

Unit II

ELECTRONIC MATERIALS

Free electron theory:

In solids, electrons in outer most orbits of atoms determine its electrical properties. Electron theory is applicable to all solids, both metals and non metals. In addition, it explains the electrical, thermal and magnetic properties of solids. The structure and properties of solids are explained employing their electronic structure by the electron theory of solids.

It has been developed in three main stages:

1. Classical free electron theory
 2. Quantum Free Electron Theory.
 3. Zone Theory.
- **Classical free electron theory:** The first theory was developed by Drude & Lorentz in 1900. According to this theory, metal contains free electrons which are responsible for the electrical conductivity and metals obey the laws of classical mechanics.
 - **Quantum Free Electron Theory:** In 1928 Sommerfield developed the quantum free electron theory. According to Sommerfield, the free electrons move with a constant potential. This theory obeys quantum laws.
 - **Zone Theory:** Bloch introduced the band theory in 1928. According to this theory, free electrons move in a periodic potential provided by the lattice. This theory is also called “Band Theory of Solids”. It gives complete informational study of electrons.

7.5 Classical Free Electron Theory of Metals

This theory was developed by Drude and Lorentz. Even though it is a macroscopic theory it successfully explained most of the properties of metals.

In this theory, the free electrons in a metal are treated like molecules in a gas; and, Maxwell-Boltzmann statistics is applied.

The main assumptions or postulates of this theory are

1. A metal is composed of positive metal ion fixed in the lattice.
2. All the valence electrons are free to move among the ionic array. Such freely moving electrons contribute towards conduction (electrical and thermal) in metals.
3. There are a large number of free electrons in a metal and they, move about the whole volume like the molecules of a gas.
4. The free electrons collide with the positive ions in the lattice and also among themselves. All the collisions are elastic, i.e., there is no loss of energy.
5. The electrostatic force of attraction between the free electrons and the metallic ions are neglected, i.e., The total energy of free electron is equal to its kinetic energy.
6. All the free electrons in metal have wide range of energies and velocities.
7. In the absence of electric field, the random motion of free electron is equally probable in all directions. So, the net current flow is zero.
8. When an electric field is applied as shown in figure 7.1 the electrons gain a velocity called drift velocity v_d and moves in opposite direction to the field resulting in a current flow in the direction of field.

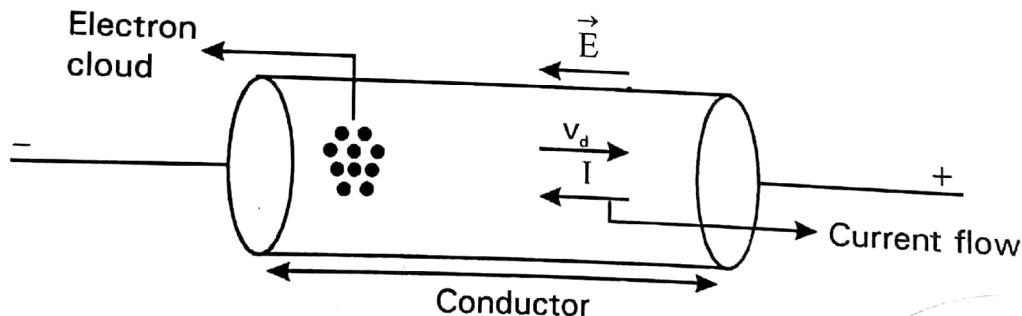


Figure 7.1 : Conduction of electrons in a metal

Thus, drift velocity is the average velocity acquired by an electron on applying an electric field.

9. Relaxation time τ

Definition - 1 : It is defined as the time required for the drift velocity to reduce to $(1/e)$ times its initial value, just when the field is switched off.

Definition - 2 : It is defined as the time taken by the free electron to reach its equilibrium position from its disturbed position just when the field is switched off.

10. Mean collision time τ_c

The average time between two consecutive collisions of an electron with the lattice points is called collision time.

11. Mean free path λ

It is the average distance travelled by the conduction electron between successive collisions with the lattice ions.

In the following sections, based on classical free electron theory, expression for electrical conductivity, thermal conductivity and Wiedemann-Franz law is derived.

Note : • **Bound Electrons** – All the valence electrons in an isolated atom bound to their parent nuclei 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; and thus, can move easily throughout the solid. All such valence electrons of its constituent atoms in a solid are called as free electrons.

The movements of the free electrons are confined to regions within the boundaries of the solid.

• **Difference between ordinary gas and the 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.

7.6 Electrical Conductivity σ

The electrical conductivity σ is defined as the rate of charge flow across a unit area in a conductor per unit potential (voltage) gradient.

$$\text{i.e., } \sigma = \frac{J}{E} \quad \text{---[1]}$$

Its unit is **mho-m⁻¹ or $\Omega^{-1} m^{-1}$** .

Expression for Electrical conductivity

Electrical conductivity of a conductor is the property by which it allows the flow of electric current.

In a metal, the valence electrons are not attached to the individual atoms and are free to move about within the lattice. Hence, the valence electrons are also called free electrons or conduction electrons.

In the absence of an electric field, the motion of the free electrons are completely random like those of the molecules of a gas in a container. But, when an electric field is applied to a metal, the electrons modify their random motion in such a way that, they drift slowly in the opposite direction to that of the applied field with an average velocity called the drift velocity v_d .

When an electric field E is applied, the free electrons in a metal experiences a force eE . Due to this force, the acceleration " a " gained by the electron is

$$F = eE$$

$$ma = eE \quad [\because F = ma]$$

$$\text{or} \quad a = \frac{eE}{m} \quad \text{---[2]}$$

Consider an electron that has just collided with an ion core. The collision momentarily destroys the tendency to drift and the electron will have truly random direction after this collision. In the next collision, the electrons velocity would have changed, to an average value v_d given by

$v_d = \sigma \tau$
where τ is called the mean free time.

Substituting equation (2) in (3), we get

$$v_d = \frac{eE\tau}{m}$$

The current density is given by

$$J = nev_d$$

where, n is the number of free electrons per unit volume.
Hence, substituting equation (4) in (5), we get

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

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

But, J is also expressed as

$$J = \sigma E$$

Therefore, substituting for J in equation (6) from equation (7)

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

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

Thus, the above expression relates the electrical conductivity to the number of free electrons per unit volume.

Expression for σ in terms of $k_B T$

The mean free time τ in terms of mean free path λ and average thermal velocity v is given by

$$\tau = \frac{\lambda}{v}$$

The kinetic energy of an electron based on kinetic theory is given by

$$\frac{1}{2} mv^2 = \frac{3}{2} k_B T$$

(where k_B is the Boltzmann constant)

$$\text{or } m = \frac{3k_B T}{v^2}$$

[10]

Substituting equation (10) for m and equation (9) for τ in equation (8)

$$\sigma = \frac{ne^2\tau}{3k_B T} = \frac{ne^2\lambda}{3k_B T \cdot v^2} \cdot v^2$$

$$\therefore \sigma = \frac{ne^2\lambda v}{3k_B T} \quad \text{--- [1]}$$

Thus, from the above expression of σ it is observed that, the electrical conductivity of a metal decreases with increase of temperature.

- Note :**
- For an isotropic material the mean collision time τ_c is equal to the relaxation time τ . i.e., $\tau_c = \tau$.
 - **Determination of density of electrons**

(Determination of number of electrons / unit volume in terms of Avagadro's number).

The density of free electrons or The number of free electrons / unit volume is

$$n = \text{Number of free electrons / atom} \times \text{Number of atoms / unit volume}$$

--- [1]

To Evaluate Number of atoms / unit volume

$$\text{In general, the volume occupied by 1 kg of a material is } = \frac{1}{D} \text{ m}^3 \quad \left[\because \text{volume} = \frac{\text{mass}}{\text{density}} \right]$$

where D, is the density of the material.

Therefore, volume occupied by a material of mass, equal to its atomic weight in kg

$$= \frac{\text{Atomic weight}}{D} \text{ m}^3 \quad \text{--- [2]}$$

But we know, the number of atoms in a material of mass equal to its atomic weight in kg = N_A (The Avagadro number expressed per k mole). --- [3]

$$\text{Therefore, number of atoms in a volume of } \left[\frac{\text{Atomic weight}}{D} \right] = N_A$$

$$\text{Hence, number of atoms / unit volume of the material} = \frac{N_A \times D}{\text{Atomic weight}} \quad \text{--- [4]}$$

Hence, substituting equation (4) in (1) we get,

The density of electrons or the number of electrons / unit volume n =

$$\text{Number of free electrons / atom} \times \frac{N_A \times D}{\text{Atomic weight}} \text{ m}^{-3}.$$

7.7 Thermal Conductivity K

The thermal conductivity is defined as the rate of heat flow across a unit area of a conductor per unit temperature gradient.

$$\text{i.e., } K = - \frac{Q'}{A \left(\frac{dT}{dx} \right)}$$

where Q' is the rate of heat flow given by $\left(\frac{dQ}{dt} \right)$

A is the cross sectional area of the conductor

$\frac{dT}{dx}$ is the temperature gradient.

The -ve sign is optional, which indicates that, the heat flows from higher to lower temperature side.

The unit for thermal conductivity is $\text{W m}^{-1}\text{K}^{-1}$.

In solids, heat transfer takes place by conduction. In the process of heat transfer both electrons and phonons take part. Hence in general, the total thermal conductivity can be written as

$$K_{\text{Total}} = K_{\text{electron}} + K_{\text{phonon}}$$

Since, thermal conductivity due to electrons is greater than the thermal conductivity due to phonons in the case of pure metals, the total thermal conductivity is given by $K_{\text{Total}} = K_{\text{electron}}$.

Expression for thermal conductivity K

Consider a uniform metallic rod AB. Let the surface A be at a higher temperature T, and the surface B be at a lower temperature $T-dT$ as shown in figure 7.2. Let the distance of separation between the surfaces be λ (Mean free path). The electrons conduct heat from A to B. During collision, the electrons near A lose their kinetic energy while, the electrons near B gain the energy.

Let,

The density of electrons = n

The average thermal velocity = v .

