

Crystal Structure

LEARNING OBJECTIVES

After reading this chapter you will be able to

- LO 1** Understand crystalline, amorphous solids, primitive lattice and Wigner-Seitz primitive cell, and types of crystals
- LO 2** Know about translation vectors, lattice planes, and significance and representation of Miller indices
- LO 3** Illustrate structures of NaCl, CsCl, and diamond, coordination number of simple cubic lattice, bcc lattice, fcc lattice
- LO 4** Learn about interplanar spacing and nearest neighbour distance and atomic radius
- LO 5** Discuss packing fraction for sc, bcc, fcc, diamond, hcp, interatomic attractive/repulsive forces
- LO 6** Explain ionic bond, covalent bond, metallic bond, van der Waals bond, hydrogen bond, crystal structure analysis i.e., Bragg's law and spectrometer, Laue method, powder method
- LO 7** Evaluate vacancies, concentration of Schottky defects and Frenkel defects, compositional and electronic defect

Introduction

A crystal structure is a unique arrangement of atoms. It consists of a set of atoms which are identical in composition, arrangement and orientation, called basis and a lattice. Bases are located upon the points of a lattice, which is an array of points repeating periodically in three dimensions. The points can be thought of as forming identical tiny boxes, called *unit cells*, that fill the space of the lattice. The lengths of the edges of a unit cell and the angles between them are called the *lattice parameters*. A crystal structure and symmetry play an important role in determining many of its properties, like electronic band structure and optical properties.

It is clear that a crystal structure is formed by the addition of a basis of atoms to every lattice point. Mathematically, it can be represented as

$$\text{Crystal structure} = \text{Lattice} + \text{Basis}$$

The solids are broadly classified into two groups, namely, crystalline solids and amorphous solids.

14.1.1 Crystalline Solids

Crystalline solids are arranged in fixed geometric patterns or lattices. Ice, methanol and sodium chloride are a few examples of crystalline solids. They have orderly arranged units and are practically incompressible. Crystalline solids also show a definite melting point and so they pass rather sharply from solid to liquid state. There are various crystalline forms which are divided into seven crystal system or shapes. They are cubic, tetragonal, hexagonal, orthorhombic, monoclinic, trigonal and triclinic. The units that constitute these systems can be atoms, molecules or ions. Ionic and atomic crystals are hard and breakable with high melting points.

14.1.2 Amorphous Solids

A rigid material whose structure lacks crystalline periodicity is called an amorphous solid. It means the pattern of its constituent atoms or molecules does not repeat periodically in three dimensions. Even amorphous materials have some short range order at the atomic length scale due to the nature of chemical bonding. They are considered supercooled liquids in which the molecules are arranged in a random manner somewhat as in the liquid state. Glass and plastic are the examples of amorphous solids. Unlike crystalline solids, amorphous solids do not have definite melting points.

14.2 UNIT CELL

LO1

The smallest portion of a space lattice which can generate the complete crystal by repeating its own dimensions in various directions is called a *unit cell*. A unit cell is defined by the length of its edges and by the angles between them, as shown in Fig. 14.1.

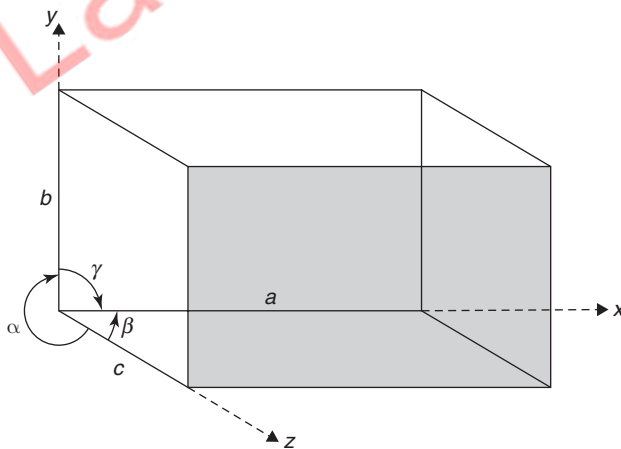


FIGURE 14.1

Vectors \vec{a} , \vec{b} and \vec{c} are called lattice vectors that form primitive axes in the crystal structure. We also call them *crystallographic axes*, as the directions defined by these vectors are nothing but crystal axes. These vec-

tors are used in translation vector and hence are called *fundamental translation vectors*. The magnitudes of vectors \vec{a} , \vec{b} and \vec{c} are called *lattice constants* that specify the distances of the bases along the crystal axes.

14.2.1 Primitive Lattice Cell

The *parallelepiped* defined by primitive axes \vec{a} , \vec{b} , \vec{c} is called a *primitive cell*. A primitive cell is a type of unit cell which fills all the space under the action of suitable crystal translation operation. A primitive cell is a minimum volume unit cell, as shown in Fig. 14.2. There is a density of one lattice point per primitive cell. The volume of a primitive cell is defined by primitive axes \vec{a} , \vec{b} , \vec{c} as $|(\vec{a} \times \vec{b}) \cdot \vec{c}|$.

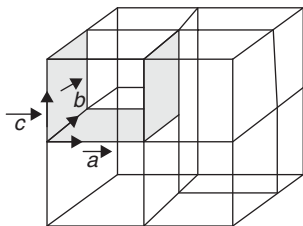


FIGURE 14.2

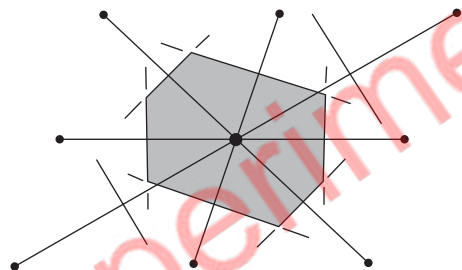


FIGURE 14.3

14.2.2 Wigner-Seitz Primitive cell

The smallest volume enclosed by the normal lines drawn from midpoints of the lines which connect lattice point to all nearby lattice points is called a Wigner-Seitz primitive cell. It is shown in Fig. 14.3.

14.3 TYPES OF CRYSTALS

LO1

All crystals are classified into seven crystal systems on the basis of the shape of the unit cells. Bravais in 1948 explained that there are fourteen different types of crystal lattices under the seven crystal systems. These seven types of crystal systems are tabulated in Table 14.1, and shown in Fig. 14.4.

TABLE 14.1

S.No.	Name of System	Relative Between		Number of Possible Lattices	Examples
		Primitives	Angles		
1.	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	3(P, F, I)	NaCl
2.	Trigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	1(R)	CaSO ₄
3.	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	2(P, I)	NiSO ₄
4.	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	1(P)	Quartz
5.	Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	4(P, C, F, I)	KNO ₃
6.	Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ, \neq \beta$	2(P, C)	FeSO ₄
7.	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	1(P)	CuSO ₄

P = Primitive, C = Base centered, I = Body Centered, F = Face centered, R = Rhombohedral

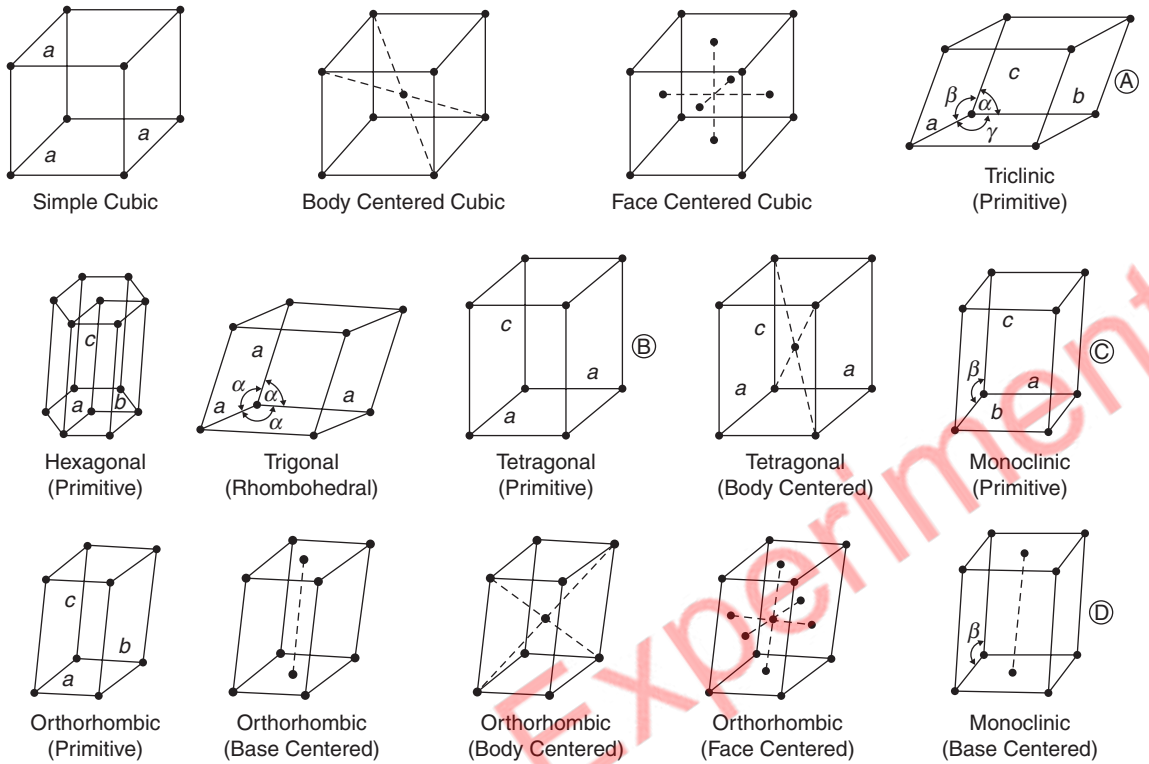


FIGURE 14.4

14.3.1 Cubic System

In a cubic system, there are three types of lattices, namely simple cubic, body centered cubic and face centered cubic. In addition to these structures, other structures are also depicted in Fig. 14.4.

- Simple Cubic*: It contains lattice points at all eight corners of the unit cell. It is represented by sc.
- Body Centered Cubic*: It contains one additional lattice point at the centre of the body of the unit cell including at all eight corners. It is represented by bcc.
- Face Centered Cubic*: It contains lattice points at the centre of each face as well as at all eight corners. It is represented by fcc.

