Electron Theory of Metals

1. INTRODUCTION

There are many fundamental properties of solids, e.g. electrical and thermal conductivities, magnetic and optical properties, etc. depend upon their electronic structure. We can understand many physical properties of solids in terms of electron theory of solids. The development of the electron theory of solids, started in the beginning of the 20th century. Today, it is the basis for the classification of all solids. When free electron theory applied to metals, it explains forces of cohesion and repulsion, binding the energy levels and the behaviour of conductors and insulators and magnetic materials. According to this model, the valence electrons of the constituent atoms become conduction electrons and move about freely through the volume of the metal.

The first version of the free electron model was introduced by P. Drude in the early 1900s, with improvements soon after by H.A. Lorentz. This is now known as *Drude-Lorentz free electron theory.* The other theories are:

(i) Sommerfeld free-electron theory
(ii) Zone Theory

2. METALLIC BONDING

In chapter 4, we have already discussed about metallic bonding. In the metal, the valence electrons are free to move in different directions. The valence electrons inside the metal are called free electrons and move inside the metal, constrained only by the surface of the sample. Collisions between electrons are neglected. The binding forces in the metals are due to the electrostatic attraction between the positive ions and negative cloud or dilute gas of electrons. Such a free electron model was first introduced by P. Drude in the early 1900s, with improvements soon after by H.A. Lorentz.

We have now a modern picture of metallic bonding. According to this picture, the metallic bond is more closely related to the covalent or electron pair bond and resembles the ionic bond. Essentially, the metallic bond can be said to be an unsaturated covalent bond which allows a large number of atoms to be held together by mutual sharing of free electrons. Furthermore, the density of electrons between the atoms in metallic bonding is much lower than allowed by Pauli exclusion principle. This permits the electrons to move freely from point to point without significant increase in energy.

We have read that the bonds between atoms in solids are made of cohesive and repulsive forces which holds the atoms at definite distances from each other. It is proper to have an understanding of these forces upon which the electron structure of atoms depends. Primarily, due to the close proximity of two atoms places too many electrons into interacting locations, mutual repulsion results. The cohesive and repulsive forces gets equal when the equilibrium position is reached. We have already remarked in chapter 4 that

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large cohesive forces produce high melting points and fairly large elastic values of materials and higher mechanical strength.

3. DRUDE-LORENTZ THEORY

Drude, in 1900, postulated that the metals consist of positive ion cores with the valence electrons moving freely among these cores. The electrons are, however, bound to move within the metal due to electrostatic attraction between the positive ion cores and the electrons. The potential field of these ion cores, which is responsible for such an interaction, is assumed to be constant throughout the metal and the mutual repulsion among the electrons is neglected. The behaviour of free electrons moving inside the metals is considered to be similar to that of atoms or molecules in a *perfect gas*. The free electrons are, therefore, also referred to as *free electron gas* and the theory is accordingly known as Drude and Lorentz's *classical free electron theory*. The movement of electrons obeys the laws of the classical kinetic theory of gases. Lorentz in 1909, applied Maxwell-Boltzmann statistics to the electron gas with the following two assumptions:

(i) The mutual repulsion between the negatively charged electrons is negligible.

(ii) The potential field due to positive ions within the crystal can be assumed to be constant everywhere.

Since the electrons move freely inside the metals irrespective of the crystal structure, the ratio of the electrical conductivity, σ, to the thermal conductivity, k, should be constant for all metals at a constant temperature, i.e.

$$\frac{\sigma}{k} = \text{constant} \tag{1}$$

This is called the *Wiedemann-Franz law* and has been realized in practice.

This theory explained a number of properties of a metal, e.g. electrical conductivity, thermal conductivity, luster and opacity. The main drawbacks of this theory are:

(i) The theory correctly predicted the room temperature resistivity of various metals but the temperature dependence of resistivity could not be established accurately. The theory predicted that resistivity varies as $\sqrt{T}$ whereas actually it is found to be linearly with temperature.

(ii) The theory yielded incorrect magnitudes of the specific heat and paramagnetic susceptibility of metals.

The above shortcomings of Drude-Lorentz theory were removed by Sommerfeld in 1928. He applied Fermi-Dirac statistics instead of Maxwell-Boltzmann statistics. The possible electronic energy states in the potential energy box and the distribution of electrons in these states are then determined using quantum statistics.

4. SOMMERFELD FREE-ELECTRON THEORY

The basic assumptions of this theory are:

(i) The valence electrons in a metal are free.

(ii) Valence electrons in a crystal are confined to move within the boundaries of a crystal. Obviously, the electrons within the crystal have a lower potential energy than outside. We must note that the potential energy of an electron is uniform or constant within the crystal (Drude theory).

(iii) The electrons are free to move within the crystal, but are prevented from leaving the crystal boundaries by very high potential energy barriers at its surface.

(iv) The allowed energy levels of an electron, bound to a single atom are quantized.

(v) The electronic specific heat of metals is very low.

We consider the one dimensional and three dimensional cases separately.

