

CRYSTAL STRUCTURE

1.1 INTRODUCTION

The solid state physics is the branch of physics dealing with physical properties of solids. A solid consists of particles (atoms, ions or molecules) or group of particles arranged in close proximity. The constituent atoms or molecules in solids are attached to one another with strong forces of attraction and hence, solids maintain a definite volume and shape. The solids may be broadly classified as crystals and amorphous solids. In amorphous solids the arrangement of particles is random while the crystals are the solids in which component atoms or ions or molecules are arranged in a regular and periodic manner. Most of the solids are crystalline in nature because the energy released during the formation of an ordered state is more than the energy released during the formation of a disordered structure (or state). Hence, crystalline state is low energy state and is, therefore, preferred by most solids in nature. The arrangement of atoms or ions or molecules in a crystal is known as *crystal structure*. The crystal structure can be described with the help of simple concepts of lattice, unit cell, basis and translation vectors.

1.2 SPACE LATTICE AND TRANSLATION VECTORS

To describe arrangement of particles in a crystal, it is very convenient to imagine points in the space about which these particles are located. These imaginary points are called *lattice points*. This set of imaginary points forms a framework upon which the actual crystal structure is based and this framework of imaginary points is known as *space lattice* or *crystal lattice* or simply *lattice*. Therefore, space lattice may be defined as a regular periodic arrangement of infinite number of imaginary points in three dimensional space in which each point has identical surrounding. The term 'identical surrounding' means that the lattice has same appearance when viewed from a point in the lattice. When all the atoms at lattice points are of same kind, then lattice is called *Bravais lattice*.

To understand concept of translation vectors, consider a part of two dimensional lattice as shown in Fig. 1.1. It is clear from the figure that the environment (or surrounding) about a point is identical with the environment around any other point in the lattice.

Choose any arbitrary lattice point, 'O' as origin. Consider two different lattice points defined by position vectors \vec{r} and \vec{r}' from the origin 'O' as shown in the figure. Also consider \vec{a} and \vec{b} as translation vectors. Then the point \vec{r}' can be obtained from point \vec{r} using the translation operation T given by

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

where n_1 and n_2 are arbitrary integers and the vectors \vec{a} and \vec{b} are known as fundamental translation vectors. i.e. the two

locations \vec{r} and \vec{r}' are related with each other by the equation

$$\vec{r}' = \vec{r} + \vec{T} = \vec{r} + n_1 \vec{a} + n_2 \vec{b}$$

Similarly, two locations \vec{r} and \vec{r}' in 3-dimensional lattice are related as:

$$\text{where } \vec{T} = n_1 \vec{a} + n_2 \vec{b} + n_3 \vec{c} \text{ is called translation operation.}$$

Hence,

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

Here, n_1, n_2, n_3 are arbitrary integers and $\vec{a}, \vec{b}, \vec{c}$ are translation vectors. These are also known as primitive vectors or crystal axes. These vectors are along three directions x, y and z known as crystallographic axes with respect to any lattice point as the origin. Clearly, we can say that with the help of translation vectors we translate or reach any lattice point from the other lattice point. In cubic crystal, translation vectors may be three adjacent edges of a cube.

1.3 UNIT CELL

It is the convenient smallest block or geometrical figure of a crystal lattice which when repeated again and again regularly along three definite directions in the space, generates the complete lattice. For a three dimensional lattice, the unit cells are of the form of a parallelopiped. The choice of the unit cell is not unique. According to the requirement of the case, either a primitive or a non primitive cell or block, can be selected as a unit cell. The parallelopiped defined by translation vectors $\vec{a}, \vec{b}, \vec{c}$ as the shortest possible sides along three crystallographic axes x, y and z is called primitive