14.4 TRANSLATION VECTORS

LO2

We take any lattice point O as an origin in a plane lattice shown in Fig. 14.5. Any other point in the two-dimensional lattice can be obtained by repeatedly translating the vectors \vec{a} and \vec{b} . These vectors are known as basis vectors. Based on these basis vectors, we obtain the plane lattice by their repeated translation. The position vector of any other lattice point, i.e., translation vector, can be represented as

$$\vec{T} = n_1\vec{a} + n_2\vec{b}$$

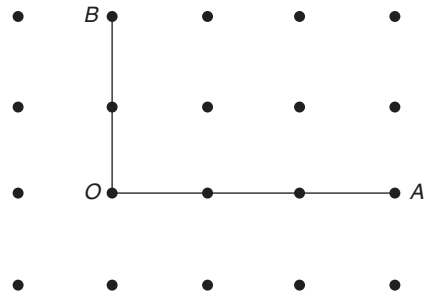


FIGURE 14.5

where n_1 and n_2 are the integers which represent the number of lattice points along the directions OA and OB , respectively, and \vec{a} and \vec{b} are the primitives. In case of three-dimensional crystal structures, the arrangement of points can be represented as

$$\vec{T} = n_1\vec{a} + n_2\vec{b} + n_3\vec{c}$$

where \vec{a} , \vec{b} and \vec{c} are the primitives along X , Y and Z axes, respectively.

14.5 LATTICE PLANES

LO2

A crystal lattice is made of a large number of parallel equidistant planes (Fig. 14.6) known as lattice planes and can be chosen in a number of ways, as shown in Fig. 14.6a, b, c and d.

14.6 MILLER INDICES

LO2

The integers which determine the orientation of a crystal plane in relation to the three crystallographic axes are called *Miller indices*. In order to find the Miller indices, the reciprocals of the intercepts of the plane on the axes in terms of lattice constants are reduced to the smallest integers in ratio. Miller indices are also called crystal indices.

Let us assume that a , b and c are the magnitudes of fundamental translation vectors along the three axes, respectively. Again we consider that ABC represents the plane whose Miller indices are to be obtained. Let OA , OB and OC are the intercepts made by this plane along the three axes (Fig. 14.7).

In order to find the Miller indices, we do the following.

- We find the intercepts along the three axes.
- We express these intercepts as multiple of lattice parameters.
- We divide these intercepts by lattice parameters.
- We take the reciprocal of these.
- We clear these fractions by taking the LCM of the denominators and multiplying it. This gives the required Miller indices.

This can be understood in a better way in the following steps corresponding to the above steps a to e.

Directions	x	y	z	
Step (a)	OA	OB	OC	
Step (b)	pa	qb	rc	
Step (c)	$\frac{pa}{a}$	$\frac{qb}{b}$	$\frac{rc}{c}$	or $p \quad q \quad r$
Step (d)	$\frac{1}{p}$	$\frac{1}{q}$	$\frac{1}{r}$	
Step (e)	$(h$	k	$l)$	

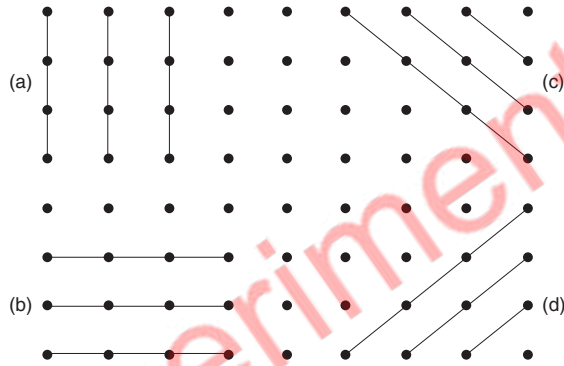


FIGURE 14.6

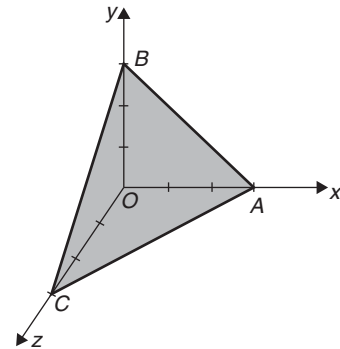


FIGURE 14.7

14.6.1 Significance of Miller Indices

Same Miller indices are assigned to all parallel planes, for example, planes with coordinates $x, y, z; 2x, 2y, 2z; -x, -y, -z;$ etc., are represented by the same Miller indices. The corresponding index for a plane, which is parallel to one coordinate axis, is zero. The corresponding index is negative for a plane that cuts an axis on the negative side of the origin. The negative index is represented by putting a bar above the index.

14.6.2 Representation of Miller Indices

Let us consider a simple cubic system ($\alpha = \beta = \gamma = 90^\circ$ and $a = b = c$). For this system in Fig. 14.8a, b, c, d, e, f and g, we show Miller planes corresponding to $(\bar{1} 0 0), (1 0 0), (0 1 0), (0 0 1), (1 1 0), (1 0 1)$ and $(1 1 1)$ planes in a cubic crystal respectively.

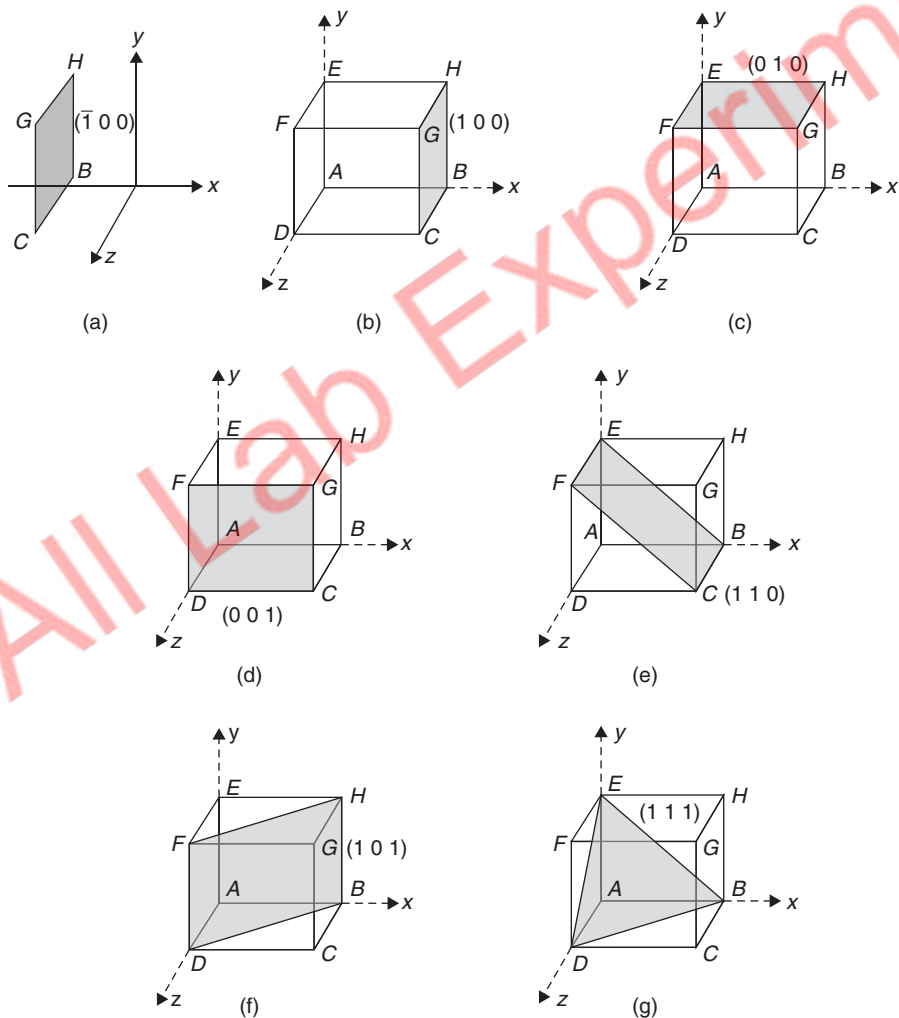


FIGURE 14.8



EXAMPLE 1 A plane cuts intercepts $2a$, $3b$ and c along the crystallographic axes in a crystal. Determine the Miller indices of plane.

SOLUTION Intercepts are $2a$, $3b$ and c .

Then from the law of rational indices, we have

$$2a \quad 3b \quad c = \frac{a}{k} \quad \frac{b}{U} \quad \frac{c}{E}$$

or
$$\frac{1}{k} \quad \frac{1}{U} \quad \frac{1}{E} = \frac{1}{2} \quad \frac{1}{3} \quad 1$$

or
$$k \quad U \quad E = \frac{1}{2} \quad \frac{1}{3} \quad 1 = 3 \quad 2 \quad 6$$

Therefore, the Miller indices of the plane are **(3 2 6)**.

EXAMPLE 2 In a triclinic crystal, a lattice plane makes intercepts at a length a , $2b$ and $-3c$. Find the Miller indices of the plane.

SOLUTION Intercepts are a , $2b$ and $-3c$.

$$a \quad 2b \quad \frac{3c}{2} = \frac{a}{k} \quad \frac{b}{U} \quad \frac{c}{E}$$

or

$$\frac{1}{k} \quad \frac{1}{U} \quad \frac{1}{E} = 1 \quad 2 \quad \frac{3}{2}$$

or

$$k \quad U \quad E = 1 \quad \frac{1}{2} \quad \frac{2}{3} = 3 \quad 4$$

Therefore, the Miller indices of the given plane are **(6 3 4)**.

EXAMPLE 3 / Reduce the Miller indices for planes in each of the following sets which intercept \vec{a} , \vec{b} and \vec{c} at (i) $3a$, $3b$, $2c$ (ii) a , $2b$, ∞ (iii) a , b , c

SOLUTION (i) Intercepts are $3a$, $3b$, $2c$.

Then,

$$3a \quad 3b \quad 2c = \frac{a}{k} \quad \frac{b}{U} \quad \frac{c}{E}$$

or

$$3 \quad 3 \quad 2 = \frac{1}{k} \quad \frac{1}{U} \quad \frac{1}{E}$$

or

$$k \quad U \quad E = \frac{1}{3} \quad \frac{1}{3} \quad \frac{1}{2}$$

or

$$h \quad k \quad l = 2 \quad 2 \quad 3$$

Therefore, the Miller indices are **(2 2 3)**.

(ii) Intercepts are a , $2b$, ∞ .

Then,

$$a \quad 2b \quad \infty = \frac{a}{k} \quad \frac{b}{U} \quad \frac{c}{E}$$

or

$$\frac{1}{k} \quad \frac{1}{U} \quad \frac{1}{E} = 1 \quad 2 \quad \infty$$

or

$$k \quad U \quad E = 1 \quad \frac{1}{2} \quad \frac{1}{\infty} = 2 \quad 1 \quad 0$$

Therefore, the Millers indices are **(2 1 0)**.