4.1 Free Electron Gas in One-Dimensional Box

Consider an electron of mass m which is bound to move in a one dimensional crystal of length as shown in Fig. 5.1. The electron is prevented from leaving the crystal by the presence of a large potential energy

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barrier at its surfaces. The potential energy everywhere within the crystal is assumed to be constant and equal to zero. Thus we have

$$V(x) = 0 \text{ for } 0 < x < L$$

$$V(x) = \infty \text{ for } x \leq 0 \text{ and } x \geq L \quad (1)$$

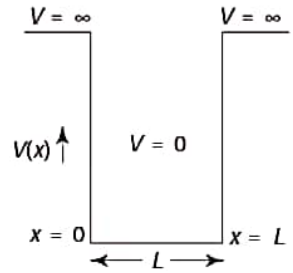

Fig. 5.1 **Potential well (one dimensional) bounded by infinite potential energy barriers**

Sommerfeld, in his free electron quantum theory assumed that the potential of an electron in a metal is uniform. He applied the one dimensional Schrödinger equation

$$\frac{d^2\psi_n}{dx^2} + \frac{8\pi^2 m}{h^2}(E_n - V)\psi_n = 0 \quad (2)$$

to calculate the total energy E_n, where ψ_n is the wave function of the electron occupying the nth state the E_n represents the kinetic energy of the electron in the nth state and V is its potential energy. The potential energy everywhere within the crystal is assumed to be constant and equal to zero. Therefore the Schrödinger equation (2) becomes

$$\frac{d^2\psi_n}{dx^2} + \frac{8\pi^2 m}{h^2}E_n\psi_n = 0 \quad (3)$$

The general solution to this equation is

$$\psi_n(x) = A \sin kx + B \cos kx \quad (4)$$

where A and B are arbitrary constants to be determined from boundary conditions. One obtains $A = \sqrt{2/L}$ and $B = 0$ and k is given by

$$k = \sqrt{\frac{4\pi m E_n}{h}} \quad (5)$$

One obtains the following expression for the allowed discrete energy values

$$E_n = \frac{h^2}{8mL^2}n^2 \quad (6)$$

where $n = 1, 2, 3 \ldots$

Obviously $E_n \propto n^2$

The number n is called the quantum number. The energy spectrum consists of discrete energy levels where the spacing between the levels is determined by the values of n and L. It decreases with increasing L. If L is of the order of a few centimeters, the energy levels form almost a continuum. But if L has atomic dimensions, the spacing between the levels becomes appreciable. The plot of E_n versus n is shown in Fig. 5.2. The energy levels and wave functions corresponding to $n = 1, 2, 3$ and 4 are shown in Fig. 5.3. Thus, we find that if the total number of electrons to be accommodated is seven, the energy levels with $n < 4$ would be occupied while the level with $n > 4$ would be empty. The topmost filled energy level at $0K$ is known as *Fermi level* and the energy corresponding to this level is called the *Fermi energy*, E_F.

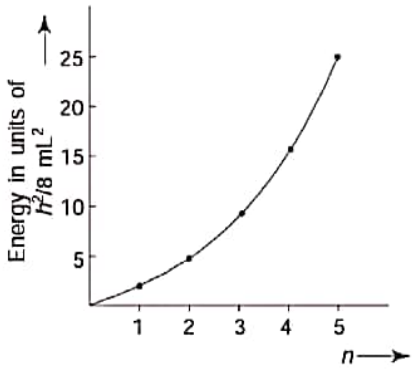

Fig. 5.2 **E_n versus n for a one-dimensional crystal**

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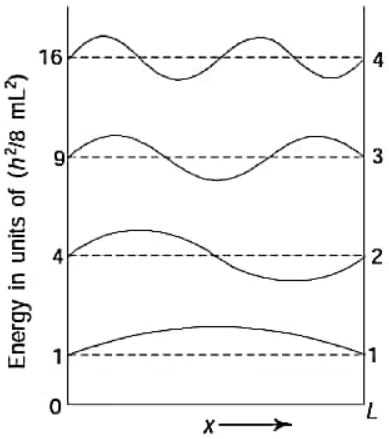

Fig. 5.3 First four wave functions (solid lines) and the corresponding energy levels (broken lines) of an electron in a one dimensional crystal

Free Electron Gas in Three Dimensions

The eq. (6) is the expression for energies in one dimension only. The corresponding three-dimensional case would be one in which an electron moves in all directions so that quantum numbers n_x, n_y and n_z are required corresponding to the three coordinate axes. In terms of a cubically shaped block of metal of side L, one obtains the expression for the allowed energies as

$$E_n = \frac{h^2}{8mL^2}\left(n_x^2 + n_y^2 + n_z^2\right) \tag{7}$$

$$= \frac{h^2}{8mv^{2/3}}\left(n_x^2 + n_y^2 + n_z^2\right) \tag{7(a)}$$

The integers n_x, n_y and n_z are the first three quantum numbers of an electron and $v = L^3$ is the volume of the assumed metal cube. The expression (7) gives the energies of free electrons in a metal. We must note that expressions (6) and (7) are of the same form, except for the number of integers. We must note that for various combinations of three integers n_x, n_y and n_z (e.g., 211, 121 and 112), one obtains the same energy value or level. However, each combination of integers represents a different wave function, having the same energy. Such an energy level is said to three fold degenerate.

From de Broglie relation, we have

$$\lambda = \frac{h}{mv} = \frac{2L}{n}$$

and wave number $$k = \frac{2\pi}{\lambda}$$

Using these relations, the expression (6) can be written as

$$E_n = \frac{k^2 h^2}{8m\pi^2} \tag{8}$$

we can see that the relation between energy and wave number obtained is parabolic (Fig. 5.4).