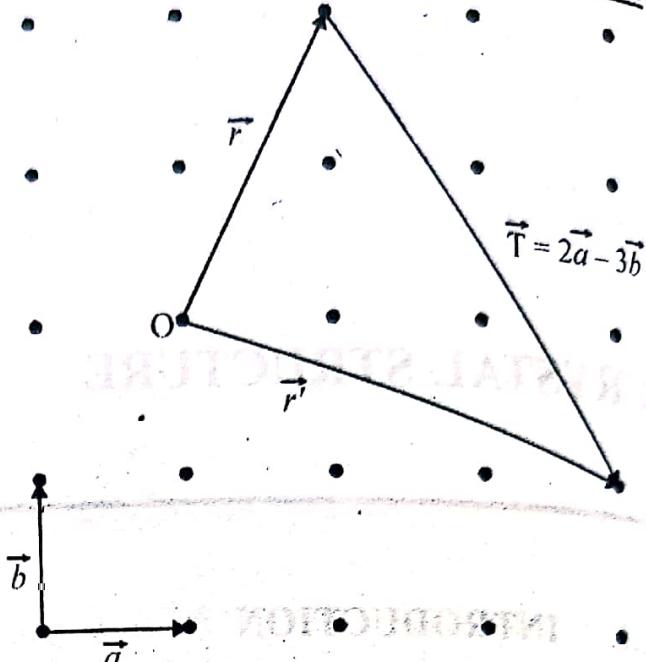


Fig. 1.1 Two dimensional lattice and translation vectors

unit cell. A primitive unit cell is a minimum volume unit cell (Fig. 1.2) and has lattice points only at its corners. Hence, A unit cell is described by six parameters out of which there are three primitive vectors \vec{a} , \vec{b} , \vec{c} and the other three are angles α, β, γ . The angles between primitives $(\vec{b}, \vec{c}), (\vec{c}, \vec{a}), (\vec{a}, \vec{b})$ are denoted as α, β, γ respectively.

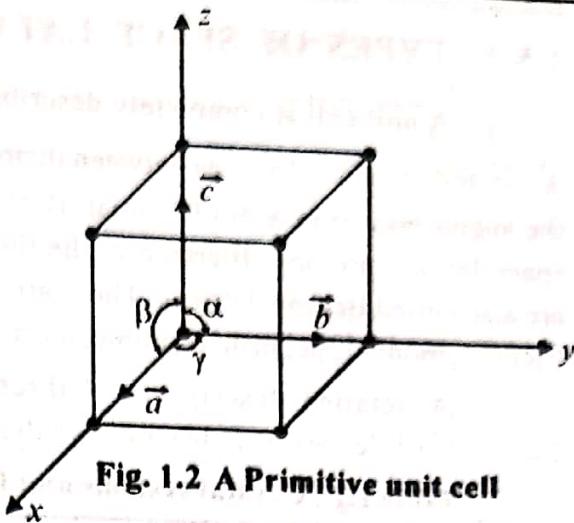


Fig. 1.2 A Primitive unit cell

Unit cell is the smallest volume of the crystal which characterizes the arrangements and positions of atoms. It se-

The volume of a primitive unit cell having \vec{a} , \vec{b} , \vec{c} as the translation vectors is given by $V = |\vec{a} \cdot (\vec{b} \times \vec{c})|$

Hence primitive unit cell has (i) smallest volume (ii) points only at its corners i.e. the effective number of lattice points in it is only one.

1.4 BASIS

The space lattice is an array of infinite number of imaginary points which are so arranged that each point has identical surroundings. The crystal structure is actually described in terms of particles rather than points. So, in order to obtain a crystal structure, particle or group of particles (atoms, ions or molecules) must be associated with each lattice point. Such a particle or group of particles is known as basis. The basis acts actually as a building unit or structural unit for the complete crystal structure. Thus a space lattice combined with a basis, generates the crystal structure. Mathematically, it is expressed as:

Clearly, space lattice is a mathematical concept and the crystal structure is a physical concept. Formation of crystal structure from a 2-dimensional lattice and basis is shown in Fig. 1.3. Here basis consists of two particles. The crystal structure is achieved by locating basis on each lattice point. The number of particles in a basis may vary from one to many. The two particles in basis are represented by O and * as shown in the Fig. 1.3.