Based on kinetic theory,

The average kinetic energy of an electron at A = $\frac{3}{2} k_B T$ -----[1]

Similarly, the average kinetic energy of an electron at B = $\frac{3}{2} k_B (T-dT)$ -----[2]

Therefore, the excess kinetic energy carried by electrons from A to B

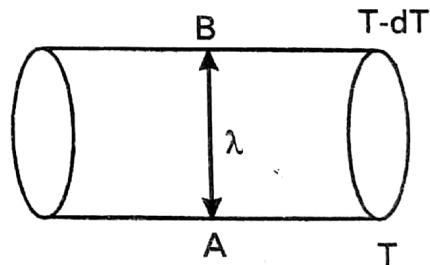


Figure 7.2

$$\begin{aligned}
 &= \frac{3}{2} k_B T - \frac{3}{2} k_B (T - dT) \\
 &= \frac{3}{2} k_B dT
 \end{aligned} \quad \text{--- [3]}$$

Since, there is equal probability for the electrons to move in all the six directions (x, y, z) and (-x, -y, -z).

$$\text{The number of electrons crossing unit area in unit time from A to B} = \frac{1}{6} nv \quad \text{--- [4]}$$

∴ The excess energy transferred from A to B per unit area in unit time

$$= \frac{1}{6} nv \times \frac{3}{2} k_B dT = \frac{1}{4} nv k_B dT \quad \text{--- [5]}$$

Similarly, the deficiency of energy carried from B to A per unit area in unit time

$$= -\frac{1}{4} nv k_B dT \quad \text{--- [6]}$$

Since, the net energy transferred from A to B per unit area per unit time is the rate of heat flow Q. Then,

$$\begin{aligned}
 Q &= \frac{1}{4} nv k_B dT - \left(-\frac{1}{4} nv k_B dT \right) \\
 &= \frac{1}{2} nv k_B dT.
 \end{aligned} \quad \text{--- [7]}$$

But, from the definition of thermal conductivity

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

In this case, $dx = \lambda$

$$\therefore K = \frac{Q}{\frac{dT}{\lambda}} \quad \text{--- [8]}$$

Hence, substituting for Q from equation (7) in equation (8), we get

$$\begin{aligned}
 K &= \frac{\left(\frac{1}{2} \right) nv k_B dT}{\frac{dT}{\lambda}} \\
 \therefore K &= \frac{nv k_B \lambda}{2}
 \end{aligned} \quad \text{--- [9]}$$

The value of K obtained with the above expression is verified experimentally and the free electron theory is found to be successful in explaining the thermal conductivity.

Note : • Thermal resistance : $R_T = \frac{\Delta T}{Q}$. It is defined as the temperature drop per unit heat flow.

Independes on both, the geometry and material. In terms of thermal conductivity, $R_T = \frac{l}{KA}$ where l is the length of the sample and A is the cross sectional area

7.8 Wiedemann-Franz Law

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

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

$$\text{or } \frac{K}{\sigma} = LT$$

where L is a constant called the Lorentz number. Its value is $2.44 \times 10^{-8} \text{ W}\Omega\text{K}^{-2}$.

Derivation

The electrical conductivity from equation (11) is [From section 7.6]

$$\sigma = \frac{ne^2\lambda v}{3k_B T}$$

The thermal conductivity from equation (9) is

$$K = \frac{nvk_B\lambda}{2} \quad [\text{From section 7.7}]$$

$$\therefore \frac{K}{\sigma} = \frac{\frac{nvk_B\lambda}{2}}{\frac{ne^2\lambda v}{3k_B T}} = \frac{nvk_B\lambda \cdot 3k_B T}{2ne^2\lambda v} = \frac{3}{2} \frac{k_B^2}{e^2} T$$

$$\therefore \frac{K}{\sigma} = \frac{3}{2} \left(\frac{k_B}{e} \right)^2 T = L T, \text{ where } L = \frac{3}{2} \left(\frac{k_B}{e} \right)^2.$$

Thus, Wiedemann-Franz law is obtained.

$$L = \frac{3}{2} \left(\frac{k_B}{e} \right)^2 = 1.12 \times 10^{-8} \text{ W}\Omega\text{K}^{-2} \text{ is known as the Lorentz number.}$$

The above value of Lorentz number obtained based on classical concept does not agree with the experimental value. Hence, the assumption that all the free electrons of a metal participate in thermal conductivity is not correct.

The actual experimental value of the Lorentz number is $2.44 \times 10^{-8} W\Omega K^{-2}$.

Thus, there is a discrepancy in the value of L between classical theory and the experimental value. This discrepancy gets eliminated on applying quantum theory.

7.9 Success of Free Electron Theory

1. It verifies ohm's law.
2. It explains the thermal and electrical conductivities of metals.
3. It is used to deduce Wiedemann-Franz law.
4. It explains the optical properties of metals.

7.10 Drawbacks of Classical Free Electron Theory

1. The theoretical value obtained for specific heat and electronic specific heat of metals based on this theory is not in agreement with the experimental value.
2. The classical free electron theory is not able to explain the electrical conductivity of semiconductors and insulators.
3. According to classical theory, $\frac{K}{\sigma T}$ is constant at all temperatures. But, this is not constant at low temperature.
4. The theoretical value of paramagnetic susceptibility χ is greater than the experimental value and ferromagnetism cannot be explained.
5. The phenomena such as photoelectric effect, compton effect and black body radiation could not be explained by this theory.

Quantum free electron theory of metals:

Advantages:

1. All the electrons are not present in the ground state at 0 K, but the distribution obeys Pauli's exclusion principle. At 0 K, the highest energy level filled is called Fermi-level.
2. The potential remains constant throughout the lattice.
3. Collision of electrons with positive ion cores or other free electrons is independent of charges and is elastic in nature.
4. Energy levels are discrete.
5. It was successful to explain not only conductivity, but also thermionic emission paramagnetism, specific heat.

Drawbacks:

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1. It fails to explain classification of solids as conductors, semiconductors and insulators.

Bloch Theorem:

According to free electron model, a conduction electron in metal experiences constant potential. But in real crystal, there exists a periodic arrangement of positively charged ions through which the electrons move. As a consequence, the potential experienced by electrons is not constant but it varies with the periodicity of the lattice. In zone theory, as per Bloch, potential energy of electrons considered as varying potential with respect to lattice 'a'.

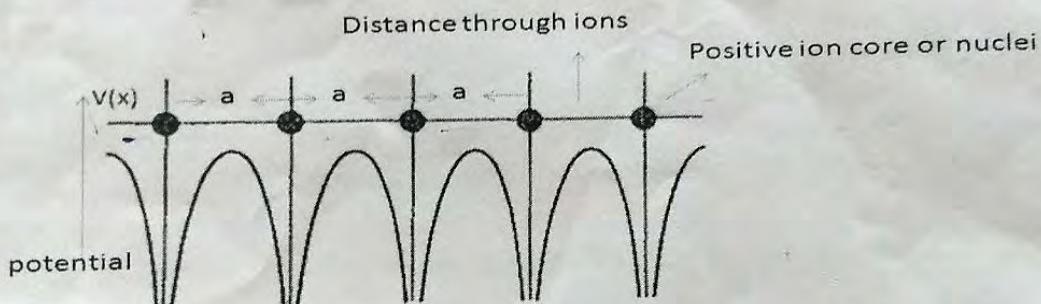


Fig: Variation of potential energy in a periodic lattice.

Let us examine one dimensional lattice as shown in figure. It consists of array of ionic cores along X-axis. A plot of potential V as a function of its position is shown in figure.

From graph:

At nuclei or positive ion cores, the potential energy of electron is minimum and in-between nuclei, the P.E. is considered as maximum w.r.to. Lattice constant 'a'.

This periodic potential $V(x)$ changes with the help of lattice constant a ,

$$V(x) = V(x + a) \quad ('a' \text{ is the periodicity of the lattice})$$

To solve, by considering Schrodinger's time independent wave equation in one dimension,

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2} [E - V(x)]\psi = 0 \dots \dots \quad (1)$$

Bloch's 1D solution for Schrodinger wave equation (1) $\psi_k(x) = u_k(x)\exp(ikx) \dots \dots \dots \quad (2)$

where $u_k(x) = u_k(x + a)$

Here $u_k(x)$ -periodicity of crystal lattice, modulating function, k - propagation vector $= \frac{2\pi}{\lambda}$
 e^{ikx} is plane wave.

By applying eq.n (2) to eq.n (1), it is not easy to solve Schrodinger wave equation and Bloch cannot explains complete physical information about an e^- in periodic potential field. Then Kronig Penny model was adopted to explains the electrical properties of an e^- .

14-1 Free Electron Theory

In solid-state electronics, the free electron theory is a simple model for the behaviour of valence electrons in a crystal structure of a metallic solid. The free electron theory was proposed by Drude and Lorentz on the basis of Maxwell-Boltzmann classical statistics. This theory tells that metals conduct electricity because of the presence of free electrons in it. The outermost shells of metal atoms are loosely bound with their nucleus. So the electrons in them are free to move anywhere in the solid. These electrons are called free electrons and the forces between them and ion cores are negligible. This theory forms the basis of a simple explanation of many properties of metals including the characteristic electrical and thermal conductivities.

This theory can explain the following physical properties of metals:

- (i) Metallic conductors obey Ohm's law according to which the current density J is proportional to the electric field strength E , i.e.

$$J \propto E \quad \text{i.e.} \quad J = \sigma E$$

Here σ is the electrical conductivity.

- (ii) The metals have a positive temperature coefficient, i.e. their resistance increases or conductivity decreases with rise of temperature.
- (iii) For pure metals, electrical conductivity ρ is inversely proportional to absolute temperature T , i.e.

$$\sigma \propto \frac{1}{T}$$

But for impure metals, electrical conductivity is inversely proportional to the square root of absolute temperature T .

- (iv) At low temperatures, the resistivity ρ is proportional to fifth power of absolute temperature T , i.e.

$$\rho \propto T^5$$

(v) For most metals, the resistivity ρ is inversely proportional to pressure P , i.e.

$$\rho \propto \frac{1}{P}$$

(vi) Metals obey Wiedmann–Franz law according to which the ratio of thermal conductivity σ_T to electrical conductivity σ is proportional to absolute temperature T , i.e.

$$\frac{\sigma_T}{\sigma} \propto T \quad \text{i.e.} \quad \frac{\sigma_T}{\sigma T} = \text{constant}$$

Limitations of free electron theory

This theory assumes that a conduction electron in a metal experiences a constant (zero) potential due to iron cores and so completely free to move in the entire metal like the gas molecules in the available volume. But, in practice, the electrons interact with the lattice and each other. Hence, the potential due to ion cores is not constant and may change with the position of electron in the metal. The actual nature of potential under which electron moves in a metal is more complicated. A more reasonable approximation of the potential experienced by an electron passing through a crystal is one which is perfectly periodic with period equal to the lattice constant for a one-dimensional case. Due to its limitations, the free electron model was unable to account for many physical phenomena. The shortcomings of free electron theory are listed below.

- (i) The temperature dependence of resistivity could not be established accurately by this theory.
- (ii) This theory failed to explain the heat capacity and paramagnetic susceptibility of free electrons.
- (iii) This theory is also unable to explain large variations in mean free paths at low temperatures.
- (iv) Since electrons are Fermi particles so Maxwell–Boltzmann classical statistics cannot be applied to free electrons in a metal.
- (v) According to this theory, law of equi-partition of energy can be applied to free electrons of metals. But experiments show that law of equi-partition of energy cannot be applied to free electrons of metals.

14-2 Classification of Solids on the Basis of Free Electron Theory

The electrical resistance of an electrical or electronic component or device is generally defined as being the ratio of the voltage difference across it to the current flowing through it (Ohm's law). The problem with using resistance as a measurement is that it depends very much on the physical size of the material being measured as well as the material out of which it is made. For example, if we were to increase the length of the material (making it longer), its resistance would also increase. Likewise, if we increase its diameter (making it fatter), its resistance would then decrease. So we want to be able to define the material in such a way as to indicate its ability to either conduct or oppose the flow of electrical current through it.

The quantity that is used to indicate this is called resistivity and is generally given by the Greek symbol ρ (rho), measured in Ohms per metre (Ω/m). If the resistivity of various materials is compared, they can be classified into three main groups—conductors, insulators and semi-conductors—as shown in Figure 14.1.