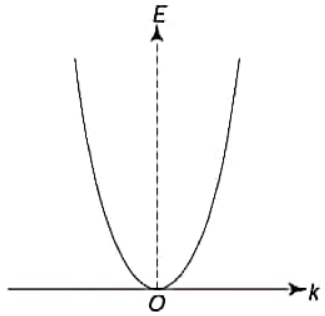

Fig. 5.4 Parabolic relationship between energy and wave number

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5. FERMI-DIRAC DISTRIBUTION FUNCTION (Electron Energies in a Metal)

The total values of energies of the valence electrons in a metal is given by Eq. (7). From Eq. (7) it is obvious that among energies E_1, E_2, E_3, etc., each energy value is greater than the preceding value by the same amount E_1. As stated earlier, for each different set of (n_x, n_y, n_z), there is an energy state. The number of states that have a given energy increases rapidly with increase in the number of different values of n_x, n_y, n_z. We must note that any change in these values influences the change in E by the square of their values $\left(n_x^2, n_y^2, n_z^2\right)$. This means the number of states in a metal is very large. If a plot is made for the number of states per interval of energy $N(E)$ or *density of states* V_s the total energy E, $N(E)$ increases parabolically with increasing E (Fig. 5.5).

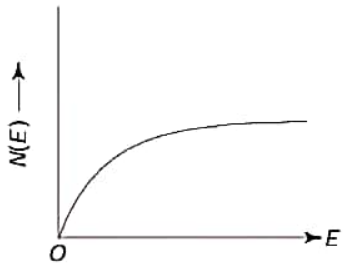

Fig. 5.5 Density of energy levels of free electrons in a solid vs energy

We know that the valence electrons have a tendency to occupy the lowest available energy states in a system. However, it is essential to consider all the electrons in the single system because of mutual interactions among all the electrons in the single system due to the mutual interactions among all the electrons forming the electron gas. This is possible only when we apply Pauli exclusion principle. We know that according to Pauli exclusion principle, only two electrons can occupy a given state, specified by the three quantum numbers (n_x, n_y, n_z), one with spin up and the other with spin down or opposite spin. If the metal is in its ground state, which occurs at absolute zero, all electrons occupy the lowest possible energy levels compatible with the exclusion principle, as indicated in Fig. 5.6. If the total number of electrons per unit volume (say n_0) is less than the total number of energy levels available in the band, the electrons will then occupy all energy states up to a maximum, designated by E_{max}. The value of E_{max} depends on how many free electrons there are. The maximum energy level (E_{max}) called the *Fermi level* and all quantum states in the energy levels above this level are empty (Fig. 5.6). The level at which the probability of occupation is 50% is the *Fermi level*, E_F. If we want to remove an electron from the Fermi level and take it out of the metal, some energy is required. This is called the *work function* and usually denoted by ϕ, which is equal to the energy normally measured when an electron is removed from the surface of the metal. Since thermal energies are very small compared with the Fermi energy, only a very few electrons are excited above the Fermi energy even at room temperatures. For that reason the work function is practically constant over a wide range of temperatures. We must note that at 0°K and electron in the Fermi level possesses the highest energy of the electrons in the metal and is the easiest to remove.

We now discuss the effect of temperature on the electron energy levels. It is apparent that, for temperatures greater than 0K, the Fermi level may not be the topmost filled level since some of the electrons from the filled energy levels may be excited to the higher levels. The probability that a state at a level of energy E is occupied by an electron at $T = 0$°K is constant and equal to 1 (unity) upto the Fermi level E_F and zero above it. When the temperature of the system is raised, excited electrons move into the new energy levels (Fig. 5.7). Thus some of the levels below E_{max} would be empty while some above it would be occupied. The probability that a particular quantum state of energy E is occupied at a temperature T is given by the so called *Fermi function.*

$$f(E) = \frac{1}{\left[1 + \exp\left\{E - E_F / kT\right\}\right]} \qquad \text{(a)}$$

The above also represents the change in electron energy distribution, i.e. $\int N(E) = f(E)$. Here $\int N(E)$ represents the probability that a state of energy E is occupied at temperature T. Thus at $T = 0$°K when $E < E_F$, the exponential term in Eq. (a) becomes zero and

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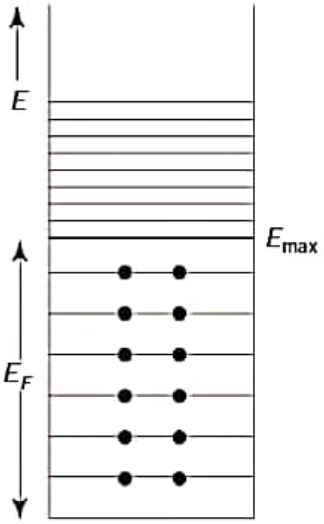

Fig. 5.6 **Filling of energy levels by electrons**

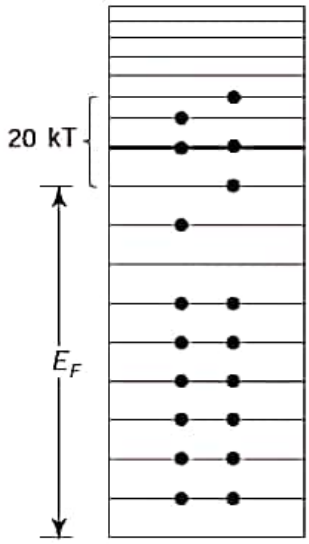

Fig. 5.7 **Distribution of free electrons among energy states (excited state)**

$$f(E) = \int N(E) = 1$$

when $E > E_F$, the exponential term becomes infinite and

$$f(E) = \int N(E) = 0$$

By putting $$\int N(E) = f(E) = \frac{1}{2}$$

one can easily see that $E = E_F$. Obviously, at absolute zero all states above $E = E_F$ are empty and all states below E_F are occupied (Fig. 5.8). The Fermi distribution function is a *step function.*

At any temperature one can define the Fermi level as that level for which the occupation probability is 1/2. The values of Fermi energy for few metals are given in Table 5.1.