(iii) Intercepts are a , b , c .

Then,

$$a \quad b \quad c = \frac{a}{k} \quad \frac{b}{U} \quad \frac{c}{E}$$

or

$$1 \quad \frac{1}{2} \quad 1 = \frac{1}{k} \quad \frac{1}{U} \quad \frac{1}{E}$$

or

$$h \quad k \quad l = 1 \quad 2 \quad 1$$

Therefore, the Miller indices are **(1 2 1)**.

As we know that the metal contains a large number of conduction electrons which are not completely free but partially, though they are not bound to any particular atomic system. The forces between conduction electrons

and ion cores are neglected in the free electron approximation so that the electrons within the metal are treated as free. Further, the energy possessed by electron is kinetic, since the potential energy is taken to be zero.

Consider an electron of mass m confined in a box of length L . Under this situation, the Schrödinger wave equation becomes

$$\left(\frac{\hbar^2}{2m} \nabla^2 + E \right) \psi = 0 \quad \text{--- (i)}$$

The solution of the above equation is

$$\psi = \psi_0 \exp(i\vec{K} \cdot \vec{r}) \quad \text{--- (ii)}$$

where \vec{K} is the wave vector with the magnitude $K = \frac{2\pi}{\lambda}$.

It can be shown from (i) that

$$\frac{\hbar^2 K_x^2}{2m} \psi; \quad \frac{\hbar^2 K_y^2}{2m} \psi; \quad \frac{\hbar^2 K_z^2}{2m} \psi$$

Then,

$$\left(\frac{\hbar^2 K_x^2}{2m} + \frac{\hbar^2 K_y^2}{2m} + \frac{\hbar^2 K_z^2}{2m} \right) \psi = E \psi \quad \text{--- (iii)}$$

$$\nabla^2 \psi = -K^2 \psi \quad \text{--- (iv)}$$

By using (iii) and (iv), we have

$$\left(\frac{\hbar^2}{2m} - E \right) \psi = 0 \quad \text{--- (v)}$$

Now we can write the total energy E in terms of momentum p with the help of following relations.

since, $K = \frac{2\pi}{\lambda}$ and $\lambda = \frac{h}{p}$

$$E = \frac{\hbar^2 K^2}{2m} = \frac{h^2}{2m} \left(\frac{2\pi}{\lambda} \right)^2 = \frac{h^2}{2m} \left(\frac{2\pi}{h} \right)^2 \left(\frac{h}{p} \right)^2 = \frac{h^2}{2m} \left(\frac{4\pi^2}{h^2} \right) \left(\frac{h^2}{p^2} \right) = \frac{2\pi^2 \hbar^2}{m} \left(\frac{1}{\lambda^2} \right) = \frac{2\pi^2 \hbar^2}{m} \left(\frac{p^2}{h^2} \right) = \frac{2\pi^2 \hbar^2}{m} \left(\frac{N^2}{2\pi} \right)^2 = \frac{2\pi^2 \hbar^2}{m} \left(\frac{N^2}{4\pi^2} \right) = \frac{\hbar^2 N^2}{2m} \quad \text{--- (vi)}$$

$$E = \frac{\hbar^2 N^2}{2m} \quad \text{--- (vi)}$$

(vi) represents the energy of a free particle i.e., electron and thus the energy is continuous. Here it may be mentioned that we have not considered the lattice periodicity and also assumed the constant potential inside the crystal to be zero. However, for cyclic boundary conditions, $K = \frac{2\pi n}{L}$, where L is the length of the cyclic chain i.e., the solid. Therefore

2 p. e Ma- oEuta-3

Consider that free electrons are contained in a box at absolute temperature. At absolute zero all the energy levels below a certain level will be filled with electrons and the levels above this level will be empty. The energy level which divides the filled and empty levels is called Fermi energy and the corresponding energy of that level is known as Fermi energy E_F . In ground state of the system of free electrons, the occupied states may be represented as a point inside a sphere in N -space as shown in Fig. 13.4. The N_x , N_y and N_z are the components of N_g along x , y and z axes, respectively. As per previous article, the energy of the electron is given by

$$E_K = \frac{\hbar^2 K^2}{2m}$$

From the above relation it is clear that the energy increases as the square of distance from the origin of the N -space coordinate system. All the electrons which lie on the same spherical shell of radius, N_g , have the same energy, which is called Fermi energy E_F . It is given by

$$E_F = \frac{\hbar^2 K_F^2}{2m}$$

hence,

$$K_F = \frac{2\pi}{L} T$$

$$K_x = \frac{2\pi}{L} T_x$$

$$K_y = \frac{2\pi}{L} T_y$$

$$K_z = \frac{2\pi}{L} T_z$$

where E_x , E_y and E_z have the values $0, \dots, 1, \dots, K$. Therefore

$$K_x = 0, \dots, \frac{2\pi}{L}, \dots, \frac{4\pi}{L}, \dots, \frac{6\pi}{L}, \dots$$

N_x and N_y also have the same values. Suppose $\left(\frac{2\pi}{L}\right)^3$ is the volume of one shell in N -space (Fig. 13.4). Then in a sphere of

FIGURE 17.2

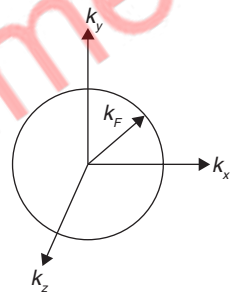


FIGURE 17.3

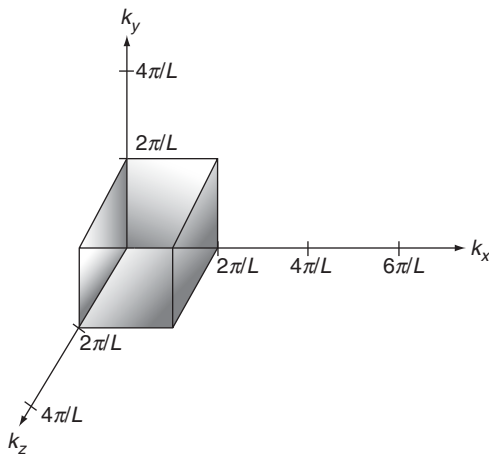


FIGURE 17.4

volume $\frac{4}{3}K_V^3$, the total number of energy states (or shells) will be

$$g_V \left[2 \left(\frac{4}{3} K_V^3 \right)^{1/3} \right] \quad \text{)iii+}$$

Here the factor C represents the two allowed values of spin quantum number $v_f \left[2 \left(\frac{1}{2} \right) \right]$ spin up and $v_f \left[\left(\frac{1}{2} \right) \right]$ spin down for each allowed value of N

If all of these energy shells are filled with electrons, then N_g will be equal to the number of electrons, i.e.,

$$2 \left(\frac{4}{3} K_V^3 \right)^{1/3} g \quad \text{or} \quad g \left[\frac{A}{3} K_V^2 \right] \quad (\because A \propto s^3) \quad \text{)iv+}$$

or $K_V \left[\frac{3g}{A} \right]^{2/3} \quad \text{or} \quad K_V \left[\frac{3g}{A} \right]^{1/3} \quad \text{)v+}$

From 2 q.)v+, it is clear that N_g depends upon electron concentration $\left(\frac{g}{A} \right)^{1/3}$ or in other words N_g depends upon number of electrons per unit volume but it does not depend on the mass of electrons. ' Now the Fermi energy is

$$E_V \left[\frac{\hbar^2}{2m} K_V^2 \right]$$

The energy can be written as

$$E_V \left[\frac{1}{2} m v_g^2 \right] \quad \text{)vii+}$$

where v_g is the velocity of electron in Fermi level, i.e., corresponding to Fermi energy. Then

$$\frac{1}{2} m v_g^2 \left[E_V \left[\frac{\hbar^2}{2m} \left(\frac{3g}{A} \right)^{2/3} \right] \right]$$

$$3 \quad J_V \left[\frac{\hbar}{m} \left(\frac{3g}{A} \right)^{1/3} \right] \quad \text{)viii+}$$

2. Density of States

It is defined as the number of energy states per unit energy range. It is denoted by the symbol $D(E)$. In other words, the density of states for electrons in a band gives the number of orbitals or states in a certain energy range. Hence, the number of filled i.e., density of electron states having the energy in the range E and $E + \Delta E$ is

$$N = \int_E^{E+\Delta E} D(E) dE \quad (i)$$

Prom the energy relation

$$E = \frac{\hbar^2 K^2}{2m} \quad (ii)$$

and

$$g = \frac{A}{3} K^3$$

we get

$$D(E) = \frac{dN}{dE} = \frac{d}{dE} \left[\frac{A}{3} \left(\frac{2mE}{\hbar^2} \right)^{3/2} \right] \quad (iii)$$

where E is total energy and N is the number of electrons. Therefore, from (iii), we have

$$\frac{3}{A} \left[\frac{2v E}{\hbar^2} \right]^{3/2} \left[\frac{\pm v E}{F^2/4} \right]^{3/2}$$

$$g \left[\frac{8 A}{3 F^3} (2v E)^{3/2} \right] \quad \text{iv+}$$

By differentiating eq. iv+ w.r.t. E , we get

$$\frac{ng}{nE} \left[\frac{8 A}{3 F^3} (2v)^{3/2} \frac{3}{2} E^{1/2} \right] \left[\frac{8 v A (2v E)^{1/2}}{F^3} \right]$$

$$\frac{ng}{nE} \left[\frac{A}{2} \right] \left[\frac{2v}{\hbar^2} \right]^{3/2} (E)^{1/2} \quad \text{v+}$$

The quantity $\left(\frac{ng}{nE} \right)$ is frequency referred to as the density of available state $D(E)$, which on multiplication with probability of occupation $f(E)$ gives density of occupied state $N(E)$, as shown in Fig. 13.5.

Thus, the number of electrons whose energies lie between m and $m + \Delta m$ is given by

$$g(E) \Delta E \left[\frac{ng}{nE} \right] f(E) \Delta E$$

$$g(E) \Delta E \left[\frac{8 v A}{F^3} (2v E)^{1/2} \frac{nE}{e^{(E - E_F)/kT}} \right] f(E) \Delta E$$

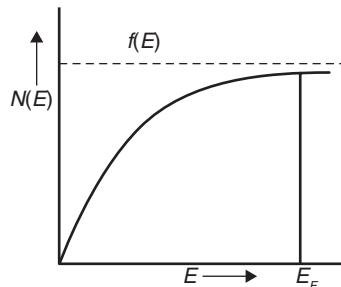


FIGURE 17.5

EXAMPLE 2 Fermi energy of a given substance is 3.9 eV . What is the average energy and speed of electron in this substance at 0 K ?