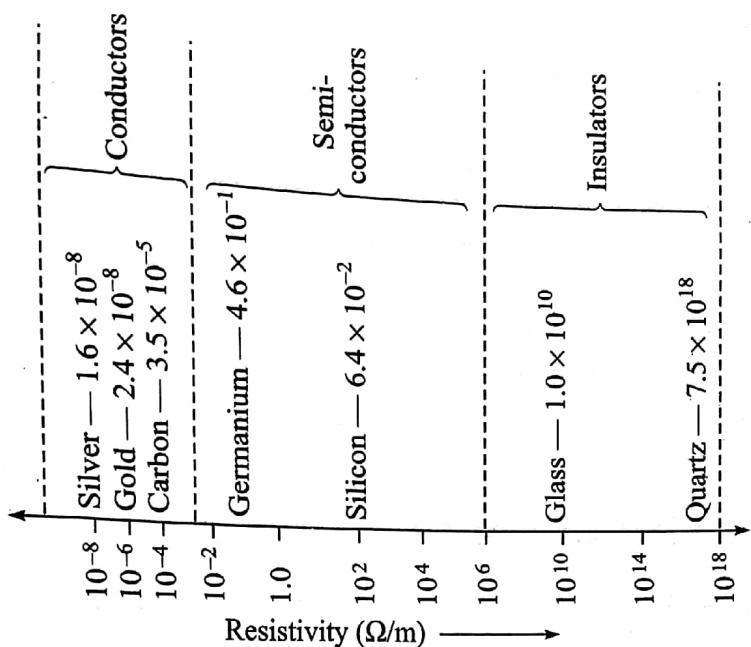


Figure 14.1 Classification of solids on the basis of free electron theory.

Conductors

From Figure 14.1, we conclude that conductors are materials that have a low value of resistivity allowing them to easily pass an electrical current due to there being plenty of free electrons floating about within their basic atom structure. When a positive voltage potential is applied to the material these free electrons leave their parent atom and travel together through the material forming an electron or current flow. Examples of good conductors are generally metals such as copper, aluminium, silver or non-metals such as carbon because these materials have very few electrons in their outer valence shell or ring, which can be easily knocked out of the atom's orbit. This allows them to flow freely through the material; thereby creating an electrical current.

Generally speaking, most metals are good conductors of electricity, as they have very small resistance values, usually in the region of micro-ohms per metre with the resistivity of conductors increasing with temperature because metals are also generally good conductors of heat.

Insulators

Insulators, on the other hand, are the exact opposites of conductors. They are made of materials, generally non-metals, that have very few or no free electrons floating about within their basic atom structure because the electrons in the outer valence shell are strongly attracted by the positively charged inner nucleus. So if a potential voltage is applied to the material, no current will flow as there are no electrons to move and which gives these materials their insulating properties. Insulators also have very high resistances, millions of ohms per metre, and are generally not affected by normal temperature changes (although at very high

temperatures wood becomes charcoal and changes from being an insulator into a conductor). Examples of good insulators are marble, fused quartz, PVC, plastics, rubber, etc.

Semiconductors

From Figure 14.1 we see that semiconductor materials such as silicon and germanium have electrical properties somewhere in the middle, between those of a conductor and an insulator. They are neither good conductors nor good insulators (hence their name semiconductors). They have very few free electrons because their atoms are closely grouped together in a crystalline pattern called a crystal lattice. However, their ability to conduct electricity can be greatly improved by adding certain impurities to this crystalline structure, thereby producing more free electrons than holes or vice versa. By controlling the amount of impurities added to the semiconductor material, it is possible to control its conductivity. This process of adding impurity atoms to semiconductor atoms (the order of 1 impurity atom per 10 million (or more) atoms of the semiconductor) is called doping.

14-3 Band Theory of Solids

The free electron theory of metals assumes that a free electron in a metal experiences a constant (zero) potential due to iron cores and so completely free to move about in the metal, restrained only by the metallic surface. In fact, the potential due to iron cores is not constant and may change with the position of electrons in metal. The actual nature of potential under which an electron moves in a metal is very complicated. A more reasonable approximation of the potential experienced by an electron in passing through a metal is one which is perfectly periodic with the period equal to the lattice constant for one-dimensional cases as shown in Figure 14.2.

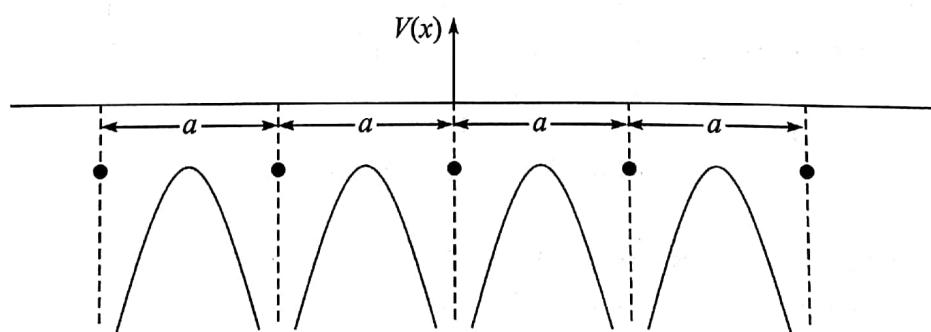


Figure 14.2 Bond theory of solids.

14-4 Kronig–Penney Model

The Kronig–Penney model is a simplified model for an electron in a one-dimensional periodic potential. It explains the behaviour of an electron in a periodic potential. This model assumes that the potential energy of an electron in a linear array of positive nuclei has the form of a periodic square well potential of period ($a + b$) such that in the region $0 < x < a$, the

potential energy is equal to zero and in the region $b < x < 0$, the potential energy is V_0 , i.e.

$$V(x) = \begin{cases} 0 & \text{for } 0 < x < a \\ V_0 & \text{for } -b < x < 0 \end{cases} \quad (14.1)$$

The possible states that the electron can occupy in such a square well potential can be determined by one-dimensional Schrödinger equation

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} [E - V(x)] \psi = 0 \quad (14.2)$$

Here m is the mass of electron.

To obtain the meaningful results, we solve above Eq. (14.2) in the two regions I and II as shown in Figure 14.3. Equation (14.2) for the two regions I and II takes the form

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2} \psi = 0 \quad [\text{for region } 0 < x < a] \quad (14.3)$$

and

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} [E - V_0] \psi = 0 \quad [\text{for region } b < x < 0] \quad (14.4)$$

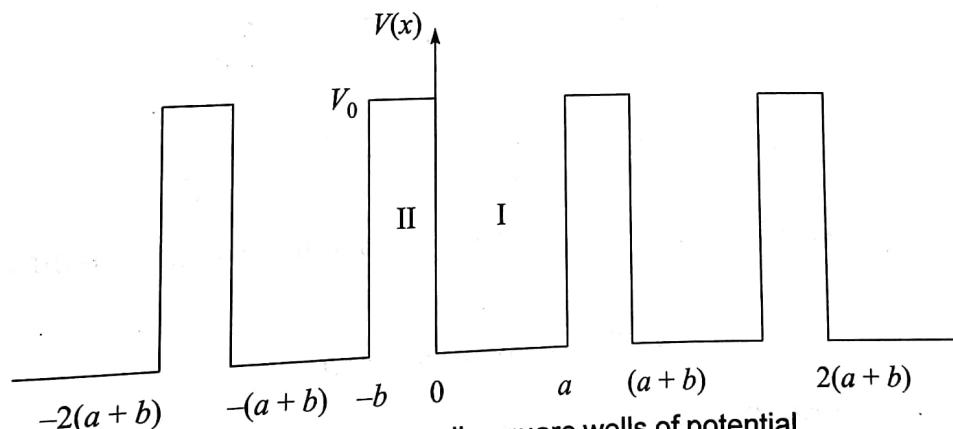


Figure 14.3 Periodic square wells of potential.

Now we define two real quantities α and β such that

$$\alpha^2 = \frac{2mE}{\hbar^2}$$

$$\beta^2 = \frac{2m}{\hbar^2} [V_0 - E]$$

and

[Here we assume that $E < V_0$]



Ralph Kronig
(1904–1995)

Kronig was a German-American physicist. He is noted for the discovery of particle spin and for his theory of x-ray absorption spectroscopy. He proposed Kronig–Penney model, which shows how the electrons in a crystal are dispersed into allowed and forbidden bands by scattering from the extended linear array of atoms.

Then Eqs. (14.3) and (14.4) become

$$\frac{d^2\psi}{dx^2} + \alpha^2\psi = 0 \quad [\text{for region } 0 < x < a] \quad (14.5)$$

and

$$\frac{d^2\psi}{dx^2} - \beta^2\psi = 0 \quad [\text{for region } b < x < 0] \quad (14.6)$$

Since $\psi(x)$ is the periodic function, it can be expressed as

$$\psi(x) = \exp(ikx)\varphi(x)$$

If φ_1 and φ_2 are the values of $\varphi(x)$ in the two regions I and II, then Eqs. (14.5) and (14.6) take the form

$$\frac{d^2\varphi_1}{dx^2} + 2ik \frac{d\varphi_1}{dx} + (\alpha^2 - k^2)\varphi_1 = 0 \quad (14.7)$$

and

$$\frac{d^2\varphi_2}{dx^2} + 2ik \frac{d\varphi_2}{dx} + (\beta^2 + k^2)\varphi_2 = 0 \quad (14.8)$$

The general solutions of Eqs. (14.7) and (14.8) are

$$\varphi_1 = A \exp[i(\alpha - k)x] + B \exp[-i(\alpha + k)x] \quad (14.9)$$

and

$$\varphi_2 = C \exp[(\beta - ik)x] + D \exp[-(\beta + ik)x] \quad (14.10)$$

Here A, B, C and D are constants to be determined by the following conditions:

$$(\varphi_1)_{x=0} = (\varphi_2)_{x=0}; \left(\frac{d\varphi_1}{dx} \right)_{x=0} = \left(\frac{d\varphi_2}{dx} \right)_{x=0}$$

and

$$(\varphi_1)_{x=a} = (\varphi_2)_{x=-b}; \left(\frac{d\varphi_1}{dx} \right)_{x=a} = \left(\frac{d\varphi_2}{dx} \right)_{x=-b}$$

Applying these conditions in Eqs. (14.9) and (14.10) and solving, we get a significant expression in the form

$$\gamma \frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos ka \quad (14.11)$$

Here quantity γ is defined as

$$\gamma = \frac{mV_0ab}{\hbar^2} \quad (14.12)$$

The solution of Eq. (14.11) for finite values of quantity γ results in an alteration of energy for real and imaginary values of k . The plot of L.H.S. of Eq. (14.11) is shown in Figure 14.4.

This curve shows that:

- (i) The energy spectrum of electrons consists of a number of allowed energy bands separated by forbidden energy bands.
- (ii) The width of the allowed energy bands increases with increase in value of α , i.e. with increase in lattice parameter a .

