text{From eqn (2) \& (3), } \boxed{\sigma \propto \frac{1}{\sqrt{T}}} \quad \text{--- (4)}$$

But experimentally it has been observed that $\sigma \propto 1/T$. Thus CFET fails to explain the dependence of σ on T .

2) Dependence of electrical conductivity on electron concentration (n):

Metal.	Concentration (n) (m^{-3}),	σ (Ωm) ⁻¹ .
Zinc	13.10×10^{28}	1.09×10^7
Aluminium	18.06×10^{28}	3.65×10^7
Copper	8.45×10^{28}	5.88×10^7
Silver.	5.85×10^{28}	6.3×10^7

According to CFET, $\sigma = \frac{ne^2\tau}{m}$

So according to this formula, the electrical conductivity for zinc and aluminium must be more than that of copper and silver. But experimentally it was found that copper and silver are having more electrical conductivity.

Drift velocity (V_d):

The average velocity with which free electrons move in a steady state opposite to the direction of the electric field in a metal is called drift velocity.

Resistivity and mobility:

Electrons tend to accelerate in the direction of the field, they are deflected in random directions by vibrating lattice points, which is scattering. The overall effect of scattering of electrons by vibrating lattice acts as resistance to electric current.

For a material of uniform cross section, the resistance R is directly proportional to length of wire (L) and inversely proportional to cross sectional area (A),

$$R \propto \frac{L}{A}$$

$$R = \rho \frac{L}{A}$$

Here ρ is called as resistivity. It is defined as the property of the material measuring opposition offered by material to the flow of current.

$$\text{Conductivity} = \frac{1}{\text{resistivity}}$$

$$\sigma = \frac{1}{\rho}$$

Mobility of electrons

It is defined as the magnitude of drift velocity acquired by the electrons in unit electric field.

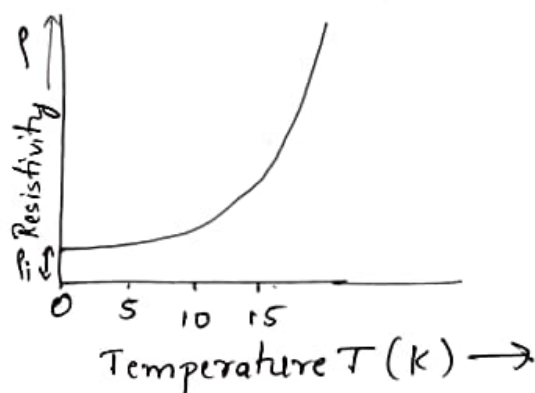
$$\text{i.e. } \mu = \frac{V_d}{E}$$

where μ is mobility

V_d is drift velocity

E is applied electric field.

Effect of temperature and impurity on electrical resistivity of metals:



From this graph, it may be noticed that ρ does not become zero even at $T=0$ K, but has a small constant value. From this value, ρ increases with T slowly in beginning, latter it assumes linear but faster variation. The linearity in variation is continued throughout till the metal melts. This variation in general applies to all the metals.

The resistivity of metals is due to the scattering of conduction electrons. In metals the scattering takes place basically under 2 mechanisms which gives rise to 2 components of resistivity which are as follows:

1) Resistivity ρ_{ph} due to scattering of electrons by lattice vibrations (phonons) which increases with temperature. ρ_{ph} is therefore temperature dependent. It is resistivity exhibited by pure specimen that is free of all defects, and hence called the Ideal resistivity.

2) Resistivity ρ_i due to scattering of conduction electrons by the presence of impurities, imperfections. This type of scattering is independent of temperature and contributes to resistivity even at the temperature $T=0K$. ρ_i is called residual resistivity.

Since the two scattering mechanisms mentioned above act independently, the two resistivities are additive. If ρ is the total resistivity of the metal, then ρ is given by,

$$\rho = \rho_{ph} + \rho_i \quad \text{--- (1)}$$

The above eqⁿ is called Matthiessen's rule. It states that the total resistivity of a metal is the sum of the resistivity due to phonon scattering which is temperature dependant and the resistivity due to scattering by impurities which is temperature independent.