SOLUTION Given $m_g = 3.9 \text{ eV}$

average energy $\bar{E}_0 = \frac{3}{5} E_F$

$$\bar{E}_0 = \frac{3}{5} \times 3.9 \text{ eV} \\ = 4.74 \text{ eV}$$

and, $\frac{1}{2} m_e v^2 = \bar{E}_0$ or $J = \sqrt{\frac{2\bar{E}_0}{m_e}}$

or $J = \sqrt{\frac{2 \times 4.74 \times 1.6 \times 10^{19}}{9.1 \times 10^{-31}}} = 1.29 \times 10^6 \text{ m/sec}$

EXAMPLE 3 There are 2.5×10^{28} free electrons per cubic meter of sodium. Calculate the Fermi energy and Fermi velocity.

SOLUTION Given $\frac{g}{V} = 2.5 \times 10^{28}$

Formula used is

$$E_F = \frac{1}{2} m_e v_F^2 = \left(\frac{\hbar^2}{2m_e} \right) \left(\frac{3}{4} \pi^2 \frac{g}{V} \right)^{2/3}$$

or $E_F = \left(\frac{\hbar^2}{2m_e} \right) \left(\frac{3}{4} \pi^2 \frac{g}{V} \right)^{2/3}$

$$= \left(\frac{6.62 \times 10^{-34}}{2 \times 9.1 \times 10^{-31}} \right) \left[\frac{3}{4} \pi^2 (2.5 \times 10^{28}) \right]^{2/3}$$

or $E_F = 5.0 \times 10^{-19} \text{ J}$

$$E_F = 3.12 \text{ eV}$$

and Fermi velocity $v_F = \left(\frac{2E_F}{m_e} \right)^{1/2}$

$$= \left(\frac{2 \times 5.0 \times 10^{-19}}{9.1 \times 10^{-31}} \right)^{1/2} = 1.05 \times 10^6 \text{ m/sec}$$

EXAMPLE 4 The density of copper is 8.9 g/cm^3 and atomic weight is 63.55 . Determine the Fermi energy of copper. Also obtain the average energy of free electrons of copper at 0 K .

SOLUTION Given atomic weight (63.55 g) and density of copper (8.9 g/cm^3).

Volume of 1 g mole of copper, $V = \frac{63.55 \text{ g}}{8.9 \text{ g/cm}^3}$

Number of atoms per cm^3 atom ($N = 10^{23}$)

or $\frac{g}{V} = \frac{6.02 \times 10^{23} \times 8.9}{63.55}$

$$\begin{aligned} \text{Permi energy } E_F &= \left[\frac{1}{2} v J_v^2 \left[\frac{\hbar^2}{2v} \right]^3 \right]^{2/3} \frac{g}{A} \\ &= \left[\frac{F^2}{8 \cdot 2v} \right]^3 \frac{g}{A} \\ &= \left[\frac{(6.62 \cdot 10^{34})^2}{8 - (3.14)^2 - 9.1 \cdot 10^{31}} \right]^3 - (3.14)^2 - \frac{6.02 \cdot 10^{26} - 8940}{63.55} \\ &= 11.261 \cdot 10^{19} \text{ F} \\ E_F &= 1.038 \text{ eA} \end{aligned}$$

$$\begin{aligned} \text{Average energy } \bar{E}_0 &= \frac{3}{5} E_F = \frac{3}{5} \cdot 1.038 \text{ eA} \\ &= 4.22 \text{ eV} \end{aligned}$$

EXAMPLE 5 Consider silver in the metallic state with one free electron per atom. Calculate the Fermi energy. Given that density of silver is 10.5 g/cm^3 and atomic weight is 108.

SOLUTION Volume of 1 g mole of silver, $V = \frac{108 \text{ g}}{10.5 \text{ g/cm}^3}$ and number of atoms per g atom $(N_A = 6.02 \cdot 10^{23})$.

$$\begin{aligned} \frac{g}{A} &= \frac{6.2 \cdot 10^{23} - 10.5}{108} \\ &= 5.85 \cdot 10^{22} \text{ per cm}^3 \\ &= 5.85 \cdot 10^{28} \text{ per cm}^3 \end{aligned}$$

$$\begin{aligned} \text{Permi energy } E_F &= \left[\frac{F^2}{8 \cdot 2v} \right]^3 \frac{g}{A} \\ &= \left[\frac{(6.62 \cdot 10^{34})^2}{8 - (3.14)^2 - 9.1 \cdot 10^{31}} \right]^3 [3 - (3.14)^2 - 5.85 \cdot 10^{28}]^{2/3} \\ &= 8.199 \cdot 10^{19} \text{ F} \\ &= 5.499 \text{ eA} \\ &= 5.5 \text{ eV} \end{aligned}$$

EXAMPLE 6 Aluminium metal crystallises in f.c.c. structure. If each atom contributes single electron as free electron and the lattice constant T is 0.356 nm , treating conduction electron as free electron Fermi gas, find (i) Fermi energy E_F and Fermi vector k_F and (ii) total kinetic energy of free electron gas per unit volume at 0 K .

SOLUTION In f.c.c. lattice number of electrons per unit cell will be 4 and volume of a unit cell is $V = (0.356 \cdot 10^{-9} \text{ m})^3$

$$\begin{aligned} \text{and } \frac{g}{A} &= \frac{4}{64 \cdot 10^{-30}} \\ &= 6.25 \cdot 10^{28} \end{aligned}$$

Permi energy $E_V \left[\frac{F^2}{8 - 2V} \right]^{2/3} \frac{\partial g}{A} \times$

$$\left[\frac{(6.62 - 10^{34})^2}{8 - (3.14)^2 - 9.1 - 10^{31}} [3 - (3.14)^2 - 6.25 - 10^{28}]^{2/3} \right]$$

$$\left[9.2 - 10^{19} \text{ F} \right]$$

$$= 5.15 \text{ eA}$$

Permi vector $K_V \left[\frac{\partial g}{A} \right]^{1/3} \left[[3 - (3.14)^2 - 6.25 - 10^{28}]^{1/3} \right]$

$$\left[1.23 - 10^{10} \text{ perkh eler} \right]$$

Total kinetic energy of free electrons per unit volume at 0 K $\left[\left(\text{g uerayekenergy7kperkevebronkalk0 w} \right) - (\text{nnh Verkofkevebronckperkmilkouwh e}) \right]$

$$= \frac{3}{5} E_V - \frac{g}{A} \left[\frac{3}{5} - 5.15 - 6.25 - 10^{28} \text{ eA} \right]$$

$$= \mathbf{21.56 \times 10^{28} \text{ eV}}$$

Band Theory of Solids and Photoconductivity

18

LEARNING OBJECTIVES

After reading this chapter you will be able to

- LO 1** Understand Kronig-Penney model, energy E versus k diagram and one- and two-dimensional Brillouin zones
- LO 2** Explain effective mass of an electron and deviation of electron behaviour in crystal lattice
- LO 3** Differentiate between Insulators, n -type, p -type semiconductors and conductors (metals)
- LO 4** Explain electron configuration in conduction band, hole concentration in valence band, Fermi level of intrinsic and extrinsic semiconductor
- LO 5** Illustrate Hall effect, Hall voltage and Hall coefficient
- LO 6** Learn simple model of photoconductor and gain factor
- LO 7** Discuss effects of traps, applications of photoconductivity

Introduction

A solid contains an enormous number of atoms packed closely together. When N atoms of the solid are well separated, then these atoms lead to N -fold degenerate levels of the solid. As the atoms approach one another to form a solid, i.e., their separation reduces, a continuously increasing interaction occurs between them. This causes each of the levels to split into N distinct levels. It is the separation distance (say r) which specifies the amount of overlap that causes the splitting. Since a solid contains about 10^{23} atoms per mole, i.e., N is very large, the splitted energy levels become so numerous and close together that they form an almost continuous **energy band**.

The amount of splitting is different for different energy levels. For example, the lower energy levels are found to spread or split less than the higher levels. It means the lowest levels remain almost unsplit. The reason is that the electrons in lower levels are the ones which are in inner subshells of the atoms. So they are not significantly influenced by the presence of nearby atoms. Since the potential barriers between the atoms are for them relatively high and wide, these electrons are localised in particular atoms, even when r is small. However, the electrons in the higher levels are the valence electrons and are not localised at all

for small r but they become part of the whole system. From the quantum point of view, the wave functions of the valence electrons overlap and the overlapping of their wave functions results in splitting or spreading of their energy levels.

The band formation of the higher energy levels of sodium, whose ground state atomic configuration is $1s^2 2s^2 2p^6 3s^1$, is shown in Fig. 18.1. In the figure, the dashed and vertical line indicates the observed interatomic separation in the solid sodium. It is clear from the figure that the bands overlap when the atomic separation decreases. This figure also shows that the allowed band corresponding to inner subshells, for example $2p$ in sodium, are extremely narrow and does not begin to split until the interatomic distance r becomes less than the value actually found in the crystal. As we move towards the higher energy states, the energy of the electrons become larger and also the region in which they can move becomes wider. Since they are also affected more by the nearby ions, it is seen that the bands become progressively wider for the outer occupied subshells and also for the unoccupied subshells of the atoms in its ground state. Therefore, with the increase of energy the successive allowed bands become wider and overlap each other in energy.

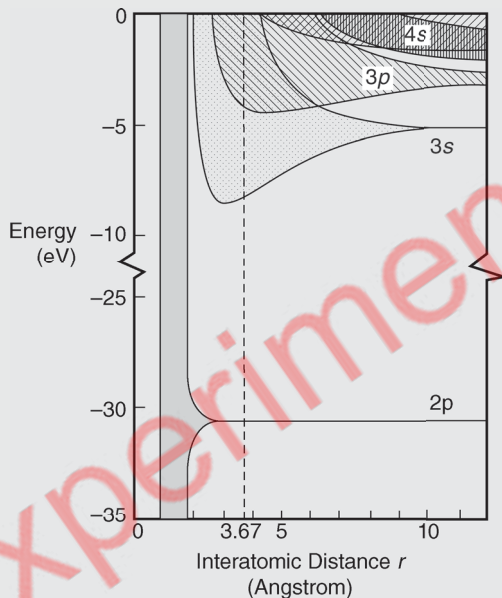


FIGURE 18.1

It is clear from the above discussion that the energy bands in a solid correspond to energy levels in an atom. Therefore, an electron in a solid can occupy only energy that falls within these energy bands. The overlapping of the bands depends on the structure of the solid. If the bands do not overlap, then the intervals between them represents energies which the electrons in the solid cannot occupy. These intervals are called *forbidden bands* or energy gaps. However, if the adjacent bands in the solid overlap, then the electrons possess a continuous distribution of allowed energies.