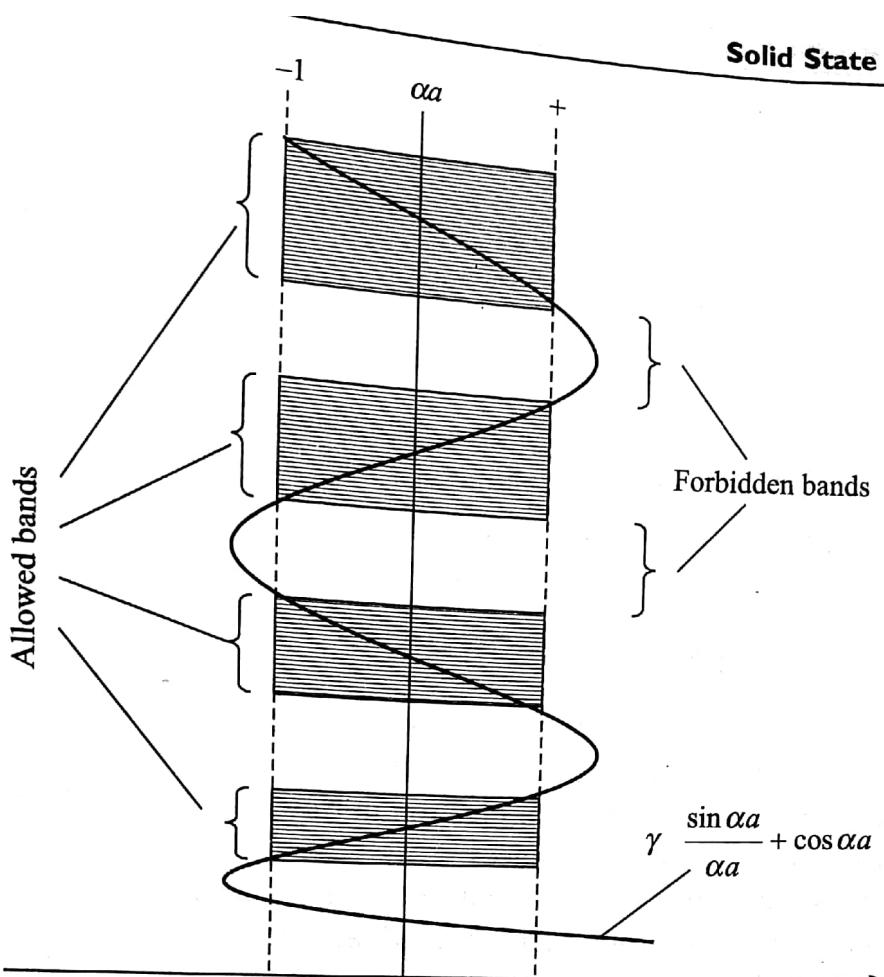


Figure 14.4 Plot of L.H.S. of Eq. (14.11) as a function of αa .

Now let us consider two important cases:

Case (i): When $\gamma \rightarrow \infty$, then Eq. (14.12) has a solution only if

$$\sin \alpha a = 0$$

or $\sin \alpha a = \sin n\pi$ [here n is an integer]

or $\alpha a = n\pi$

or $\alpha^2 a^2 = n^2 \pi^2$

or $\frac{2mE}{\hbar^2} a^2 = n^2 \pi^2$ [since $\alpha^2 = \frac{2mE}{\hbar^2}$]

or $E = E_n \text{ (say)} = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$

This expression represents the energy levels of a particle in one-dimensional box of atomic dimension. This is an expected result, since for large values of γ ; the electrons cannot tunnel through the potential barrier.

Case (ii): When $\gamma \rightarrow 0$, then Eq. (14.11) reduces to

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

or $\alpha a = ka$

or $\alpha^2 = k^2$

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

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

This expression represents the energy of a completely free particle. In this case, the allowed energy bands of electrons are continuous. This is also an expected result which agrees with the free electron theory.

14-5 Effective Mass of Electron

When an electron is moving inside a solid material, the force between other atoms will affect its movement and it will not be described by Newton's law. So we introduce the concept of effective mass to describe the movement of electron in Newton's law. The effective mass can be negative or different due to circumstances.

Let us consider an electron inside a crystal in a state k with the electronic wave function $\exp(ik)$. For a wave packet the group velocity is given by

$$v = \frac{d\omega}{dk} = \frac{1}{\hbar} \frac{d(\hbar\omega)}{dk} = \frac{1}{\hbar} \frac{dE}{dk} \quad (14.13)$$

In presence of an electric field ξ , the force experienced by the electron is

$$F = \frac{dp}{dt} = m \frac{dv}{dt}$$

Here p is the electron's momentum.

Now since $p = \hbar k$, so we can say that

$$\hbar \frac{dk}{dt} = m \frac{dv}{dt}$$

or $\frac{\hbar}{m} \frac{dk}{dt} = \frac{dv}{dt} \quad (14.14)$

Substituting the value of v from Eq. (14.13) to Eq. (14.14), we get

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

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

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

or

$$\frac{1}{m} = \frac{1}{\hbar^2} \frac{d^2 E}{dk^2}$$

Replacing m by m^* in above equation, we get

$$m^* = \frac{\hbar^2}{\frac{d^2 E}{dk^2}}$$

This is the expression for the effective mass of electron.

Significance of effective mass of electron

Effective mass of electron has a special importance in solid state electronics because the results of free electron theory can be applied in band theory of solids by replacing the rest mass m of electron by effective mass of electron. The effective mass is used in transport calculations, such as transport of electrons under the influence of fields or carrier gradients in different semiconductors. It is also used to calculate the density of states.

9.4 Fermi Distribution Function

The fermi distribution function, also called the fermi function gives the probability of occupancy of energy levels by fermions in terms of fermi energy, temperature and Boltzmann constant.

Fermions are half integer spin particles like electrons which obey pauli exclusion principle.

Consider a system of electrons in thermal equilibrium at a temperature T_K . The probability $f(E)$ of an electron occupying a particular energy level (state) E is given by

$$f(E) = \frac{1}{1 + \left(\frac{E - E_F}{e^{k_B T}} \right)} \quad \text{--- [1]}$$

where

$f(E)$ is the fermi function.

E_F is the fermi energy (also called fermi level)

k_B is the Boltzmann constant

and,

T is the absolute temperature.

Thus, a system is characterised by its temperature and its fermi energy E_F .

For a filled energy level, $f(E) = 1$ and for an unfilled level $f(E) = 0$.

The dependence of fermi function under different conditions of temperature and the effect on occupancy of energy levels are as follows.

Case 1:

At $T = 0K$

At absolute zero temperature, the electrons occupy the lowest energy level first, followed by the next higher ones as per Pauli's exclusion principle. i.e., A pair of electrons, one with spin up and the other with spin down occupy the lowest level. The next pair of electrons occupy the next higher level and so on, till all the electrons of the metal are accomadated as shown in figure 9.4.

The uppermost filled energy level is referred as fermi level and the energy of the electrons in the fermi level at absolute zero degree is called the fermi energy.

Thus, at a temperature of absolute zero, all the energy levels lying above the fermi level are empty and those lying below are completely filled. Hence, fermi level helps to distinguish between an occupied and an unoccupied state. Since there are two electrons in each energy level, out of the N allowed

energy levels, $\frac{N}{2}$ of them will be occupied.

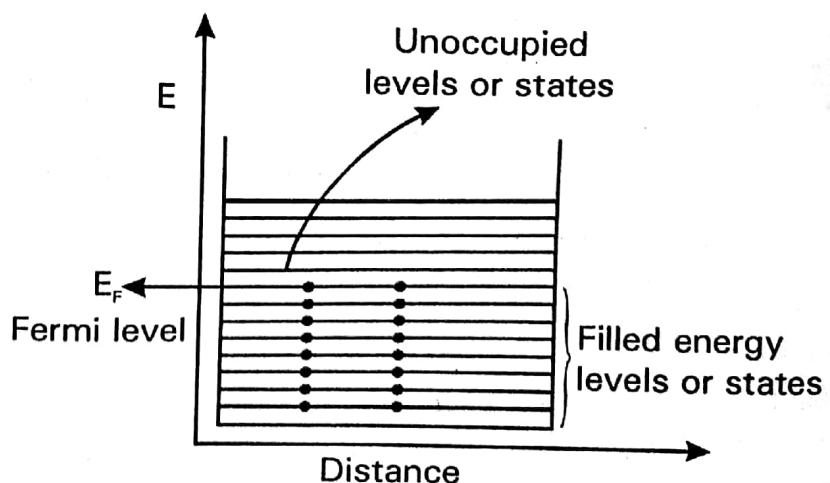


Figure 9.4 : Distribution of electrons in a band.
Electrons occupy all the levels below E_F

Special cases :- Probability of occupation

(a) At $T = 0K$ for $E < E_F$

For energy levels E lying below E_F , the term $(E - E_F)$ takes a negative value. Hence, the argument $\left(\frac{E - E_F}{k_B T}\right)$ in the exponential function becomes $-\infty$. Therefore,

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

$\therefore f(E) = 1$ implies that, all the energy levels below E_F are occupied by electrons.

(b) At $T = 0K$ for $E > E_F$

For energy levels above E_F , the term $(E - E_F)$ takes a positive value. Hence, the argument

$\left(\frac{E - E_F}{k_B T}\right)$ in the exponential function becomes ∞ . Therefore,

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

$\therefore f(E) = 0$ implies that, all the energy levels above E_F are vacant, i.e., there is no chance of an electron occupying an energy level above E_F .

Thus, the variation of $f(E)$ at $T = 0K$ for different energy values takes a step function as shown in figure 9.5.

Case 2 :

Probability of occupation at $T > 0K$

At ordinary temperature (room temperature) the value of probability starts reducing from 1 for values of E close to but larger than E_F .

At $T > 0K$ for $E = E_F$, the argument in the exponential function becomes zero.

$$\therefore f(E) = \frac{1}{1 + e^0} = \frac{1}{1 + 1} = \frac{1}{2} = 0.5 \quad [\because e^0 = 1]$$

Thus $f(E) = \frac{1}{2}$ implies that, the probability of occupancy of an electron is 50% at any temperature above 0K. Further for $E > E_F$, the $f(E)$ value falls off to zero rapidly as shown in figure 9.5.

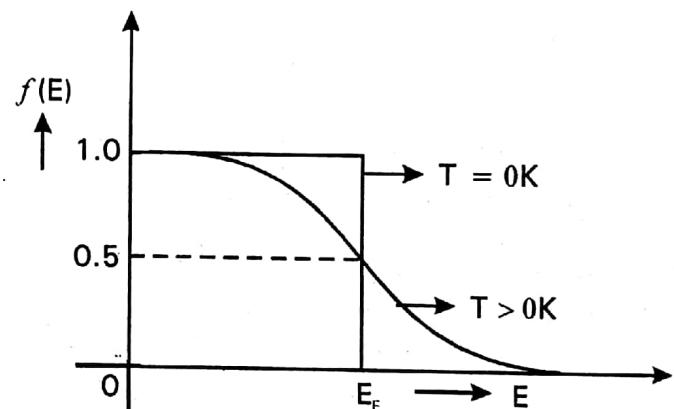


Figure 9.5 : Fermi function at 0K

Case 3 :

Probability of occupation at very high temperatures

At very high temperatures it is observed that, the transition between completely filled states and completely empty states is gradual rather than abrupt, i.e., $f(E)$ changes from 1 to 0 more and more gradually. Hence, as temperature increases an electron may get energy of the order of $k_B T$ and go to higher vacant state. As a result, fermi function falls. But, for energies below E_F , such that $(E_F - E) \gg k_B T$ the value of $f(E)$ will be unity i.e., only in the region of E_F , $f(E)$ begins to fall as shown in figure 9.6.