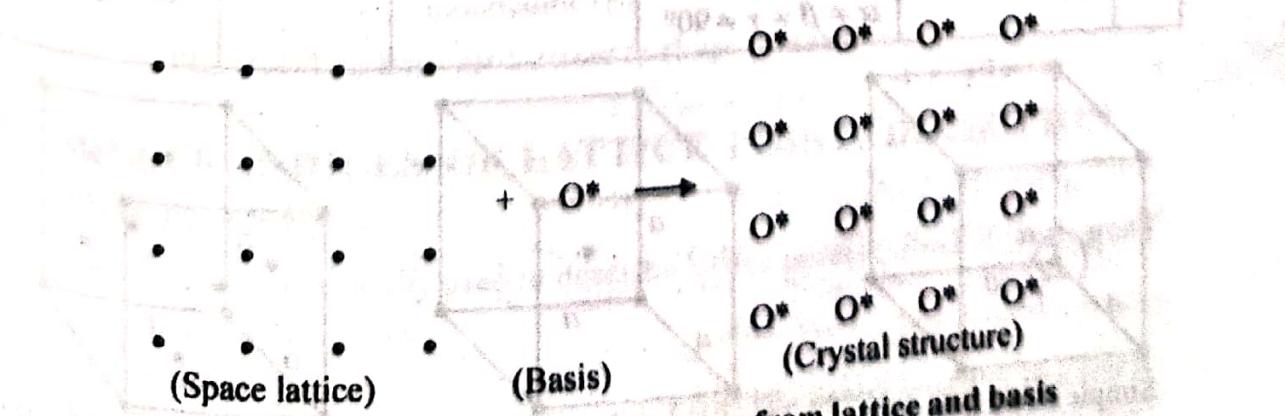


Fig. 1.3 Generation of Crystal Structure from lattice and basis

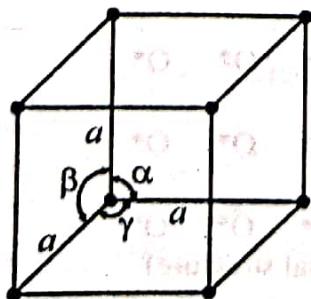
1.5 TYPES OF SPACE LATTICES OR CRYSTAL SYSTEMS

A unit cell is completely described by three primitive translation vectors \vec{a} , \vec{b} , \vec{c} and interfacial angles between them α , β and γ . The primitives \vec{a} , \vec{b} , \vec{c} and the angles may or may not be equal. Bravais showed that the total number of different space lattices are only fourteen in the three dimensions. After Bravais, space lattices are also called Bravais lattices. These are divided into seven crystal systems. These are triclinic, monoclinic, orthorhombic, tetragonal, trigonal, hexagonal and cubic.

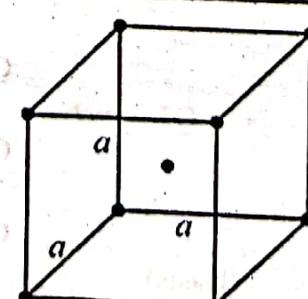
A detailed description of three dimensional Bravais lattices is given in Table 1.1, while they have been shown diagrammatically in Fig. 1.4.

Table 1.1 : Crystal systems and Bravais lattices in three dimensions

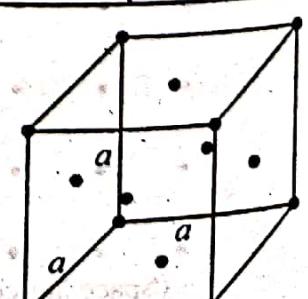
S. No.	Crystal System	Lattice Parameters Axes & Angles	Bravais Lattice	Common Abbreviation	Examples
1.	Cubic	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	Simple	sc	Cu, Ag, Fe,
2.	Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	Body-centred	bcc	Na, NaCl,
3.	Orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	Face-centred	fcc	CsCl
4.	Rhombohedral or Trigonal	$a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$	Simple	st	β -Sn, TiO_2
5.	Hexagonal	$a = b \neq c$ $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$	Body-centred	bct	Ga,
6.	Monoclinic	$a \neq b \neq c$ $\alpha = \gamma = 90^\circ \neq \beta$	End-centred	so	Fe_3C
7.	Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$	Face-centred	bco	(cementite)
			Simple	eco	
			Simple	fco	
			—	—	As, Sb, Bi
			—	—	Mg, Zn, Cd,
			—	—	NiAs
			—	—	$CaSO_4 \cdot 2H_2O$
			—	—	(gypsum)
			—	—	$K_2Cr_2O_7$



Simple cubic (P)



Body - centred cubic (I)



Face - centred cubic (F)