Since the resistivity $\rho = \frac{1}{\sigma}$ & $\sigma = \frac{ne^2\tau}{m}$,
the eqⁿ for ρ can be written as, $\rho = \frac{m}{ne^2\tau}$

$\therefore \epsilon_{qn}$ ① can be written as,

$$\rho = \frac{m}{ne^2\tau_{ph}} + \frac{m}{ne^2\tau_i}$$

For lower temperatures, the amplitude of vibrations become small. Therefore the scattering of electrons by the lattice ions also become less. This results in τ_{ph} becoming large, and ρ_{ph} tends to zero at very low temperatures.

It means that $\rho = \rho_i$ at very low temperatures. Accordingly, in above fig, the resistivity has a residual value ρ_i at $T=0K$. On the other hand, when the temperature becomes high, the amplitude of lattice vibrations increases proportionately which results in large scale scattering of electrons.

Consequently, the resistance curve takes an upswing, and the resistivity becomes linearly dependent on temperature. At high temperatures, the scattering effect due to phonons overtakes the effect due to scattering by impurities.

Quantum free electron theory

After the development of quantum mechanics, a new free electron theory was proposed by Sommerfeld in 1928. He succeeded in overcoming many of the drawbacks of classical free electron theory while retaining all its essential features. He treated electrons quantum mechanically and included the effects of Pauli's exclusion principle. This new theory proposed by Sommerfeld is known as Quantum free electron theory.

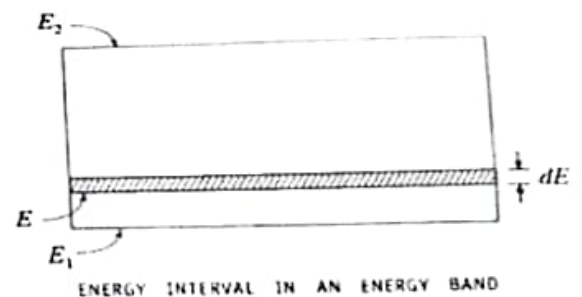
Assumptions of Quantum free electron theory:

- 1) The energy values of the conduction electrons are quantized. The allowed energy values are realized in terms of a set of energy levels.
- 2) The distribution of electrons in the various allowed energy levels occurs as per Pauli's exclusion principle.
- 3) The free electrons travel in a constant potential inside the metal but stay confined within its boundaries.
- 4) The attraction between the free electrons and the lattice ions, and the repulsion between the electrons themselves are ignored.

Density of states:

We know that the permitted energy levels for electrons in a solid material will be in terms of bands. Each band is spread over an energy range of few electron volts. The number of energy levels in each band will be extremely large. Therefore, in a small energy range, the energy values appear to be virtually continuous over the band spread. However, number of energy levels per unit energy range varies with energy in band. This variation is realized through a function $g(E)$, which is known as density of states function. Density of states $g(E)$ can be defined as it is the number of available energy states per unit volume per unit energy centred at E . It is mathematically continuous function and the product $g(E) dE$ gives the number of states per unit volume in an energy interval dE at E .

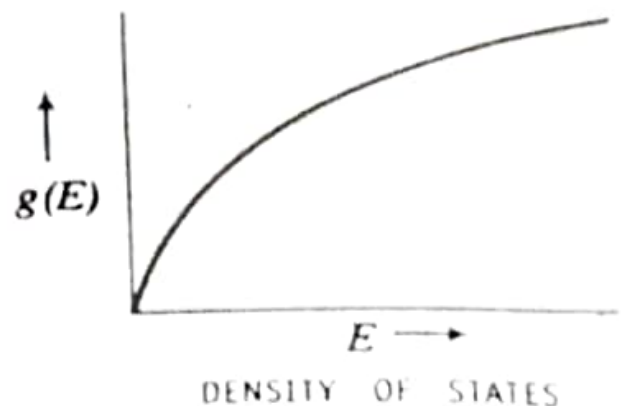
Let us consider the case of free electrons in a material. The possible energy values for the free electrons corresponds to only the set of energy levels available vacant but adjacent to the filled energy levels in the band. Consider such a band as shown in fig below. Let the energy band be spread in an energy interval between E_1 and E_2 .