Note : • The relation between fermi energy E_F , fermi velocity v_F and fermi temperature T_F is

$$v_F = \sqrt{\frac{2E_F}{m}} \quad \text{and} \quad T_F = \frac{E_F}{k_B}$$

- The probability of an electron definitely occupying an energy state is given by $f(E) = 1$.
- The probability of an electron not occupying an energy state i.e., the unoccupancy of an energy state is given by $1 - f(E)$.

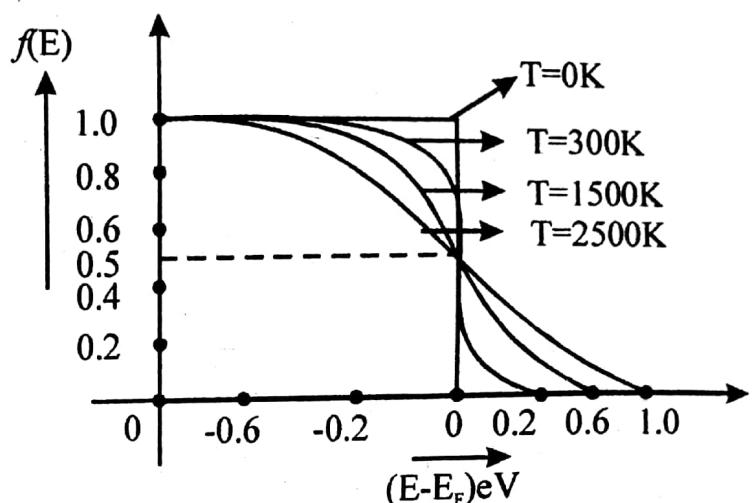


Figure 9.6 : The Fermi function at very high temperatures

9.5 Density of States

The fermi function gives us only the probability of occupation of an energy state by an electron. But, it does not give the actual number of electrons with a given energy.

Hence, to know the actual number of electrons with a given energy, the number of available energy states in the system with a particular energy has to be determined first. Then, by multiplying the number of energy states by the probability occupation we get the actual number of electrons.

If $Z'(E)dE$ is the number of available states and $f(E)$ the probability of occupation of any given energy state by the electron; then, the number of electrons $N(E)$ in a system with energy dE is given by

$$N(E)dE = Z'(E)dE f(E) \quad \text{---- [1]}$$

Derivation to determine the number of available of energy states

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

To find $Z'(E)dE$

We know that, the equation for the energy of a particle in 3d potential well is given by

$$E = \frac{h^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2) \quad [2]$$

where n_x , n_y and n_z are positive integers and m is the mass of the electron.

$$\text{Let us take } n_x^2 + n_y^2 + n_z^2 = n^2 \quad [3]$$

\therefore Equation (2) becomes,

$$E = \frac{h^2}{8ma^2} n^2 \quad [4]$$

The allowed energy states are governed by the values of n_x , n_y and n_z . For a single set of n_x , n_y and n_z we get one energy value as per equation (2).

Since, equation $n^2 = n_x^2 + n_y^2 + n_z^2$ represents a sphere, and if we take n_x , n_y and n_z along three mutually perpendicular axes of a co-ordinate system then, each set of such values can be represented as a point in the system. Hence, for a very large number of such set of values we get a spherical distribution of points.

Therefore, to know the actual number of energy states with all possible energies a sphere of radius n is constructed. Thus, every point within this sphere represents an energy state, i.e., a unit volume of this sphere contains exactly one state. Also, since the values of n_x , n_y and n_z are restricted to be positive; only one octant [i.e., (1/8)] of the sphere is available. Therefore,

$$\frac{\text{The number of allowed energy states in any volume}}{\text{Numerical value of volume of one octant of the sphere of a definite radius}} = \frac{1}{8} \cdot \frac{4\pi n^3}{3} \quad [5]$$

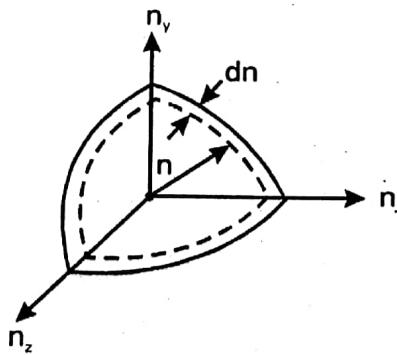


Figure 9.7: An octant of a sphere

Hence, in order to calculate the number of energy states with small energy dE , we construct two spheres, one with radii n and the other with radii $n + dn$ with energies E and $E + dE$ respectively. Within the sphere and octant is considered as shown in figure 9.7.

Therefore, the number of available states with sphere of radius n is $\frac{1}{8} \times \frac{4\pi}{3} n^3$

Applying equation (5)

$$= \frac{1}{6} \pi n^3 \quad [6]$$

Similarly, the number of available states with sphere of radius $(n + dn)$ is $\frac{1}{8} \times \frac{4}{3} \pi(n + dn)^3$

$$= \frac{1}{6} \pi(n + dn)^3$$

---- [7]

Thus, the number of allowed energy states in an energy range E and $E + dE$ (i.e., in the energy interval dE) is

$$\begin{aligned} Z'(E)dE &= \frac{1}{6}\pi(n + dn)^3 - \frac{1}{6}\pi n^3 \\ &= \frac{\pi}{6} (n^3 + dn^3 + 3n^2dn + 3dn^2n - n^3) \end{aligned}$$

[Neglecting higher power of dn and on simplification]

$$Z'(E)dE = \frac{\pi}{6} [3n^2dn] \quad ---- [8]$$

$$Z'(E)dE = \frac{\pi}{2} n^2dn$$

$$\text{or} \quad Z'(E)dE = \frac{\pi}{2} n(ndn) \quad ---- [9]$$

From equation (4)

$$\begin{aligned} E &= \frac{n^2 h^2}{8m\alpha^2} \\ n^2 &= \frac{8m\alpha^2 E}{h^2} \end{aligned} \quad ---- [10]$$

$$\text{Therefore, } n = \left(\frac{8m\alpha^2}{h^2} E \right)^{\frac{1}{2}} \quad ---- [11]$$

On differentiating equation (10) we get,

$$\begin{aligned} 2ndn &= \frac{8m\alpha^2}{h^2} dE \\ \therefore ndn &= \frac{8m\alpha^2}{2h^2} dE \end{aligned} \quad ---- [12]$$

substituting equation (11) and (12) in equation (9)

$$\begin{aligned} Z'(E)dE &= \frac{\pi}{2} \left(\frac{8m\alpha^2 E}{h^2} \right)^{\frac{1}{2}} \frac{8m\alpha^2}{2h^2} dE \\ \text{or} \quad Z'(E)dE &= \frac{\pi}{4} \left(\frac{8m\alpha^2}{h^2} \right)^{\frac{3}{2}} E^{\frac{1}{2}} dE \end{aligned} \quad ---- [13]$$

According to Pauli's exclusion principle, since there can be two electrons, one with spin up and the other with spin down in a single energy state, The actual number of available energy states is

$$Z'(E)dE = 2 \times \frac{\pi}{4} \left(\frac{8ma^2}{h^2} \right)^{3/2} E^{1/2} dE$$

$$Z'(E)dE = \frac{\pi}{2} \left(\frac{8ma^2}{h^2} \right)^{3/2} E^{1/2} dE \quad ---- [14]$$

$$\text{or} \quad Z'(E)dE = \frac{4\pi}{h^3} (2m)^{3/2} E^{1/2} dE \quad ---- [15]$$

Therefore, the density of states i.e., the number of energy states per unit volume with energy interval dE is

$$Z(E) dE = \frac{Z'(E)dE}{\text{Volume}} = \frac{\frac{\pi}{2} \left(\frac{8m}{h^2} \right)^{3/2} a^3 E^{1/2} dE}{a^3}$$

$$\text{or} \quad Z(E) dE = \frac{\pi}{2} \left(\frac{8m}{h^2} \right)^{3/2} E^{1/2} dE. \quad ---- [16]$$

Equation (16) is the expression for density of states, in a 3d solid of unit volume.

2.21 Direct and Indirect band gap semiconductor

The picture of the electronic energy levels in a crystal is known as the energy band model of the crystal. The lowest point in the conduction band is called the conduction band edge. The highest point in the valence band is called valence band edge. The band gap is the difference in energy between the lowest point of the conduction band and the highest point of the valence band.

The ratio of the band gap ' E_g ' to the temperature T , $E_g/K_B T$ controls the intrinsic conductivity and intrinsic carrier concentrations. The best values of the band gap are obtained by optical absorption process. The band gap $E_g = \hbar\omega_g$ is determined by the threshold of continuous optical absorption at frequency ω_g .

In the direct band gap semiconductor the lowest point of conduction band occurs at the same value of 'k' as the highest point of valence band. That is, at $k = 0$, the valence band edge and the conduction band edge lie on the same vertical line as shown in the figure (2.19 a). Hence in the direct absorption process a photon is absorbed by the crystal with the creation of electron and hole pair. When the electron in the valence band edge absorbs a photon of energy $\hbar\omega_g$ it goes to the conduction band.