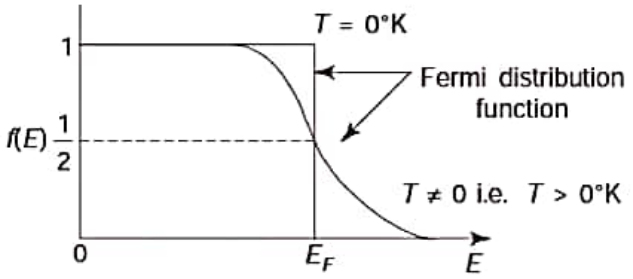

Fig. 5.8 **Probability of occupancy by an electron at various temperatures different from absolute zero**

Table 5.1 Fermi energy

Metal	*Li*	*Na*	*K*	*Rb*	*Cs*	*Cu*	*Ag*	*Mg*	*Al*
Fermi energy, E_F (eV)	4.72	3.12	2.14	1.82	1.53	4.07	5.54	7.3	11.9

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11. EQUATION OF MOTION OF AN ELECTRON

According to Drude-Lorentz theory, the motion of electrons is random (when no electric field is applied). Obviously, the number of electrons in a metal moving from left to right at any time is the same as that moving from right to left. This shows that no net current flows through the metal. However, if we apply an electric field across a metal, the electrons move in the positive direction of the field and current is produced.

Let us consider that an electron within a metal moving in any direction and at any time under the applied field 'E'. Let m is the mass of an electron, v is the velocity of the electron and e be the charge on the electron. The force experienced by an electron due to the applied electric field, E is

$$F = eE \tag{13}$$

Due to this force, the electron moves with an average acceleration, d^2x/dt^2 (= dv/dt). The force with which the electron moves,

$$F = m \frac{dv}{dt} \tag{14}$$

from (13) and (14), we have

$$m \frac{dv}{dt} = eE$$

or $$\int dv = \frac{eE}{m} \int dt$$

or $$v = \frac{eE}{m} t + K \tag{15}$$

where K is constant of integration, which represents the random velocity of the electrons. The average value of random velocity must be zero, otherwise there will be a flow of current even in the absence of external field. Thus $K = 0$. We have from Eq. (15)

$$v = \frac{eE}{m} t \tag{16}$$

Obviously, velocity is directly proportional to time 't'. This clearly reveals that the velocity of an electron continues to increase with time till the collision does not occur. Now, if 't' is the collision time, i.e. average time between the two successive collisions, we have the average velocity of the electron

$$v = \frac{eE \cdot t}{m} \quad \text{or} \quad \frac{v}{e} = \frac{et}{m} \tag{17}$$

Equation (17) is called the equation of motion of an electron under the applied electric field. The average velocity is also called as '*drift velocity*', because the drift in electrons is due to applied field (E).

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15. MEAN FREE PATH

One can define a metal as a substance, which consists of a lattice of a positive ion cores held together by means of a loosely bound valence electrons, also called gas of electrons or delocalized electrons. We know that these electrons have a wave characteristics as they move throughout the metal. When waves travelling through a periodic structure, i.e., a structure which has uniform repetition, proceed with a minimum interruption. Any irregularity in the periodic, i.e. repetitive structure, through which the wave travels, will deflect the wave. Obviously, when an electron is travelling towards the positive electrode, a foreign or displaced atom could cause it to be reflected towards the negative electrode.

We must note that while moving towards the positive electrode, electrons continuously acquire additional momentum and hence more velocity. And when electrons move towards the negative electrode, they continuously lose momentum and hence velocity. Thus the distance between reflections and deflections determines the *net* or *drift* velocity of electrons. Obviously, *mean free path is an average* distance which an electron covers in its wavelike pattern without any reflection or deflection. Mathematically, one finds the following relation for mean free path,

$$\lambda = vt \tag{27}$$

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where $v \rightarrow$ velocity of an electron and $t \rightarrow$ collision time or mean free time.

For metals, the velocity of an electron corresponds to that of Fermi energy (E_F) and is given by the relation

$$v_F = \sqrt{\frac{2W_F}{m}} \tag{28}$$

where $W_F \rightarrow$ Fermi energy in Joules (= 1.602×10^{-19} times the Fermi energy in electron volts, i.e. $1.602 \times 10^{-19} E_F$) and $m = 9.1 \times 10^{-31}$ kg.

Example 7 *(i) Estimate the maximum velocity of an electron in a metal in which Fermi energy has a value of 3.75 eV. Given $e = 1.602 \times 10^{-19}$ C and $m = 9.1 \times 10^{-31}$ kg. (ii) What will be the mobility of electrons when the mean free time between the collisions is 10^{-14} S?* [M.Sc.]

Solution

$$W_F = 1.602 \times 10^{-19}$$
$$E_F = 1.602 \times 10^{-19} \times 3.75$$
$$= 6 \times 10^{-19} \text{ J}$$

(i) $$v_F = \sqrt{\frac{2W_F}{m}} = \sqrt{\frac{2 \times 6 \times 10^{-19}}{9.1 \times 10^{-31}}} \text{ m/s}$$
$$= 1.76 \times 10^6 \text{ m/s}$$

(ii) $$\mu = \frac{et}{m} = \frac{1.602 \times 10^{-19} \times 10^{-14}}{9.1 \times 10^{-31}} = 1.76 \times 10^{-3} \text{ m}^2/\text{V-s}$$

Example 8 *The Fermi level for Potassium is 2.1 eV. Estimate the velocity of electrons at the Fermi level. Given $e = 1.6 \times 10^{-19}$ C and $m = 9.109 \times 10^{-31}$ kg.* [B.E.]