18.1 KRONIG-PENNEY MODEL

LO1

Free electron model ignores the effects those arise when the electrons interact with crystal lattice. However, now we consider this by making some general remarks about the effect of the periodic variation in the potential. Due to this periodicity in potential for an infinitely long lattice, the wave function does not remain sinusoidal travelling waves of constant amplitude but now they include the lattice periodicity in their amplitudes, and electrons may be scattered by the lattice. When the deBroglie wavelength of the electron corresponds to a periodicity in the spacing of the ions, the electron interacts strongly with the lattice. This situation is the same as an electromagnetic wave suffers Bragg's reflection, when the Bragg's condition is satisfied.

In order to find the allowed energies of electrons in solids, we consider the effect of formation of a solid when the individual constituent atoms are brought together. We solve the Schrödinger equation for periodic potential seen by an electron in a crystal lattice. We also consider that the periodic potential is a succession of rectangular wells and barriers. The solution of Schrödinger equation is a sinusoidal wave in certain energy ranges, i.e., allowed states, and real decaying exponential wave in the other ranges, i.e., the forbidden bands. For this purpose, here we present only qualitative approach.

It is found that the potential is not constant but varies periodically. The effect of periodicity is to change the free particle travelling wave eigen function. Therefore, the travelling wave eigen function has a varying amplitude which changes with the period of the lattice. If we consider that the space periodicity is a (Fig. 18.2), then according to Bloch, the eigen function for one-dimensional system has the form

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

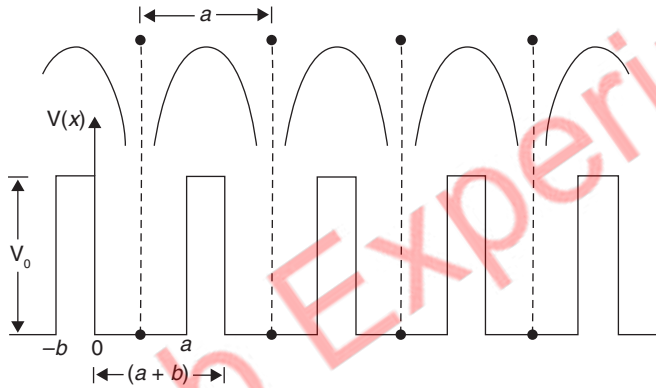


FIGURE 18.2

As is clear, this is different from the free travelling wave function $\psi(x) = Ae^{ikx} \cdot u_k(x)$ is the periodic function with the periodicity a of the periodic potential, i.e.,

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

In general,

$$u_k(x) = u_k(x + na)$$

where n is an integer. Hence, with the effect of periodicity, the complete wave function is

$$\psi(x, t) = u_k(x)e^{i(kx - \omega t)} \quad (i)$$

In the above equation, the exponential term indicates a wave of wavelength $\lambda = \frac{2\pi}{k}$ which travels along $+x$ direction if k is positive and it moves along $-x$ direction if the value of k is negative.

The exact form of the function $u_k(x)$ depends on the particular potential assumed and the value of k .

In 1930, *Kronig and Penney* proposed a one-dimensional model for the shape of rectangular potential wells and barriers having the lattice periodicity, as shown in Fig. 18.2. Each well represents an approximation to the potential produced by one ion. In the region such as $0 < x < a$, the potential energy is assumed to be zero while in the region $-b < x < 0$ or $a < x < (a+b)$, the potential energy is taken as V_0 . The relevant Schrödinger equations for these two regions are

$$\frac{d^2\psi}{dx^2} + \left[\frac{2m}{\hbar^2} \right] E\psi = 0 \quad \text{(ii) } [0 < x < a]$$

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

The electron of not too high energy is practically bound within one of the wells that are deep and widely spaced. So the lower energy eigen values are those of a single well. However, for the wells those are closer together the eigen function can penetrate the potential barriers more easily. Because of this, spreading of previously single energy level into a band of energy levels takes place. The band becomes wider with the decrease in the separation of the wells. Under the limit of zero barrier thickness, we obtain an infinitely wide single well in which all energies are allowed. So the present case is reduced to the free electron model. The comparison between the allowed energies of a single well and an array of wells (Kronig-Penney model) is shown in the Fig. 18.3. In this figure, we have assumed $b = a/16$ and the well strength as $2mV_0a^2/\hbar^2 = 121$. It is clear from the figure that each band corresponds to a single energy level of the single well. The forbidden bands appear even for energies $E > V_0$.

Here we will solve the Schrödinger wave equation for electron for Kronig-Penney potential under the condition that ψ and $\frac{d\psi}{dx}$ are continuous at the boundaries of the well. A complicated expression for the

allowed energies in terms of k shows that gaps in energy are obtained at values such that

$$k = \pm \frac{\pi}{a}, \pm \frac{2\pi}{a}, \pm \frac{3\pi}{a}, \dots \quad \text{(iv)}$$

The solution of the Schrödinger wave equation for free-electrons results in the energy values given by

$$E = \frac{\hbar^2 k^2}{8\pi^2 m} = \frac{\hbar^2 k^2}{2m} \quad \text{(v)}$$

18.1.1 Energy E versus Wave Number k Diagram

From Eq. (v), it is clear that the relation between E and k is parabolic. The parabolic relation between E and k , valid in case of free electrons, is therefore, interrupted at different values of k , as shown in Fig. 18.4. It means the energies corresponding to the values of k given by Eq. (iv) are not permitted for electrons in the crystal. Thus, the energies of electrons are divided into forbidden and allowed bands (Fig. 18.4).

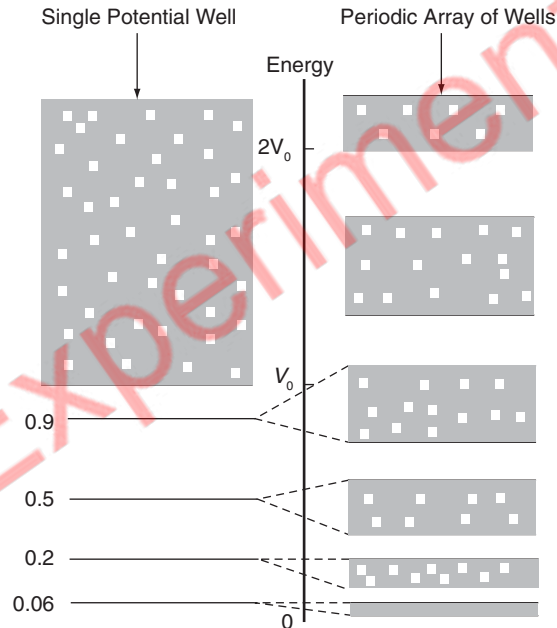


FIGURE 18.3

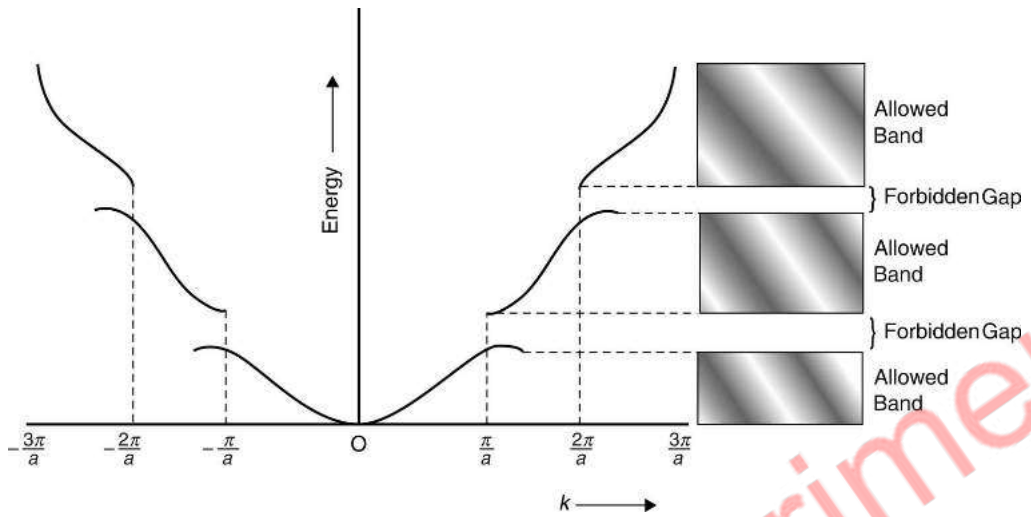


FIGURE 18.4

The occurrence of the gaps can be understood on the basis of Bragg's condition for the diffraction, given as

$$2a \sin \theta = n\lambda \quad n = 1, 2, 3, \dots \quad (\text{vi})$$

where a is spacing between the ions of the lattice and θ is the angle of incidence.

Eq. (vi) can be written as

$$2a = n\lambda \quad (\text{for } \theta = 90^\circ)$$

or
$$2a = n \frac{2\pi}{k}$$

or
$$k = \frac{n\pi}{a} \quad (\text{vii})$$

or
$$k = \pm \frac{\pi}{a}, \pm \frac{2\pi}{a}, \pm \frac{3\pi}{a}, \dots$$

We have put \pm signs because the incident wave can travel along $+x$ -axis as well as along $-x$ -axis. At all these values of k the gaps in energy occur, as shown in Fig. 18.4.

The waves corresponding to values of k satisfying the Bragg's condition are reflected and resulted in standing waves. On each subsequent Bragg reflection, the direction in which the wave is travelling is reversed again. The eigen function of incident and corresponding reflected waves for $k = \pm n \frac{\pi}{a}$ are therefore $e^{i(\pi/a)x}$ and $e^{-i(\pi/a)x}$. These two eigen functions can be combined in two different ways to give total eigen function

$$\psi_1 = e^{i(\pi/a)x} + e^{-i(\pi/a)x} = \cos(\pi/a)x$$

$$\psi_2 = e^{i(\pi/a)x} - e^{-i(\pi/a)x} = \sin(\pi/a)x$$

or
$$\psi_1 \propto \cos(\pi/a)x \quad (\text{viii})$$

and
$$\psi_2 \propto \sin(\pi/a)x \quad (\text{ix})$$

Hence, the two standing waves are obtained. The probability density curves for these two stationary waves, i.e., $|\psi_1|^2$ and $|\psi_2|^2$, are shown in Fig. 18.5. From this figure and Eq. (viii) it is clear that the value of $|\psi_1|^2$ is maximum at the positions of positive ions (i.e., $x = 0, \pm a, \pm 2a, \dots$). The value of $|\psi_2|^2$ is maximum in between the position of the ions. From Fig. 18.2, it is evident that the potential energy of an electron is maximum between the ions and minimum at the positions of the ions. So an electron can have two different values of energies, i.e., E_1 and E_2 for $k = \frac{\pi}{a}$ corresponding to the two standing waves ψ_1 and ψ_2 . Hence, no electron can have any energy between E_1 and E_2 . This phenomenon creates a difference in energy ($E_1 \sim E_2$) which is known as *energy gap*.