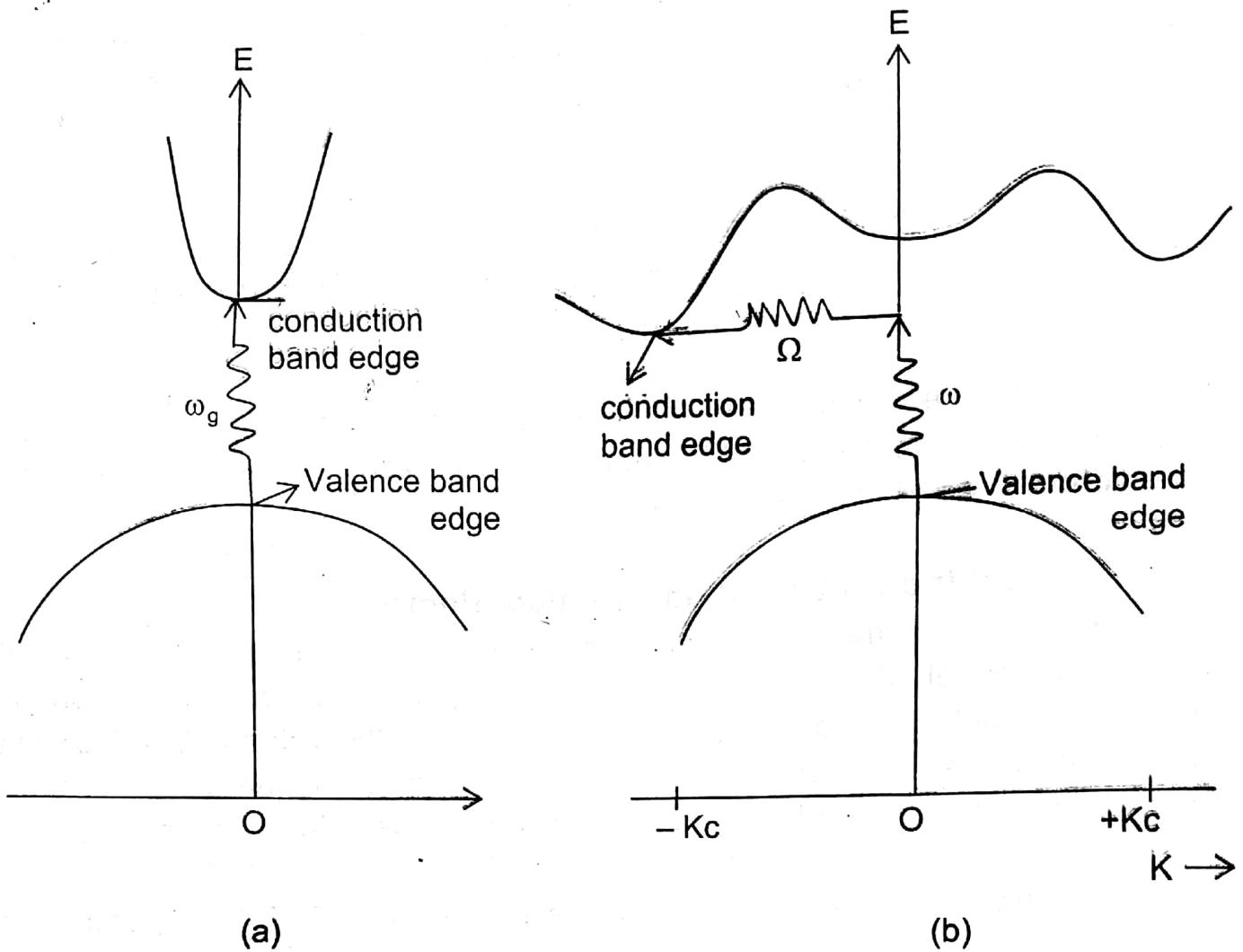


Figure (2.19) (a) **Direct band gap semiconductor**
(b) **Indirect band gap semiconductor**

In the indirect band gap semiconductor, the valence band edge and the conduction band edge are not lie on the same vertical line at $k = 0$. The conduction band edge and the valence band edge have different k values as shown in the figure (2.19 b)

In the indirect absorption process, the minimum energy gap of the band structure involves electrons and holes separated by wave vector k_c . Here a photon of wave vector k and frequency Ω is created for the conservation of wave vector. Thus, $k(\text{photon}) = k_c + k$ and $\hbar\omega = E_g + \hbar\Omega$. That is, to shift an electron from the valence band edge to the conduction band edge a photon of energy $\hbar\omega_g$ and a phonon of energy $\hbar\Omega$ are required. The band gap may also be deduced from the temperature dependence of conductivity.

14-6 Formation of Energy Bands in Solids

We know that each electronic orbit in an atom has a fixed amount of energy. The electron moving in an orbit has the same energy as that of the orbit. The method of representing the energy of different orbits is known as energy level diagram. The concept of energy level diagram is shown in Figure 14.5. The first orbit represents the first energy levels. The second orbit represents the second energy levels and so on.

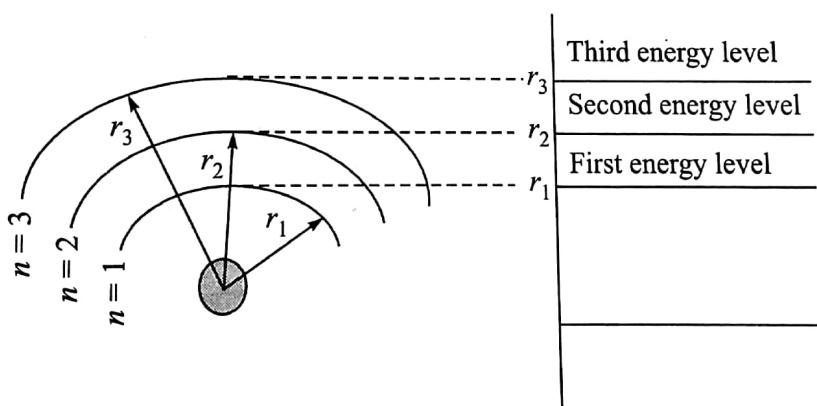


Figure 14.5 Energy level diagram of an atom.

In case of a single isolated atom, the electron in any orbit has definite amount of energy. A solid consists of a large number of atoms. Each atom has interaction effect on the other atom. Due to this effect, the electrons in any orbit have a range of energies. When atoms combine to form substances, the outermost shells, subshells, and orbitals merge, providing a greater number of available energy levels for electrons to assume. When a large number of atoms are close to each other, these available energy levels form a nearly continuous band wherein electrons may move as illustrated in Figure 14.6 for metals.

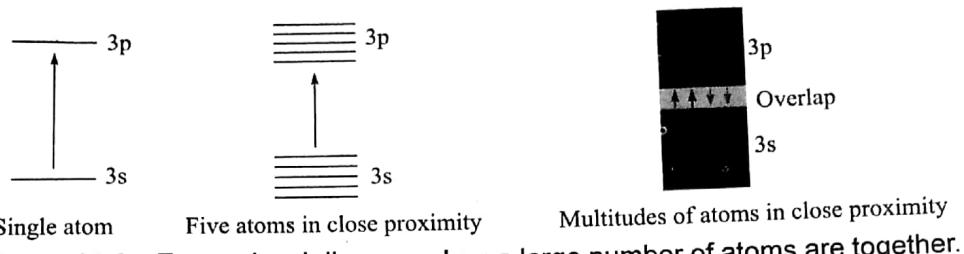


Figure 14.6 Energy level diagram when a large number of atoms are together.

The range of energies possessed by an electron in a solid is known as energy band as shown in Figure 14.7. A useful way to visualize the difference between conductors, insulators and semiconductors is to plot the available energies for electrons in the materials. Instead of having discrete energies as in the case of free atoms, the available energy states form bands. Crucial to the conduction process is whether or not there are electrons in the conduction band. In insulators, the electrons in the valence band are separated by a large gap from the conduction band, in conductors like metals the valence band overlaps the conduction band, and in semiconductors there is a small enough gap between the valence and conduction bands that thermal or other excitations can bridge the gap. With such a small gap, the presence of a small percentage of a doping material can increase conductivity dramatically.

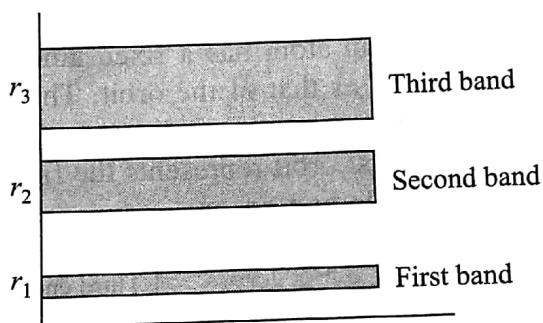


Figure 14.7 Different energy bands.

An important parameter in the band theory is the Fermi level, the top of the available electron energy levels at low temperatures. The position of the Fermi level with relation to the conduction band is a crucial factor in determining electrical properties.

Further, band theory explains distinction between metals and insulators, which free electron theory cannot do (since it assumes all valence electrons become conducting).

Classification of energy bands in solid

These are three important energy bands in solids.

(i) Valence band: The electrons in the outermost orbits are called valence electrons. The range of energies possessed by the valence electron is known as valence band. In a normal atom, valence band has the electrons of highest energy. This band may be completely or partially filled.

(ii) Conduction band: In some solids, the valence electrons are loosely attracted to the nucleus. At room temperature these valence electrons may become free electrons, thus electrons are called conduction electrons. The range of energies possessed by conduction electrons is

known as conduction band. For insulators, this band is completely empty and for conductors this band is partially filled.

(iii) **Forbidden energy gap:** The separation between conduction band and valence band or band to conduction band internal energy equal to forbidden energy gap must be required. The three bands are shown in Figure 14.8.

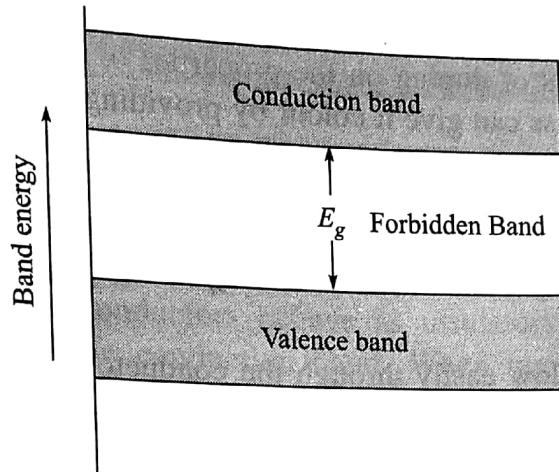


Figure 14.8 Conduction, forbidden and valence bands in solids.

14-7 Classification of Solids on the Basis of Band Theory of Solids

The solids may be divided into the following three main groups:

Insulators

Most solid substances are insulators, and in terms of the band theory of solids this implies that there is a large forbidden gap between the energies of the valence electrons and the energy at which the electrons can move freely through the material (the conduction band). Thus, in the insulators, the valence band is full and conduction band is empty. The forbidden energy gap is very large, i.e. of the order of 6 eV as shown in Figure 14.9

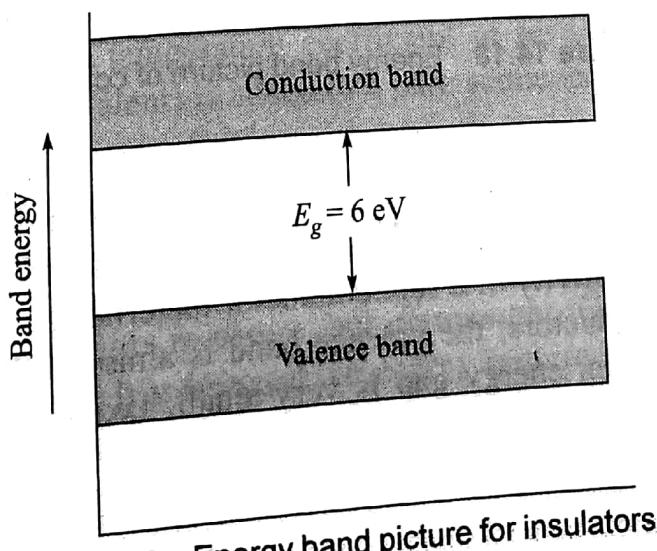


Figure 14.9 Energy band picture for insulators.

At room temperature, the valence electrons of insulator do not have sufficient amount of energy to cross over to the conduction band. When temperature is increased, these electrons gain enough energy and cross the energy gap. Hence the resistance of insulator decreases with increases in temperature. Thus insulator has negative temperature coefficient of resistance.