Solution

$$E_F = 2.1 \text{ eV}$$
$$e = 1.602 \times 10^{-19} \text{ C}$$
$$m = 9.109 \times 10^{-31} \text{ kg}$$
$$t = 10^{14} \text{ s}$$
$$W_F = 1.602 \times 10^{-19} E_F$$
$$= 1.602 \times 10^{-19} \times 2.1 \text{ J}$$
$$= 3.364 \times 10^{-19} \text{ J}$$

The velocity of electrons,

$$v_F = \sqrt{\frac{2W_F}{m}} = \sqrt{\frac{2 \times 3.364 \times 10^{-19}}{9.109 \times 10^{-31}}} = 0.86 \times 10^6 \text{ m/s.}$$

Example 9 *Estimate the mean free path of free electrons in pure copper at 4 K. The collision time for photon scattering at 4 K is 10^{-9} s. The Fermi energy level for copper is 7 eV. Given: $e = 1.602 \times 10^{-19}$ C and $m = 9.109 \times 10^{-31}$ kg.*

Solution

$$t = 10^{-9} \text{ s}$$
$$E_F = 7 \text{ eV}$$
$$e = 1.602 \times 10^{-19} \text{ C}$$
$$m = 9.109 \times 10^{-31} \text{ kg}$$
$$W_F = 1.602 \times 10^{-19} E_F$$
$$= 1.602 \times 10^{-19} \times 7$$
$$= 11.2 \times 10^{-9} \text{ J}$$

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Velocity of electrons,

$$v_F = \sqrt{\frac{2W_F}{m}} = \sqrt{\frac{2 \times 11.2 \times 10^{-19}}{9.109 \times 10^{-31}}} \text{ m/s}$$

$$= 1.57 \times 10^6 \text{ m/s}$$

Mean free path

$$\lambda = v_F \, t = 1.57 \times 10^6 \times 10^{-9} = 1.57 \times 10^{-3} \text{ m} = 1.57 \text{ mm}$$

Example 10 *Find the conductivity of copper at 300 K. The collision time (τ) for electron scattering 2×10^{-14} s at 300 K. Given e = 9.1 $\times$ 10^{-31} kg and m = 9.1 $\times$ 10^{-31} kg.* [B.E.]

Solution The number of electrons per m^3 of copper is obtained as

$$n = \frac{6.023 \times 10^{23} \times 8960}{0.06354}$$

$$= 8.50 \times 10^{23}/m^3$$

We have, conductivity

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

$$= \frac{8.50 \times 10^{28} \times (1.602 \times 10^{-19})^2 \times 2 \times 10^{-14}}{9.1 \times 10^{-31}}$$

$$= 4.8 \times 10^7 \text{ Ohm}^{-1}\text{-m}^{-1}$$

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2. ELECTRICAL CONDUCTION

One of the most important characteristics of a solid material is the ease with which it transmits an electric current. Ohm's law relates the current I (i.e., the time rate of charge passage, Q/t, $Q \rightarrow$ Charge and $t \rightarrow$ time) to the applied voltage V as follows:

$$V = I\,R \tag{1}$$

where R is the resistance of the material through which the current I is passing. The units of V, I and R are Volt, ampere and Ohm respectively. The electrical resistivity (ρ) of solids is probably the most important of all physical properties. The value of electrical resistance is influenced by specimen configuration, and for many materials is independent of current. However, the resistivity (ρ) of material is independent of specimen geometry but it is related to R through the relation

$$\rho = \frac{RA}{l} \tag{2}$$

where l is the distance between the two points of the specimen at which the voltage is measured, and A is the area of cross-section perpendicular to the direction of the current. The units of ρ are Ohm-meters (Ω – m). From Eqs. (1) and (2),

$$\rho = \frac{VA}{Il} \tag{3}$$

Many factors influence the value of ρ for a given material. Values of resistivity of common materials at 20°C are given in Table 14.1 and few engineering materials are given in Table 14.1(a).

Table 14.1 Resistivity of some common materials at 20°C

Material	*Resistivity (ρ) (Ω – m)*	*Material*	*Resistivity (ρ) (Ω – m)*
Silver	1.6×10^{-8}	Germanium	10^{-5} to 0.6
Aluminium	2.66×10^{-8}	Silicon	10^{-5} to 2.5×10^{3}

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Table 14.1 (*Contd.*)

Material	*Resistivity (ρ) (Ω – m)*	*Material*	*Resistivity (ρ) (Ω – m)*
Iron	9.1×10^{-8}	PVC	1.0×10^{10}
Copper	1.67×10^{-8}	Bakelite	1.0×10^{11}
Nickel	13.3×10^{-8}	Mica	1.0×10^{11}
Carbon-steel	1.7×10^{-7}	Glass	1.0×10^{16}
Polythene	1.0×10^{16}	Stainless steel	7.0×10^{-7}
Graphite	1.4×10^{-7}	Steatite Porcelain	1.0×10^{13}
		Alumina	10^{11}
		Diamond	10^{12}

Table 14.1(a) Room temperature electrical resistivity for few engineering materials