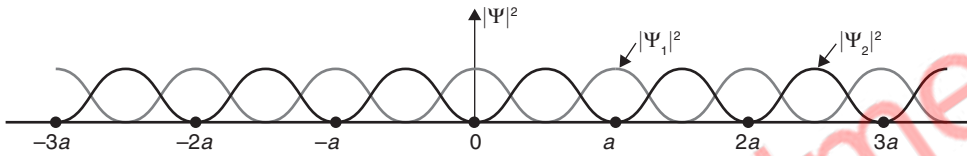


FIGURE 18.5

18.2 ONE-AND TWO-DIMENSIONAL BRILLOUIN ZONES

LO1

In Kronig-Penney model, we have seen that the discontinuities in energy occurs when the wave number k satisfies the condition $k = n\pi/a$, where n takes the values $\pm 1, \pm 2, \pm 3, \dots$ etc. The graph between the total energy E and wave number k is shown in Fig. 18.4. It is clear from the figure that an electron has allowed energy values in the region between $-\pi/a$ to $+\pi/a$. This region is called the first Brillouin zone. As discussed earlier, there is a discontinuity of gap in the energy values after this allowed energy value. This gap is called forbidden gap or forbidden zone. Again there is another allowed energy zone, which is observed after this forbidden gap and is extended from $-\pi/a$ to $-2\pi/a$ and π/a to $2\pi/a$. This zone is called second Brillouin zone. Similarly, the other higher order Brillouin zones can be defined.

The first two Brillouin zones in one-dimensional case are shown in Fig. 18.6. We can extend the concept of the Brillouin zones to two-dimension by considering that the electron is moving in the two-dimensional square lattice. In this case, the wave number k has the two components, i.e., along the x -axis and y -axis. Let us represent them as k_x and k_y , respectively. The two-dimensional Brillouin zones are shown in Fig. 18.7. It can be seen that $k_x = k_y = \pm\pi/a$ limits the first Brillouin zone. In the figure, the first Brillouin zone is represented by a square passing through the points A, B, C and D . The second Brillouin zone for a two-dimensional lattice is represented by a square passing through E, F, G and H .

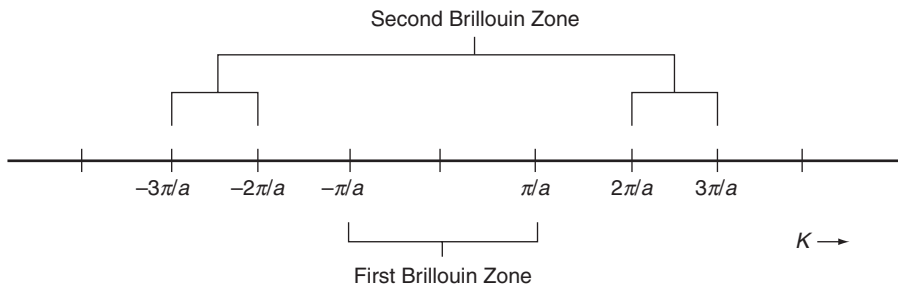


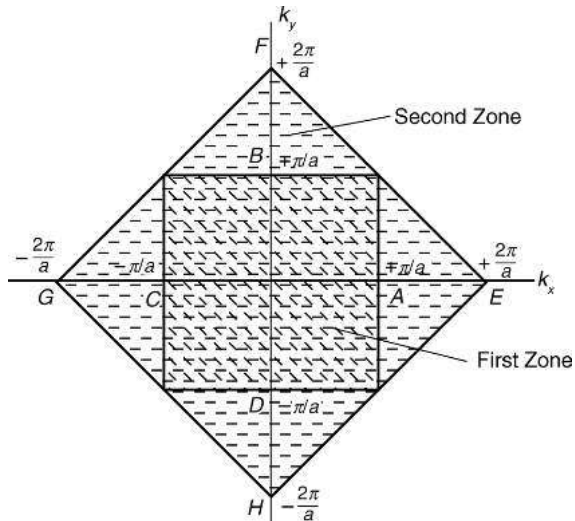
FIGURE 18.6

It is clear that the boundary for the second zone is given by $k_x = \pm 2\pi/a$ and $k_y = \pm 2\pi/a$. Thus the region between the squares $ABCD$ and $EFGH$ is called the second Brillouin zone.

18.3 EFFECTIVE MASS OF AN ELECTRON

LO2

The electrons in a crystal are not completely free but interact with the crystal lattice. As a result, their behaviour towards external forces is different from that of a free electron. The deviation of electron behaviour in the crystal lattice from the free electron behaviour can be taken into account simply by considering the electron to have an altered value of mass called the 'effective mass' m^* rather than its



18.4

DISTINCTION BETWEEN INSULATORS, SEMICONDUCTORS AND CONDUCTORS (METALS)

LO3

The formation of bands in solids has already been discussed and it was shown that there is an energy gap, called forbidden band, representing energies which the electrons cannot occupy. Based on this energy gap and the conduction, the solids are classified into different categories named as insulators, semiconductors and conductors.

18.4.1 Insulators

For these types of solids, the band formation is like the one shown in Fig. 18.8a. In this case, the forbidden gap between the highest filled band (valence band) and the lowest empty band (conduction band) is very wide; it is about 3 eV to 6 eV. It is seen that a very few electrons from the filled band reach the empty band, even if we thermally excite them or apply an electric field to them. Moreover, Pauli exclusion principle restricts the electrons for moving about in the filled band. For this reason, a free electron current cannot be obtained and the solids of this type are poor conductors of electricity. This class of solid is known as insulators. Diamond, quartz, and most covalent and ionic solids like ZnO and AgCl are the examples of insulators.

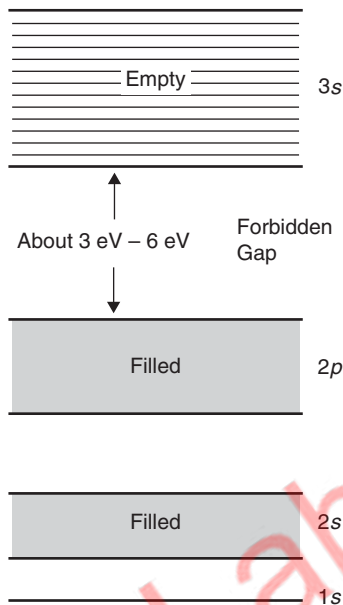


FIGURE 18.8a

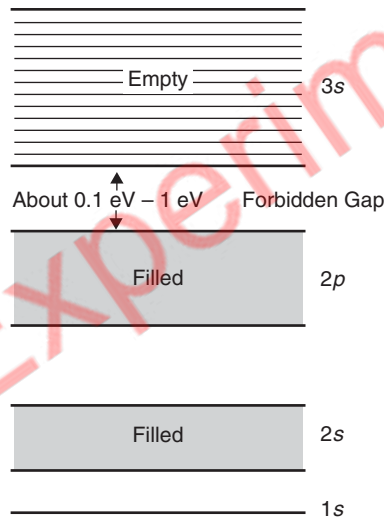


FIGURE 18.8b

18.4.2 Semiconductors

For these types of solids the band formation is like the one shown in Fig. 18.8b. In this case, the forbidden gap between the highest filled band (valence band) and the lowest empty band (conduction band) is very narrow; it is about 0.1 eV to 1 eV. Under this situation we can easily move the electrons from the highest filled band to the empty band. This can be achieved by thermal excitation or also by applying an electric field. For this reason, a free electron current can be obtained as a few electrons are available in the empty band. This class of solids is known as semiconductors. Silicon and germanium are the examples of semiconductors.

In semiconductors, there also exists another mechanism that causes the generation of electric current. Actually there are vacancies or the empty places left behind when the electron moves, which remain near the top of the uppermost filled band. These vacancies are called holes. The holes behave as positive electrons and can contribute to the generation of electric current. This is possible as the electron below the hole may gain enough energy to jump and occupy the hole due to the applied electric field. With such successive jumps of the electrons, the hole moves towards the lower energy state and contribute to the generation of electric current.

The semiconductors are mainly of two types, defined below.

18.4.2.1 *n*-type Semiconductors

The *n*-type semiconductors are the ones in which the electron conduction (negative) exceeds the hole conduction (positive). In such semiconductors, the donor impurity predominates. This can be understood if we introduce a small amount of phosphorous (*P*) or arsenic (*As*), i.e., an element of fifth group of the periodic table, as an impurity into a crystal of silicon (*Si*) or germanium (*Ge*). This addition of *P* or *As* means replacing an atom of *Si* or *Ge* at a lattice site by an atom of the impurity. Atoms of fifth group elements have five valence electrons whereas *Si* or *Ge* has four valence electrons. So four electrons of *P* or *As* form covalent bonds with the electrons of the atoms of *Si* or *Ge*. However, the fifth electron remains only very weakly bound to the *P* or *As* atom by electrostatic forces and this cannot be accommodated in the already filled original valence band. So, it occupies a discrete energy level which is just below the conduction band (with only a few tenths of an *eV*). Hence these extra electrons jump easily into the conduction band and contribute to the electric conductivity in addition to the electron hole pairs produced by thermal excitation of the pure semiconductor. This way the number of electrons sits more than holes to serve as charge carriers.

18.4.2.2 *p*-type Semiconductors

The *p*-type semiconductors are the one in which the hole conduction (positive) exceeds the electron conduction (negative). In such semiconductors, the acceptor impurity predominates. This can be understood if we introduce a small amount of *Al*, *Ga* or *In*, i.e., an element of third group of the periodic table, as an impurity into a crystal of silicon (*Si*) or germanium (*Ge*). Atoms of third group elements have three valence electrons whereas *Si* or *Ge* has four valence electrons. So three electrons of *Al* or *Ga* form covalent bonds with the electrons of the atoms of *Si* or *Ge*. However, the fourth available electron of the semiconductor lacks an electron with which it can form a bond. This is equivalent to as if a vacancy or hole has been created at the site of the impurity atom. Hence, the impurity atoms introduce vacant discrete energy levels very near the top of completely filled valence band of *Si* or *Ge*. So these extra holes move from an impurity atom. These holes behave as positive charge carriers and are available in excess. Since the crystals of this type have an excess of positive charge carriers, they are called positive semiconductors or *p*-type semiconductors.