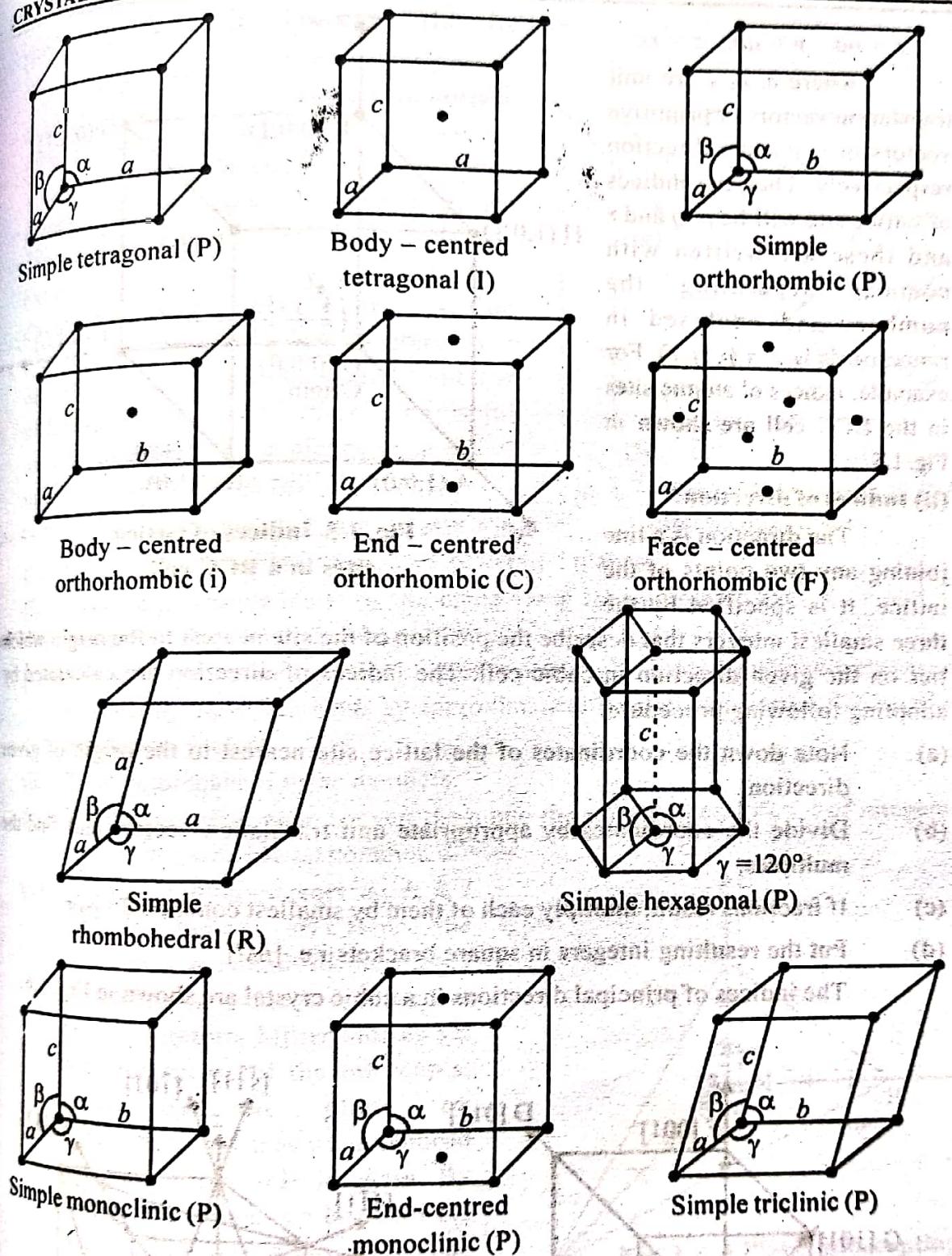


Fig. 1.4 The Bravais lattices in three dimensions

1.6

MILLER INDICES OF LATTICE POINT, DIRECTION AND PLANES

A notation conventionally used to describe lattice points (sites), direction and planes is known as Miller indices.