Material	*Electrical Resistivity (Ω – m)*
Steel alloy 1020 (annealed)	1.60×10^{-7}
Steel alloy 4140 (quenched and tempered)	2.20×10^{-7}
Steel alloy 4340 (quenched and tempered)	2.48×10^{-7}
Stainless steel alloy 440 A (annealed)	6.0×10^{-7}
Stainless steel alloy 17-7 PH (annealed)	8.3×10^{-7}
Gray irons	
• Grade G 1800	15.0×10^{-7}
• Grade G 3000	9.5×10^{-7}
• Grade G 4000	8.5×10^{-7}
Ductile irons	
• Grade 60-40-18	5.5×10^{-7}
• Grade 80-55-06	6.2×10^{-7}
• Grade 120-90-02	6.2×10^{-7}
Aluminium alloy 7075 (T 6 treatment)	5.22×10^{-8}
Aluminium alloy 356.0 (T 6 treatment)	4.42×10^{-8}
Copper alloy C 3600 (free cutting brass)	6.6×10^{-8}
Copper alloy C 71500 (copper-nickel, 30%)	37.5×10^{-8}
Magnesium alloy A Z 91 D	17.0×10^{-8}
Titanium alloy Ti – 5Al – 2.5Sn	15.7×10^{-7}
Nickel 200	0.95×10^{-7}
Inconel 625	12.90×10^{-7}
Monel 400	5.47×10^{-7}
Haynes alloy 25	8.9×10^{-7}
Invar	8.2×10^{-7}
Super invar	8.0×10^{-7}
Kovar	4.9×10^{-7}
Lead-tin-solder (60 Sn – 40 Pb)	1.50×10^{-7}

The resistivity of some widely used metal and their alloys along with their temperature coefficient are given in Table 14.2.

Table 14.2 Electrical resistivity of some metals and their alloys

Metals and alloys	*Resistivity (ρ) at 20°C (Ω-m)*	*Temperature coefficient α/°C*
• Copper, annealed	1.67×10^{-8}	4.29×10^{-3} (0-100°C)
• Copper, reduced 75% by cold drawing	1.71×10^{-8}	—

(*Contd.*)

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Table 14.2 *(Contd.)*

Metals and alloys	*Resistivity (ρ) at 20°C (Ω-m)*	*Temperature coefficient α/°C*
• Cartridge brass annealed 70% Cu and 30% Zn	6.20×10^{-8}	1.48×10^{-3} (20°C)
• Aluminium, annealed	2.65×10^{-8}	4.29×10^{-3} (20°C)
• Iron, annealed	9.71×10^{-8}	6.57×10^{-3} (20°C)
• Constantan 55% Cu and 45% Ni	49×10^{-5}	0.02×10^{-3} (25°C)
• Manganin 84% Cu, 12% Mn and 4% Ni	44×10^{-7}	0.009×10^{-3} (25°C) -0.42×10^{-3} (100°C)
• Nichrome 80% Ni and 20% Cr	108×10^{-5}	0.14×10^{-3} (0-500°C)

3. ELECTRICAL CONDUCTIVITY (σ)

Sometimes, electrical conductivity (σ) is used to specify the electrical character of a material. Electrical conductivity is simply the reciprocal of resistivity (ρ), i.e.

$$\sigma = \frac{1}{\rho} \tag{4}$$

Electrical conductivity is indicative of the ease with which a material is capable of conducting an electrical current. The units of σ are reciprocal Ohm-meters $[(\Omega\text{-m})^{-1}]$ or mho/m. It is also expressed in Siemens/m.

When an electric field E is applied to a conductor an electric current begins to flow and the current density by Ohm's law is

$$J = \sigma E \tag{5}$$

The conductivity may be defined as the movement of electrical charge from one point to another and it depends on the number of charge carriers (n), the charge per carrier (e) and the mobility of carriers (μ), i.e.

$$\sigma = ne\mu \tag{6}$$

The unit of mobility (μ) is $m^2\ V^{-1}s^{-1}$. Mobility is an important term in the study of semiconductors.

One can obtain the expression (6) from first principle as follows:

Let E be the electric field applied to a conductor, e be the charge on the electron and m the mass of the electron. The electrons move in a specific direction under the influence of the electric field. The directional motion of a free electron is called a *drift*. The average velocity gained during this drift motion is termed as *drift velocity*.

As electron is being negatively charged particle, the force acting on it under the electric field intensity E is,

$$F = -eE \tag{7}$$

The electron drift is in a direction opposite to that of the applied field. During the accelerated motion, the electron collides with the defects in the lattice. As a result of the consequence scattering, the electron loses the velocity it gained from the electric field. The effect of the crystal lattice may be reduced considerably due to a retarding force (may be due to damping). This force is proportional to the velocity v and mass m of the electron. The retarding force is represented as $-\alpha mv$, where α is a constant. We can write the equation of motion of the electron as

$$m\frac{dv}{dt} = -eE = -\alpha mv \tag{8}$$

or

$$dv = -\frac{eE}{m}\,dt$$

or

$$v = -\frac{eE}{m}\,t + \text{constant} \tag{9}$$

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If the average time between collisions is 2τ then, during this time, the electron is acted upon by a force F given by Eq. (7). But at $t = 0$, $v = 0$ (immediately after each collision) and hence the integeration constant in (9) is zero. Thus (9) takes the form

$$v = -\frac{eE}{m}\tau$$

Obviously, the mean velocity $= -eE\,\tau/m$, where τ is called the relaxation time and is time interval in which there is unit probability of a collision.

When there is a collision of lattices (resistance), the current density J due to n electrons per unit volume of charge e and drift velocity v is expressed as

$$J = nev \tag{10}$$

$$= ne\left(\frac{eE\tau}{m}\right) \tag{11}$$

$$= \sigma E \tag{12}$$

$$\therefore \quad \sigma = \frac{J}{E} = \frac{ne^2\,\tau}{m} = \frac{ne(e\tau)}{m} \tag{13}$$

The velocity in a unit electric field, i.e. v/E is the mobility (μ) of the electron. Hence

$$\mu = \frac{v}{E} = \frac{1}{E/v}\left(\frac{Ee\tau}{m}\right) = \frac{e\tau}{m}$$

Using Eqs. (10) and (12), one obtains

$$J = ne\mu E$$

and

$$\sigma = ne\mu \tag{14}$$

Equation (14) is of immense importance for solid materials. From (14), we note that the electrical conductivity depends on two factors: *(i)* the number n of charge carriers per unit volume and *(ii)* their mobility, μ.