18.4.3 Conductors or Metals

For these types of solids, the band formation is like the one shown in Fig. 18.8c. In this case, the valence band is either partially filled or the next allowed empty band overlaps with the filled band. In both the cases, there are unoccupied states for electrons in the uppermost band. So these electrons are available to generate the current. This class of solids is known as conductors. The conductors offer a low resistance to

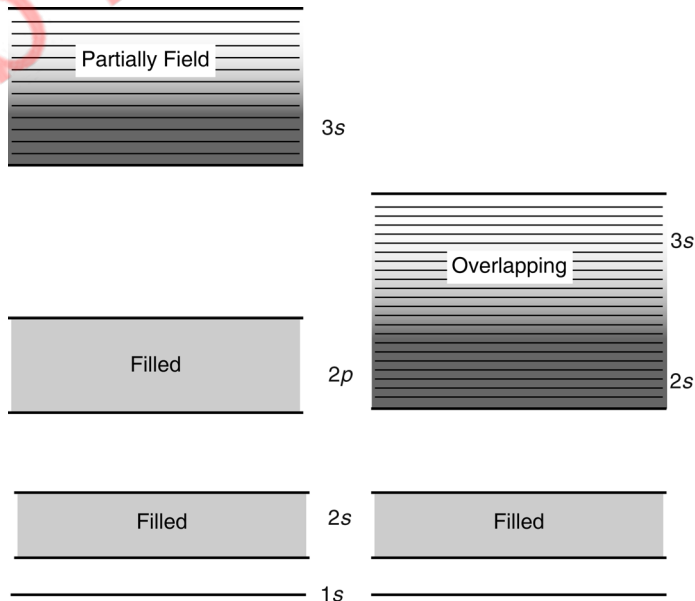


FIGURE 18.8c

18.5.4 Energy Band Diagram and Fermi Level

In an intrinsic semiconductor, the electrons and holes are always generated in pairs, i.e., $n = p = n_i$. Substituting the values of n and p from Eqs. (vi) and (vii) of the previous sections, we get

$$2 \left[\frac{2\pi m k T}{h^2} \right]^{3/2} e^{(E_F - E_C)/kT} = 2 \left[\frac{2\pi m_h k T}{h^2} \right]^{3/2} e^{(E_V - E_F)/kT}$$

$$e^{(2E_F - E_C - E_V)/kT} = \left(\frac{m_h}{m} \right)^{3/2}$$

r 6

Taking the logarithm of both sides

$$\frac{2E_F - E_C - E_V}{kT} = \frac{3}{2} \ln \left(\frac{m_h}{m} \right)$$

r 6

$$2E_F - E_C - E_V = \frac{3}{2} kT \ln \left(\frac{m_h}{m} \right)$$

r 6

$$E_F = \frac{E_C + E_V}{2} + \frac{3}{4} kT \ln \left(\frac{m_h}{m} \right)$$

If the effective mass of hole and a free electron is the same i.e., $m_h = m$, then

$$E_F = \frac{E_C + E_V}{2}$$

This shows that the Fermi level E_F lies exactly in the centre of the forbidden energy gap E_g as depicted in Fig. 18.9. The Fermi level can also be defined as the energy level at which there is a 0.5 probability of finding an electron. It depends on the distribution of energy levels and the number of electrons available.

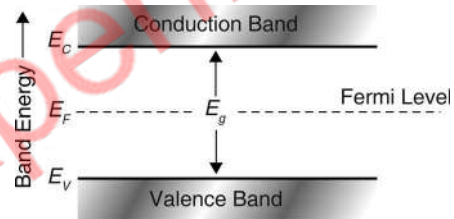


FIGURE 18.9

18.6 EXTRINSIC SEMICONDUCTOR

LO4

The conductivity of an intrinsic semiconductor can be increased significantly by adding certain impurities to it. By doing so, we get impurity semiconductor which is also known as extrinsic semiconductor. In extrinsic semiconductors, current carriers are introduced by donor and acceptor impurities with locked energy levels near the top or bottom of the forbidden gap.

18.6.1 Energy Band Diagram and Fermi Level

(i) *n*-type Extrinsic Semiconductor

When a small amount of pentavalent impurity is added to the crystal, it creates extra electrons without adding any new holes. This impurity introduces new energy levels into the energy band picture. The location of these new levels is slightly below the bottom of the conduction band for intrinsic semiconductor. The width of the gap for germanium was previously stated as 0.72 eV. The energy required to move an electron from a donor impurity into the conduction band is of the order of 0.01 eV, and since at normal ambient temperature the thermal energy is considered to be about 0.02 eV, it is concluded that almost all the electrons are detached from the donor atoms and have conduction band energies. In the case of silicon doped with donor impurities, the energy required to move an electron from donor impurity into the conduction band is of the order of 0.05 eV. The energy band diagram for an *n*-type semiconductor is shown in Fig. 18.10. Here E_g represents the energy level corresponding to donor impurities.

In intrinsic semiconductor, Fermi level lies in the middle of the forbidden energy E_g indicating equal concentrations of free electrons and holes. When a donor type impurity is added to the crystal, then if we assume that all the donor atoms are ionised, the donor electrons will occupy the states near the bottom of the conduction band. Hence, it will be more difficult for the electrons from the valence band to cross the energy gap by thermal agitation. Consequently, the number of holes of the valence band is decreased. Since Fermi level is a measure of the probability of occupancy of the allowed energy states, E_F for n -type semiconductors must move closer to the conduction band, as shown in Fig. 18.10. At usual temperatures all the donor levels will be fully activated and the donor atoms will be ionised. It means the density of electrons in the conduction band will be approximately equal to the density of donor atoms, i.e., $n \approx N_d$ (N_d being the density of donor atoms). Then from Eq. (vi), we have

$$\begin{aligned} n &= N_d = 2 \left[\frac{2\pi mkT}{h^2} \right]^{3/2} e^{(E_F - E_C)/kT} \\ &= N_c e^{(E_F - E_C)/kT} \end{aligned}$$

where $N_c = 2 \left[\frac{2\pi mkT}{h^2} \right]^{3/2} = \text{constant}$

$$\frac{N_c}{N_d} = e^{-(E_F - E_C)/kT}$$

Taking the logarithm of both the sides

$$\ln \frac{N_c}{N_d} = - \frac{E_F - E_C}{kT}$$

or $E_F = E_C - kT \ln \frac{N_c}{N_d}$

It shows that the Fermi level lies below the bottom of the conduction band, as shown in Fig. 18.10.

(ii) *p-type Extrinsic Semiconductor*

When an acceptor-type impurity is added, it also modifies the energy level diagram of semiconductor and makes the conduction easier. The presence of impurity creates new energy levels which are in the gap in the neighbourhood of the top of valence band of energies, as shown in Fig. 18.11. Ambient temperature results in ionisation of most acceptor atoms and thus an apparent movement of holes takes place from the acceptor levels to the valence band. The energies for holes are highest near the valence band and decrease vertically upward in the energy level diagram. Alternatively, one may say that electrons are accepted by the acceptors and these electrons are supplied from the valence band, thus leaving a preponderance of holes in the valence band.

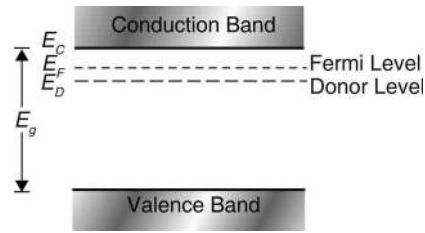


FIGURE 18.10

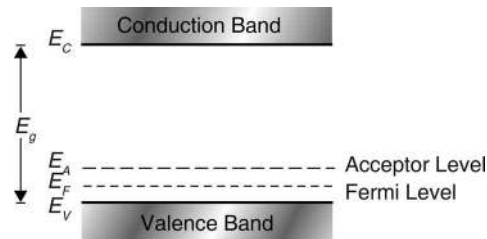


FIGURE 18.11

The energy band diagram for a p -type semiconductor is shown in Fig. 18.11 where E_A represents the energy level corresponding to the acceptor impurity. When an intrinsic semiconductor is doped with acceptor type impurity, the concentration of holes in the valence band is more than the concentration of electrons in the conduction band and the Fermi level shifts towards the valence band, as shown in Fig. 18.11. The acceptor level lies immediately above the Fermi level.

If we assume that there are only acceptor atoms present and that these are all ionised, we have $p = N_a$. Then from Eq. (vii), we get

$$p = N_a = 2 \left[\frac{2\pi m_h kT}{h^2} \right]^{3/2} e^{(E_V - E_F)/kT}$$

$$= N_v e^{(E_V - E_F)/kT}$$

where $N_v = 2 \left[\frac{2\pi m_h kT}{h^2} \right]^{3/2} = \text{constant}$

$$\approx \frac{N_v}{N_a} = e^{-(E_V - E_F)/kT}$$

Taking logarithm of both the sides,

$$\ln \frac{N_v}{N_a} = - \frac{E_V - E_F}{kT}$$

or

$$E_F = E_V + kT \ln \frac{N_v}{N_a}$$

It shows that the Fermi level lies above the top of valence band, as shown in Fig. 18.11.

EXAMPLE 1 Consider two-dimensional square lattice of side 3.0 \AA . At what electron momentum values do the sides of first Brillouin zone appear? What is the energy of free electron with this momentum?

SOLUTION Given $a = 3.0 \times 10^{-10} \text{ m}$.

Formula used for momentum of electron

$$p = \hbar k$$

For first Brillouin zone $k = \pm \frac{\pi}{a}$, then

$$p = \frac{\hbar \pi}{2a} = \frac{h \pi}{2a} = \frac{1.054 \times 10^{-34}}{2 \times 3 \times 10^{-10}}$$

$$= 1.76 \times 10^{-24} \text{ kg m/s}$$

$$E = \frac{p^2}{2m} = \frac{(1.76 \times 10^{-24})^2}{2 \times 9.1 \times 10^{-31}}$$

$$= 1.76 \times 10^{-1} \text{ eV}$$

$$= \mathbf{4.155 \text{ eV}}$$

EXAMPLE 2 Find the position of Fermi level E_F at room temperature ($= 27^\circ\text{C}$) for germanium crystal having $5 \times 10^{22} \text{ atoms/m}^3$.