Glass is an insulating material which may be transparent to visible light for reasons closely correlated with its nature as an electrical insulator. The visible light photons do not have enough quantum energy to bridge the band gap and get the electrons up to an available energy level in the conduction band. The property of transparency of glass can also give some insight into the effects of doping on the properties of solids. A very small percentage of impurity atoms in the glass can give it colour by providing specific available energy levels which absorb certain colours of visible light. The ruby mineral (corundum) is aluminium oxide with a small amount (about 0.05%) of chromium which gives it its characteristic pink or red colour by absorbing green and blue light.

Conductors

We know that current can flow easily through the conductors because it has free electrons. In terms of the band theory of solids, metals are unique as good conductors of electricity. This can be seen to be a result of their valence electrons being essentially free. In the band theory, this is depicted as an overlap of the valence band and the conduction band so that at least a fraction of the valence electrons can move through the material. In conductors, valance band and conduction band overlap each other as shown in Figure 14.10. Copper, aluminium, gold, and silver are a few examples of good conductors.

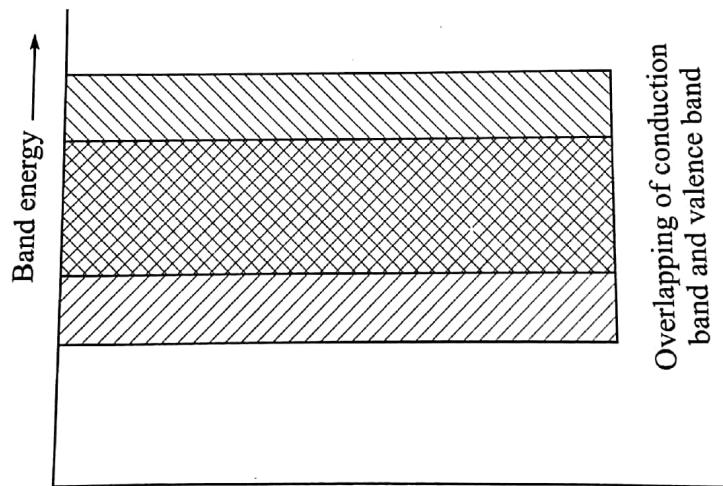


Figure 14.10 Energy band picture of conductors.

Semiconductors

A semiconductor is a material that has electrical conductivity between those of a conductor and an insulator. The conductivity of a semiconductor material can be varied under an external electrical field. In semiconductors, the valence band is almost filled and conduction band is almost empty. The forbidden energy gap is very small, i.e. of the order of 0.5 to 1 eV as shown in Figure 14.11.

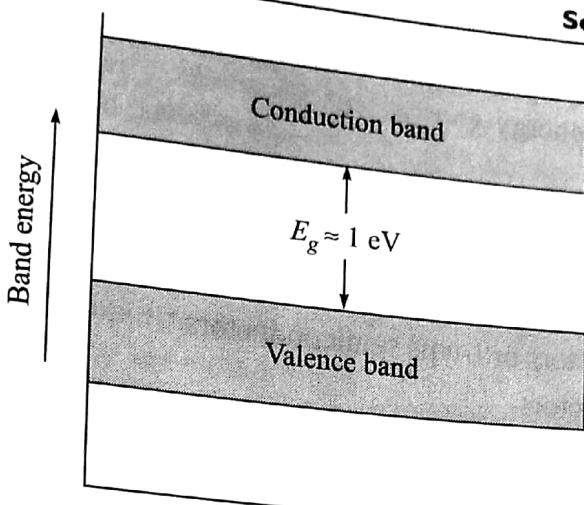


Figure 14.11 Energy band picture of semiconductors.

At low temperature, semiconductors behave as insulators. But at room temperature some electrons cross over the conduction band. When temperature is increased more valence electrons cross over to the conduction band. This increases the conductivity of the substance. This indicates that electrical conductivity of a semiconductor increases with the increase in temperature. Thus the semiconductor has negative temperature coefficient of resistance.

14-8 Significance and Important Properties of Semiconductors

Semiconductors form the heart of modern electronics. Devices made from semiconductor materials are the basic elements of modern electronics, including radio, computers, telephones, and many other devices. Semiconductor devices include the transistor, many kinds of diodes including the light-emitting diode, the silicon controlled rectifier, and digital and analog integrated circuits.

These materials are insulators in normal condition. Their resistivity lies between conductors and insulators. The range of resistivity for semiconductors is $10^{-4} \Omega\text{-m}$ to $0.5 \Omega\text{-m}$. In other words, a semiconductor is a substance, which has resistivity in between conductors and insulators. Examples of semiconductors include germanium (Ge), silicon (Si), selenium, carbon, etc. These solids have negative temperature coefficient of resistance. When some metallic impurity (like trivalent or pentavalent) is added to a pure semiconductor, then its conductivity increases.

In solids, each atom has a tendency to complete its outermost orbits. To achieve this, an atom may transfer or share electrons with other atoms. In this process, bonds are formed. In semiconductors, bonds are formed by sharing of electrons, i.e. covalent bond.

There are many semiconductors in nature, but germanium (Ge) and silicon (Si) are most commonly used semiconductors. It is because the energy required to break the covalent bond (i.e. forbidden energy gap) is very small in these materials. It is 0.7 eV for Ge and 1.1 eV for

Si. The semiconductors have almost filled valence band and nearly empty conduction band. There is a small forbidden energy gap (≈ 1 eV).

14-9 Classification of Semiconductors

The semiconductors can be divided into two types:

- (i) Intrinsic semiconductors or I-type semiconductors
- (ii) Extrinsic semiconductors

Intrinsic semiconductors

An intrinsic semiconductor, also called an undoped semiconductor or I-type semiconductor, is a pure semiconductor without any significant dopant species. The number of charge carriers is therefore determined by the properties of the material itself instead of the amount of impurities. The conductivity of intrinsic semiconductors can be due to crystal defects or to thermal excitation. In an intrinsic semiconductor, the number of electrons in the conduction band is equal to the number of holes in the valence band.

Extrinsic semiconductors

An extrinsic semiconductor is a semiconductor that has been doped, that is, into which a doping agent has been introduced, giving it different electrical properties than the intrinsic (pure) semiconductor. Doping involves adding dopant atoms to an intrinsic semiconductor, which changes the electron and hole carrier concentrations of the semiconductor at thermal equilibrium. Dominant carrier concentrations in an extrinsic semiconductor classify it as either an *n*-type or *p*-type semiconductor. The electrical properties of extrinsic semiconductors make them essential components of many electronic devices.

Extrinsic semiconductors are further divided into the following two categories

- (i) *n*-type semiconductors
- (ii) *p*-type semiconductors

***n*-type semiconductors**

When a small amount of pentavalent impurity like arsenic ($Z = 33$) or phosphorus ($Z = 15$) is added to a pure tetravalent semiconductor like silicon or germanium, it is known as *n*-type semiconductor. An addition of a small amount of phosphorus in pure silicon crystal causes the formation of four covalent bonds between four valance electrons of one phosphorus atom with four silicon atoms. The fifth valance electron of phosphorus remains free. Therefore, one free electron is created for each phosphorous atom. This extra electron is only weakly bound to the atom and can easily be excited into the conduction band. At normal temperatures, virtually all such electrons are excited into the conduction band. Since excitation of these electrons does not result in the formation of a hole, the number of electrons in such a material far exceeds the number of holes. In this case, the electrons are the majority carriers and the holes are the minority carriers.

The addition of pentavalent impurities contributes free electrons, greatly increasing the conductivity of the intrinsic semiconductor. Phosphorus may be added in pure silicon by diffusion of phosphine gas (PH_3). The formation of *n*-type semiconductor is shown in Figure 14.12.

Because the pentavalent impurity atoms have an extra electron to donate, they are called donor atoms. Note that each movable electron within the semiconductor is never far from an immobile positive dopant ion, and the *n*-type semiconductor normally has a net electric charge of zero.

Thus, the features of *n*-type semiconductor are as follows:

1. The donors are positively charged.
2. There are a large number of free electrons.
3. A small number of holes in relation to the number of free electrons.
4. Doping gives positively charged donors and negatively charged free electrons.
5. Supply of energy gives negatively charged free electrons and positively charged holes.

***p*-type semiconductor**

When a small amount of trivalent impurity such as gallium ($Z = 31$) or boron ($Z = 5$) is added to a pure tetravalent semiconductor like silicon or germanium, then it is known as *p*-type semiconductor. An addition of a small amount of boron in pure silicon crystal causes the formation of three covalent bonds between the three valence electrons of one boron atom with three silicon atoms. The fourth bond is incomplete; there is a vacancy of one electron. This missing electron is called a hole. Therefore for each boron atom added one hole is created. A small amount of indium produces a millions of holes.

Thus, the addition of trivalent impurities to an intrinsic semiconductor creates deficiencies of valence electrons, called holes. Diborane gas B_2H_6 is used to diffuse boron into the intrinsic silicon material. The formation of *p*-type semiconductor is shown in Figure 14.13.

Because the trivalent impurity atoms have less number of valence electrons than the atoms they replace in the intrinsic semiconductor, they accept electrons from the semiconductor's valence band. Hence, they are called acceptor atoms. Like *n*-type semiconductor, the net electric charge of *p*-type semiconductor is zero.

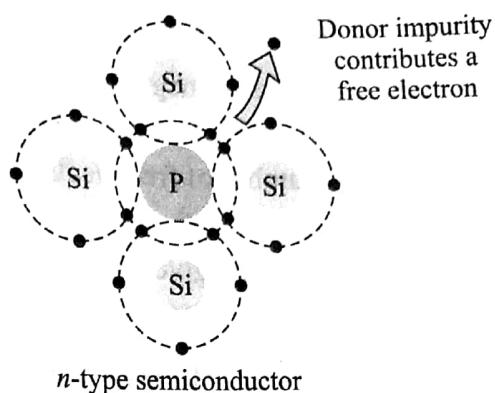


Figure 14.12 Formation of *n*-type semiconductor.

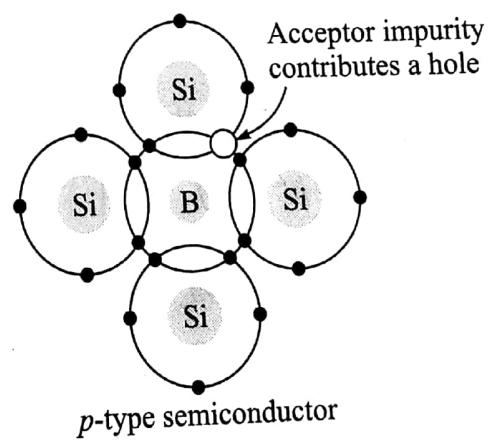


Figure 14.13 Formation of *p*-type semiconductor.

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Thus, the features of *n*-type semiconductor are as follows:

1. The acceptors are negatively charged.
2. There are a large number of holes.
3. A small number of free electrons in relation to the number of holes.
4. Doping gives negatively charged acceptors and positively charged holes.
5. Supply of energy gives positively charged holes and negatively charged free electrons.

ENERGY BANDS IN SOLIDS

9.1 The Band Theory of Solids

Formation of Energy Bands in Solids

Formation of Energy Bands in Solids
In the case of a single isolated atom, the electron in any orbit as shown in figure 9.1 have a definite energy. As a result, they occupy discrete energy levels, as shown in figure 9.2a.