Solid materials exhibit an amazing range of electrical conductivities, extending over 27 orders of magnitude; probably no other physical property experiences this breadth of variation. In fact, one way of classifying solid materials is according to the ease with which they conduct an electric current. Within this classification scheme, one can classify materials into three broad categories:

(i) Conductors (ii) Semi conductors and *(iii) Insulators*

Metals and their alloys are good conductors. Copper, silver and gold are among the best conductors of electricity, followed by aluminium, iron and nickel. Some semimetals, e.g. graphite also fall in this group. According to free electron theory, when the outer orbit of an atom has less than one half of the maximum 8 electrons, the material is usually a metal and a good conductor of electricity. Metals have conductivities on the order of 10^7 $(\Omega\text{-m})^{-1}$. The electrical resistivity of conductor range from 10^{-9} to 10^{-4} $(\Omega\text{-m})$.

Semiconductors are materials which behave are insulators at 0 °K but a significant rise in electrical conductivity is observed as the temperature rises. At room temperature, the electrical conductivity of semiconductor falls between that of a conductor and insulator. The electrical conductivity semiconductors ranges from about 10^5 to 10^{-7} $(\Omega\text{-m})^{-1}$, as compared with the conductivity on the order of 10^7 $(\Omega\text{- m})^{-1}$ for good conductors and minimum conductivity of 10^{-15} $(\Omega - \text{m})^{-1}$ for good insulators. Semiconductors form the base materials for a number of electronic devices. Germanium and silicon are the widely used common semiconductors. According to free electron theory, when the outer orbit of an atom has exactly one-half the maximum eight electrons, the material has both metal and non-metal properties and usually exhibit semiconducting properties. We must note that the electrical resistivity of a semiconductor is usually strongly dependent on temperature.

There are also materials with very low conductivities, ranging between 10^{-10} and 10^{-20} $(\Omega\text{-m})^{-1}$. These are electrical *insulators*. Mica, PVC, rubber, porcelain and bakelite are few examples of insulators. The

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resistivity range of insulators extends from 10^4 to 10^{17} (Ω-m). According to electron theory, when the outer orbit of an atom has more than one half of the maximum eight electrons, the material is usually a non-metal and non-conductor.

A brief comparison between metals, semiconductors and insulators is presented in *Table* 14.3.

Table 14.3 A comparison between conductors, semiconductors and insulators

Conductors	*Semiconductors*	*Insulators*
1. Conductivity decreases with increase in temperature upto nearly zero value	• Conductivity increases with increase in temperature. Conductivity is particularly sensitive to impurity type and content.	• Conductivities increases with increase in temperature
2. Conductivity of metals is of the order of 10^7 $(\Omega\text{-m})^{-1}$	• Conductivity of semiconductors range from 10^{-6} to 10^4 $(\Omega\text{-m})^{-1}$	• Conductivity of insulators range between 10^{-10} to 10^{-20} $(\Omega\text{-m})^{-1}$
3. Electrical resistivity is very low and range from 10^{-9} to 10^{-4} (Ω-m)	• Resistivity is normally high and range between 10^{-3} to 10^3 (Ω-m)	• Resistivity is very high and range between 10^4 to 10^{17}(Ω-m)
4. Temperature coefficient of resistance is not constant	• Temperature coefficient of resistance is negative	• Negative resistance temperature coefficient. Probably with the rise in temperature some electrons reach to the conduction band.
5. At low temperatures they exhibit semiconductivity. At very low temperatures, some elements and their alloys exhibit infinite conductivity, i.e. super conductivity	• At low temperature semiconductors become *dielectrics* (insulators)	• No change in the properties of the insulators observed
6. Have unfilled overlapping energy bands	• Have filled energy bands and small forbidden zones	• There is a large energy gap in between valence and conduction band
7. Current carriers in conductors are free electrons which exist whether external field is applied or not	• Current carriers are originated due to absorption of electrical, radiant or thermal energy from external source. Electrons and holes, both serve as current carriers	• Energy required for electrons to cross the energy gap between conduction band and valence band is very large and hence no conduction

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7. ELECTRICAL RESISTIVITY OF METALS

Most metals are extremely good conductors of electricity. Room temperature conductivities of few common metals are given in Table 14.3. Metals have high conductivities due to the large number of free electrons that have been excited into empty states above the Fermi energy. Obviously, n has a large value in the conductivity expression (14).

Table 14.3 Room-temperature electrical conductivity for few metals and alloys

Metal or alloy	*Electrical conductivity* $(\Omega\text{-m})^{-1}$
Copper	6.0×10^7
Silver	6.8×10^7
Gold	4.3×10^7
Aluminium	3.8×10^7
Iron	1.0×10^7
Platinum	0.94×10^7
Brass (70 Cu – 30 Zn)	1.6×10^7
Plain carbon steel	0.6×10^7
Stainless steel	0.2×10^7

Let us now discuss conduction in metals in terms of the resistivity (the reciprocal of conductivity).