SOLUTION Given $T = 27^\circ\text{C} = 300 \text{ K}$ and $n_C = 5 \times 10^{22} \text{ per m}^3$

Formula used is

$$n_C = 2 \left(\frac{2\pi m k T}{h^2} \right)^{3/2} e^{(E_F - E_C)/kT}$$

$$e^{(E_F - E_C)/kT} = \frac{n_C}{2 \left(\frac{2\pi m k T}{h^2} \right)^{3/2}}$$

$$e^{(E_F - E_C)/kT} = \frac{10^{22}}{2 \left[\frac{2 \times 3.14 \times 1 \times 10^{-31} \times 1.381 \times 10^{-23} \times 300}{(1.054 \times 10^{-34})^2} \right]^{3/2}}$$

$$= \frac{10^{22}}{2 \times 1.1 \times 10^{24}}$$

$$e^{-(E_C - E_F)/kT} = 0.1 \quad 1 \quad 10^{-2}$$

$$e^{(E_C - E_F)/kT} = 10 \quad 0.2 \quad 2 \quad 1 \quad r6 \quad E_C - E_F = 0.2 \quad 2 \quad 1$$

$$\frac{E_C - E_F}{kT} = 6.2192 \quad r6 \quad E_C - E_F = 0.161 \text{ eV}$$

EXAMPLE 3 Consider the Fermi level 0.3 eV below the conduction band at room temperature ($=27^\circ\text{C}$) in an n -type semiconductor. If the temperature is raised to 57°C , what would be the new position of Fermi level?

SOLUTION Given $E_C - E_F = 0.3 \text{ eV}$, $T_1 = 27^\circ\text{C} = 300 \text{ K}$ and $T_2 = 57^\circ\text{C} = 330 \text{ K}$.

Formula used is

$$E_F = E_C - kT \ln\left(\frac{N_c}{N_d}\right)$$

$$E_C - E_F = kT \ln\left(\frac{N_c}{N_d}\right)$$

At temperature T_1 , $E_C - E_F = kT_1 \ln\left(\frac{N_c}{N_d}\right)$

At temperature T_2 , $E_C - E'_F = kT_2 \ln\left(\frac{N_c}{N_d}\right)$

$$\frac{E_C - E'_F}{E_C - E_F} = \frac{T_2}{T_1}$$

or $E_C - E'_F = \frac{T_2}{T_1}(E_C - E_F)$

$$= \frac{330}{300} \times 0.3 \text{ eV}$$

$$= 0.33 \text{ eV}$$

EXAMPLE 4 For an intrinsic semiconductor having band gap $E_g = 0.7 \text{ eV}$, calculate the density of holes and electrons at room temperature ($= 27^\circ\text{C}$).

SOLUTION Given $E_g = 0.7 \text{ eV}$.

In intrinsic semiconductor, the concentration of electrons and holes are same. So

$$n_e = n_h = 2 \left[\frac{2\pi kTm}{h^2} \right]^{3/2} e^{(E_F - E_C)/kT}$$

The Fermi level lies exactly in the middle of conduction and valence band.

$$E_F = \frac{E_C + E_V}{2}$$

$$E_F - E_C = \frac{E_C + E_V}{2} - E_C = -\frac{(E_C - E_V)}{2} = -\frac{E_g}{2}$$

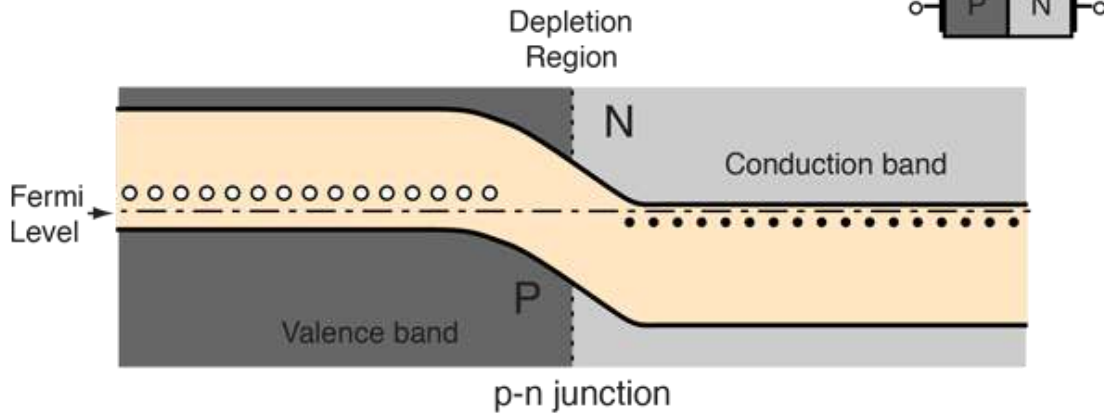
\approx

$$\begin{aligned}n_e = n_h &= 2 \left[\frac{2\pi k T m}{h^2} \right]^{3/2} e^{-E_g/2kT} \\&= 2 \left[\frac{2 \cdot 3.14 \cdot 1.38 \cdot 10^{-23} \cdot 300}{1.112 \cdot 10^{-34}} \cdot 1 \cdot 10^{-31} \right]^{3/2} e^{-\left[\frac{0}{2 \cdot 0.021} \right]} \\&= \mathbf{3.6 \cdot 10^{19} \text{ per m}^3}\end{aligned}$$

For a p-n junction at equilibrium, the fermi levels match on the two sides of the junctions. Electrons and holes reach an equilibrium at the junction and form a depletion region. The upward direction in the diagram represents increasing electron energy. That implies that you would have to supply energy to get an electron to go up on the diagram, and supply energy to get a hole to go down.

Band Structure of P-N Junction:

- at equilibrium
- reverse biased
- forward biased

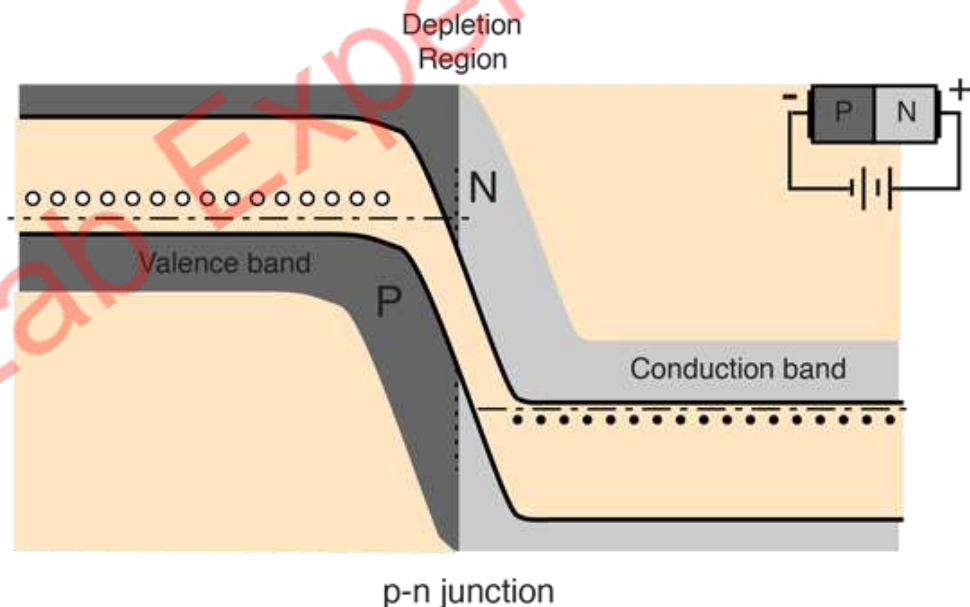


P-N Energy Bands

To reverse-bias the p-n junction, the p side is made more negative, making it "uphill" for electrons moving across the junction. The conduction direction for electrons in the diagram is right to left, and the upward direction represents increasing electron energy.

Band Structure of P-N Junction:

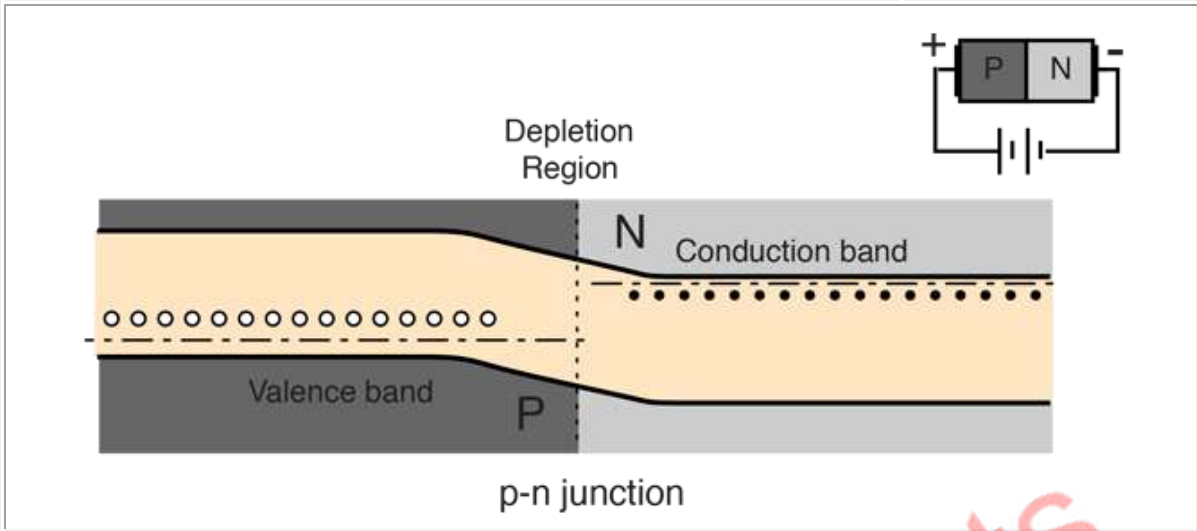
- at equilibrium
- reverse biased
- forward biased



To forward bias the p-n junction, the p side is made more positive, so that it is "downhill" for electron motion across the junction. An electron can move across the junction and fill a vacancy or "hole" near the junction. It can then move from vacancy to vacancy leftward toward the positive terminal, which could be described as the hole moving right. The conduction direction for electrons in the diagram is right to left, and the upward direction represents increasing electron energy.

Band Structure of P-N Junction:

- at equilibrium
- reverse biased
- forward biased



Forward Biased Conduction

When the p-n junction is forward biased, the electrons in the n-type material which have been elevated to the conduction band and which have diffused across the junction find themselves at a higher energy than the holes in the p-type material. They readily combine with those holes, making possible a continuous forward current through the junction.

Band Structure of P-N Junction:

- at equilibrium
- reverse biased
- forward biased