(i) Point (site) indices:

We will confine our study to cubic system here. The position of a lattice site is described by three coordinates x, y, z which can be expressed as

$x = pa, y = qb, z = rc$
 where a, b, c are unit translation vectors or primitive vectors in x, y and z direction respectively. Then the indices of lattice site will be p, q and r and these are written with commas separating the numbers and enclosed in parenthesis i.e. as (p, q, r) . For example, indices of atomic sites in the BCC cell are shown in Fig. 1.5.

(ii) Indices of direction:

The direction is a line joining any two points of the lattice. It is specified by the three smallest integers that describe the position of the site nearest to the origin which lies on the given direction in cubic cell. The indices of direction are calculated by adopting following procedure:

- Note down the coordinates of the lattice site nearest to the origin of given direction.
- Divide the coordinates by appropriate unit translation vectors and find the multiples.
- If fractions result, multiply each of them by smallest common divisor.
- Put the resulting integers in square brackets i.e. $[hkl]$.

The indices of principal directions in a cubic crystal are shown in Fig. 1.6.

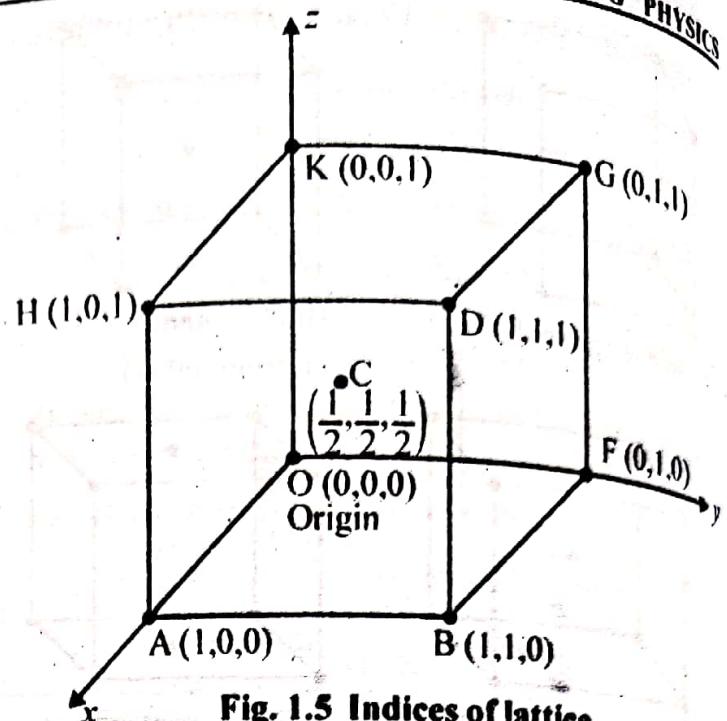


Fig. 1.5 Indices of lattice sites in a BCC cell

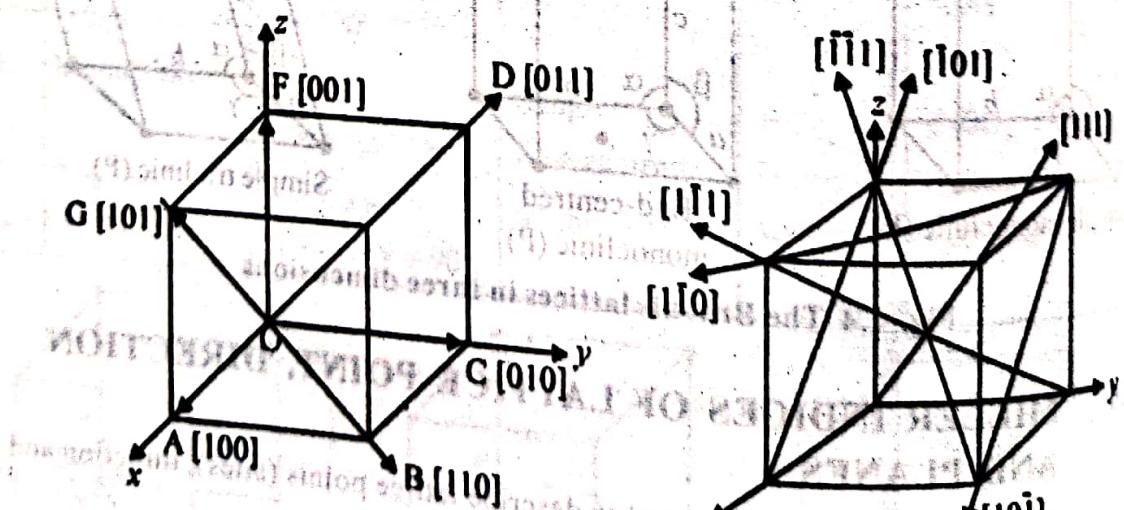


Fig. 1.6 (a) Indices of directions

It should be noted that a negative component is denoted by a minus sign placed above the index.