Consider an infinitesimally small increment dE at arbitrary energy value E in the band. Since dE is an infinitesimally small increment in E , we can assume that $g(E)$ remains constant between E and $E+dE$. Then the number of energy levels in the range E and $(E+dE)$ is obtained by evaluating the product of $g(E)$ and dE

$$\text{i.e } g(E) * dE = \left[\frac{8\sqrt{2}\pi m^{\frac{3}{2}}}{h^3} \right] \sqrt{E} dE$$

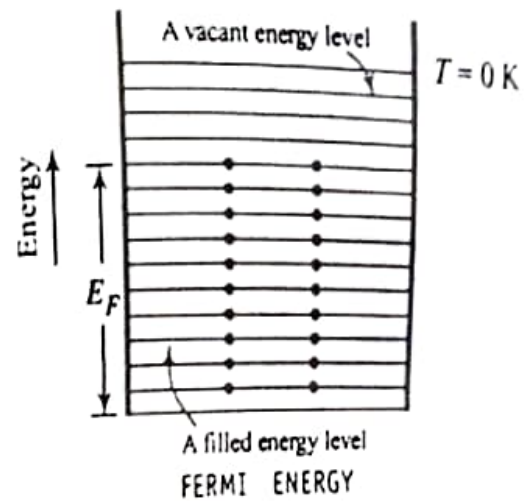
As per this equation, the number of energy levels in an energy interval dE is proportional to \sqrt{E} . A plot of $g(E)$ verses E is shown in fig below.



Fermi energy:

The energy corresponding to the highest occupied levels at zero degree absolute is called the Fermi energy, and the energy level is referred to as Fermi level. The Fermi energy is denoted as E_F .

Thus at $T=0^\circ\text{K}$ all the energy levels lying above the Fermi level are empty and those lying below are completely filled as shown in fig below.



Fermi factor and its temperature dependence:

Fermi factor is the probability of occupation of a given energy state for a material in thermal equilibrium. The probability $f(E)$ that a given energy state with energy E is occupied at a steady temperature T , is given by

$$f(E) = \frac{1}{e^{\frac{E-E_F}{KT}} + 1}$$

Where E_F is the Fermi energy and K is the Boltzmann constant.

The dependence of Fermi factor on temperature, and the effect on occupancy of energy level is as shown in fig below. Let us consider different cases of distribution as follows.

(i) **Probability of occupation for $E < E_F$ at $T=0$**

When $T=0$ and $E < E_F$, we have for the probability,

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

Therefore $f(E) = 1$, for $E < E_F$. Here $f(E) = 1$ means the energy level is certainly occupied, and $E < E_F$ applies to all the energy levels below E_F .

Therefore, at $T=0$, all the energy levels above Fermi level are occupied.

(ii) **Probability of occupation for $E > E_F$ at $T=0$**

When $T=0$ and $E > E_F$, we have for the probability,

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

Therefore $f(E) = 0$, for $E > E_F$. i.e at $T=0$, all the energy levels above Fermi levels are unoccupied.

(iii) **Probability of occupation at ordinary temperature:**

At ordinary temperature the value of probability remains 1 for $E \ll E_F$. But it starts decreasing from 1 as E reaches closer to E_F .

The value of $f(E)$ becomes $\frac{1}{2}$ at $E=E_F$

This is because, for $E = E_F$,

$$e^{\frac{(E-E_F)}{KT}} = e^0 = 1$$

$$\text{Therefore, } f(E) = \frac{1}{e^{\frac{(E-E_F)}{KT}} + 1} = \frac{1}{1+1} = \frac{1}{2}$$

Further, for $E > E_F$ the probability value falls off to zero rapidly.