The crystalline defects serve as scattering centers for conduction electrons in metals and increase in their number raises the resistivity, i.e. lowers the conductivity. The concentration of these imperfections depends on temperature, composition, and the degree of cold work of a metal specimen. It has been observed experimentally that the total resistivity of a metal is the sum of the contributions from the thermal vibrations, impurities and plastic deformation; i.e., the scattering mechanism act independently of one another. Mathematically, we can write this as follows:

$$\rho_{\text{total}} = \rho_t + \rho_i + \rho_d \tag{15}$$

where ρ_t, ρ_i and ρ_d are the individual thermal, impurity and deformation resistivity contributions, respectively. Equation (15) is sometimes called as *Matthiessen's rule*. Figure 14.6 shows a plot of resistivity versus temperature for copper and several copper-nickel alloys in annealed and deformed states. Figure also show the influence of each ρ variable on the total resistivity. The additive character of the individual resistivity contributions is demonstrated at –100°C.

7.1 Factors Affecting Resistivity

(i) Influence of Temperature: Any rise in temperature of a conductor (which contains small amounts of impurities) increases thermal agitation of the metallic ions as they vibrate about their mean position. This reduces the mean free path and restricts the free movement of electrons, thus reducing the conductivity of the metal, i.e. this increases the resistivity of metal. For the pure metal and all the copper-nickel alloys shown in Fig. 14.6, the resistivity rises linearly with temperature above about –200°C. Thus

$$\rho_t = \rho_o + aT \tag{16}$$

where ρ_o and a are constants for each particular metal.

(ii) Influence of Impurities: Another factor which reduces the mean free path of electrons is the impurity or solute atoms. The solute atoms provide the breakage in the regular crystalline structure, thus presenting an obstacle in the movement of electron waves. A solid solution alloy will always have lower conductivity than its pure components though both individual components have higher conductivity than the alloy. For additions of a single impurity that forms a solid solution, the impurity resistivity ρ_i is related to the impurity concentration C_i in terms of the atom fraction (at %/100) as follows:

$$\rho_i = AC_i (1 - C_i) \tag{17}$$

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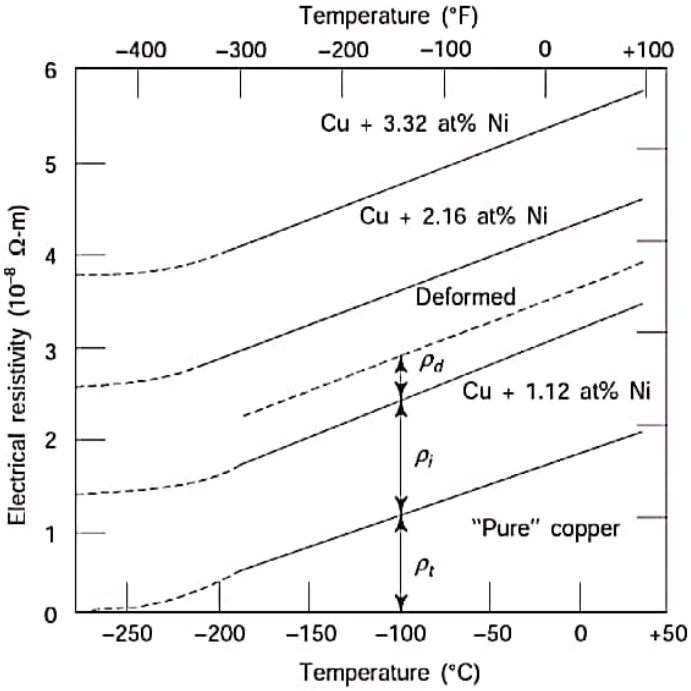

Fig. 14.6 The electrical resistivity vs. temperature curves for Cu and three copper-nickel alloys, one of which has been deformed. The contributions to the resistivity due to thermal, impurity and deformation are shown at –100°C

where A is a composition-independent constant that is a function of both the impurity and host metals. The influence of Ni impurity additions at about room temperature resistivity of Cu is shown in Fig. 14.7, upto 50 Wt% Ni; over this composition range Ni is completely soluble in Cu.

We may note that Ni atoms in Cu act as scattering centres, and increasing the concentration of Ni in Cu results in the enhancement of resistivity.

One can use the rule of mixtures expression for a two-phase alloy consisting of α and β phases to approximate the resistivity as follows:

$$\rho_l = \rho_\alpha V_\alpha + \rho_\beta V_\beta \qquad (18)$$

where the V's and ρ's represent volume fractions and individual resistivities for the respective phases.

(iii) Influence of Plastic Deformation: Plastic deformation also raises the electrical resistivity as a result of increased number of electron-scattering dislocations. The effect of plastic deformation on resistivity is also shown in Fig. 14.6.

(iv) Effect of Pressure: At room temperature the general behaviour of ρ of metal is to decrease initially with increasing pressure and it may pass through a minimum. The initial decrease is due to the effect of pressure in reducing the amplitude of lattice vibrations. The subsequent increase is probably due to modification of the electron band structure which leads to increased phonon scattering.

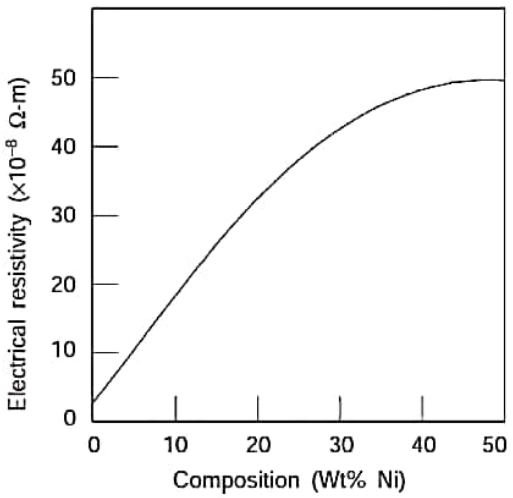

Fig. 14.7 Room temperature electrical resistivity vs. composition for Cu-Ni alloys

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