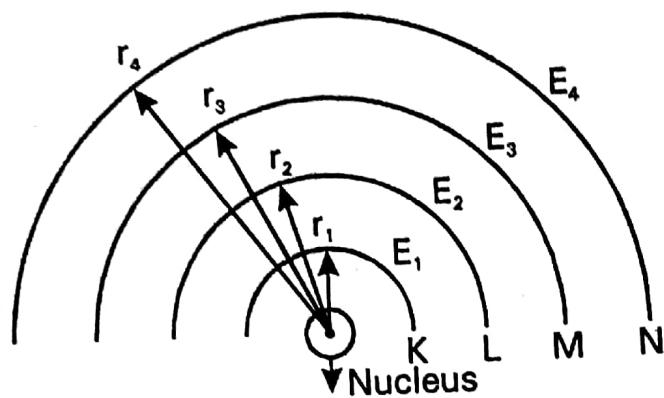


Figure 9.1 : The energy levels of a single isolated atom

The pauli exclusion principle allows each energy level to contain only two electrons. For example, the 2s level of a single atom contains one energy level with two electrons and 2p level contains 3 energy levels with two electrons in each level thus, with a total of six electrons as shown in figure 9.2a.

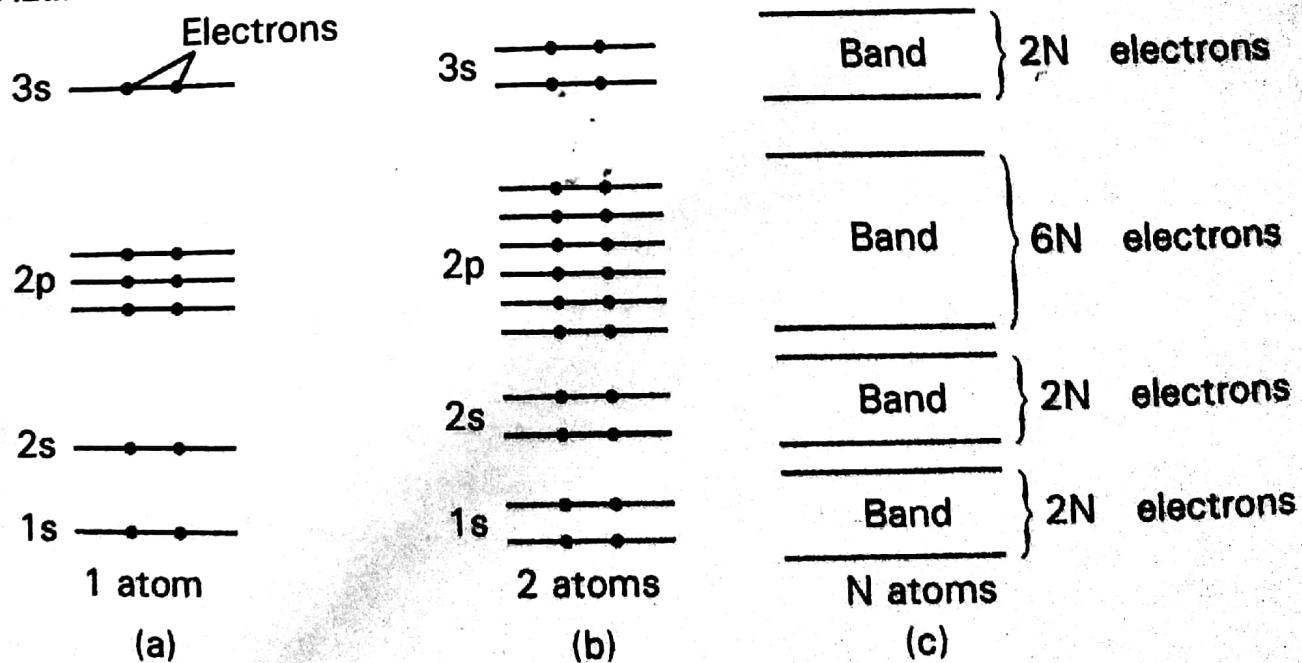


Figure 9.2 : The energy levels broaden into energy bands

Band structure in solid

Let us consider the formation of bands in a solid sodium.

The single energy level of an isolated sodium ($Z = 11$) based on the electron configuration $1s^2 2s^2 2p^6 3s^1$ is shown in figure 9.2a.

When another sodium is brought close to it, the electrons will be subjected to the effect of an additional field. As a result, each energy level is split into two as shown in figure 9.2b. Similarly, when three atoms come close together, the original level splits into three levels and so on.

More generally, when a solid is formed by bringing N atoms together, the Pauli principle still demands that only two electrons in the entire solid should have the same energy. Hence, in a solid the different split energy levels of electrons come together to form continuous bands of energies as shown in figure 9.2c.

Consequently, the 2s band in a solid sodium contain N discrete energy levels and $2N$ electrons, two in each energy level. Similarly, each of the 2p level contain N energy levels and $2N$ electrons. Hence, a broad 2p band will contain $3N$ energy levels and $6N$ electrons since the three 2p bands overlap.

Hence in general, each energy band has a total of N individual levels and each energy band can hold a maximum of $2(2l + 1)N$ electrons.

[Each energy level can hold $2(2l + 1)$ electrons. 2 corresponds to the electrospin and $(2l + 1)$ corresponds to the orientation of the electron orbital angular momentum].

The result is that, electrons in any orbit of atom within a solid can have a range of energies rather than a single value. *Thus, the range of energies possessed by an electron in a solid is known as energy band.* i.e., Each energy level of an isolated atom becomes a band in a solid as shown in figure 9.2c.

Note :

- In general, it is the outermost energy levels that are mostly affected whereas, the innermost levels barely suffer any splitting during the formation of a band. In the case of sodium it is the outermost energy levels i.e., 3s and 3p energy levels that are mostly affected. Whereas, the 1s, 2s and 2p levels barely suffer any splitting during the formation of a band.

9.2 Energy Bands in Solids ✓

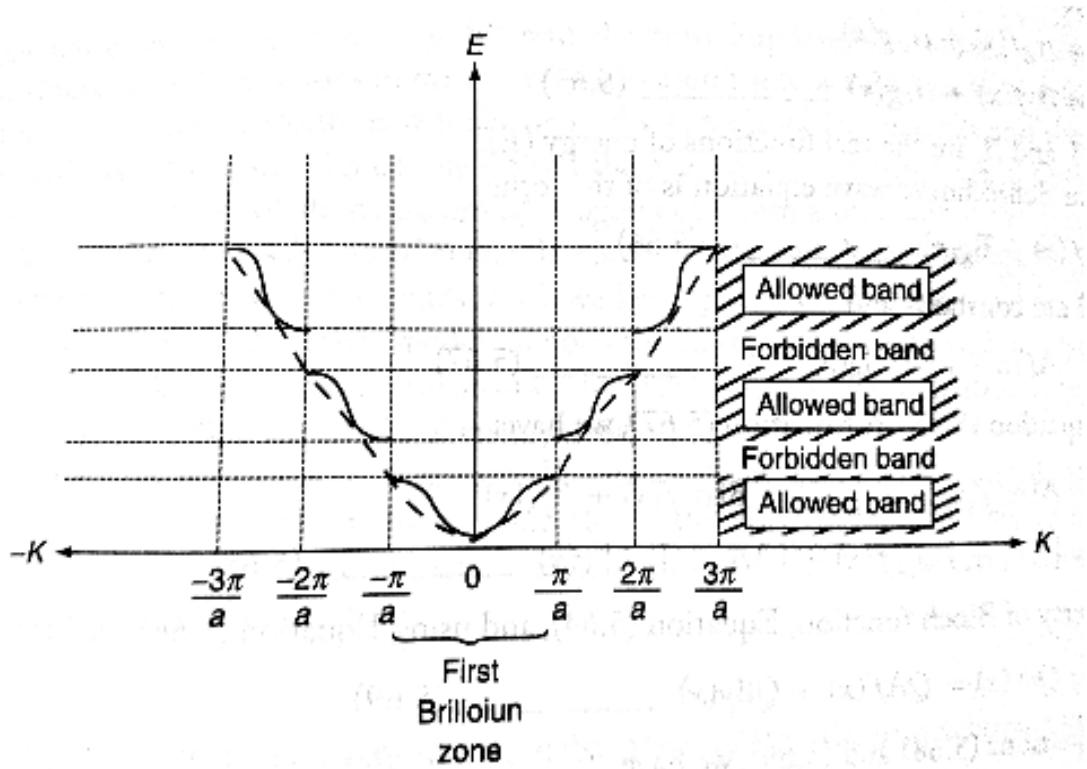
As explained in the case of solid sodium, the discrete energy levels of an atom becomes bands during the formation of solid due to the influence of the constituent atoms. Each band consists of a large number of energy levels which correspond to a range of energy values. The energies within the bands depend on the spacing between the atoms.

The highest occupied band is called the valence band below which all the lower bands are occupied fully. The valence band may even be partially filled. In the case of sodium, the 3s energy levels are the valence band which is partially filled.

The empty band which is immediately above the valence band is called the conduction band. In the case of sodium atom the empty 3p energy levels which are separated from the 3s band by an energy gap is the conduction band.

The gap between the valence band and conduction band is called the forbidden band or the energy gap.

EK Diagram



The Brillouin zone are the boundaries that are marked by the values of wave vector k , in which electrons can have allowed energy values. These represent the allowed values of k of the electrons in 1D, 2D,&3D.

We have ,the energy of the electron in a constant potential box is,

$$E = \frac{n^2 h^2}{8ma^2} \dots \text{(1)} \quad \text{where } a = \text{length of the box.}$$

But,

$$k = \frac{n\pi}{a} \Rightarrow k^2 = \frac{n^2 \pi^2}{a^2}$$

$$\frac{n^2}{a^2} = \frac{k^2}{\pi^2} \dots \dots \dots \text{(2)}$$

Substitute eqn (2) in (1) ,we get $E = \frac{k^2 h^2}{8m\pi^2}$; $E \propto k^2$. It represents parabolic equation.

A graph is drawn between the total energy (E) and the wave vector k ,for various values of k .

$$\text{i.e. } k = \frac{n\pi}{a} ; n = \pm 1, \pm 2, \pm 3, \dots \dots$$

It is the energy spectrum of an electron moving in presence of a periodic potential field and is divided into allowed energy regions (allowed zones) or forbidden energy gaps (forbidden zones).

Allowed energy values lie in the region $k=-\pi/a$ to $=+\pi/a$. This zone is called the first Brillouin zone. After a break in the energy values, called forbidden energy band, we have another allowed zone spread from $k=-\pi/a$ to $-2\pi/a$ and $+\pi/a$ to $+2\pi/a$. This zone is called the second Brillouin zone. Similarly, higher Brillouin zones are formed

* 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 its 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 a definite energy and momentum.

These waves are treated as a particle called 'phonons'.

- Thus a phonon can be defined as a discrete unit of vibrational mechanical energy.
- 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, \hbar = planck constant

- Phonons can carry heat and sound and they play a major role in determining heat capacities of solids and liquids.