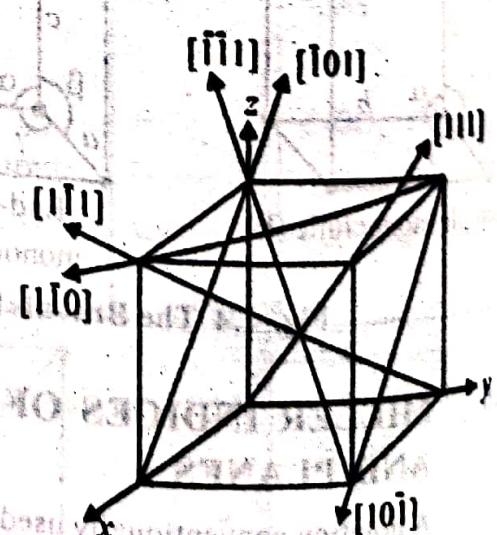


Fig. 1.6 (b) Indices of directions

(iii) Crystal lattice Planes and Miller Indices:

A crystal lattice may be considered as an aggregate of a set of parallel equidistant planes passing through the lattice points. Those equidistant planes are known as lattice planes. For a given lattice, these sets of planes can be selected in a number of ways for examples (a), (b), (c), (d) etc. in two dimensional lattice shown in Fig. 1.7. The spacing between the successive planes and density of lattice points is different for different sets of planes. There is an useful method to design these planes by a set of three integers known as Miller indices.

The following steps are involved in determination of Miller indices of a set of parallel planes.

- (i) Find the intercepts made by the plane along the coordinate axes X, Y and Z in terms of lattice parameters or primitives.
- (ii) Express the intercepts as the multiples of primitive vectors (or unit cell dimensions) by dividing these intercepts by approximate unit cell dimensions or by lengths of translation vectors.
- (iii) Take reciprocals of these numbers.
- (iv) If fractions result, then convert them into the smallest possible set of integers by multiplying with lowest common divisor.
- (v) Put the resulting integers say h, k, l into parenthesis as (hkl) . Hence, the required planes and all the planes parallel to the plane is specified as (hkl) . Therefore, Miller indices are the reciprocals of the intercepts, made by the plane on crystallographic axes when reduced to smallest possible integers. By taking reciprocals, we bring all the planes in a single unit cell. The following example explains these steps. Fig. 1.8 shows a plane ABC having intercepts $6a, 4b$ and $3c$ on x, y and z axes respectively.

Intercepts:

$6a \quad 4b \quad 3c$

Multiples:

$6 \quad 4 \quad 3$

Reciprocals:

$\frac{1}{6} \quad \frac{1}{4} \quad \frac{1}{3}$

After clearing fractions:

$\frac{1}{2} \quad \frac{1}{4} \quad \frac{1}{3}$

Miller indices of plane (234)

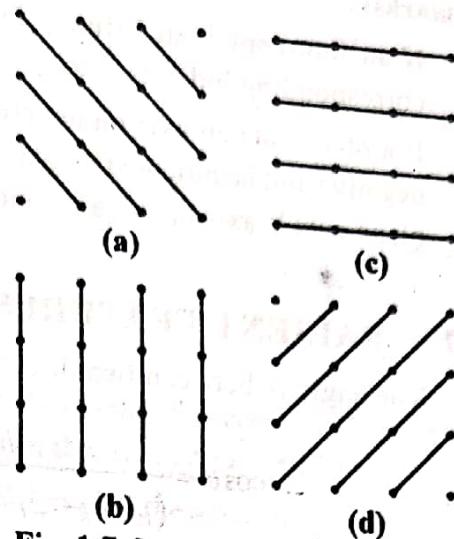


Fig. 1.7. Some lattice planes in two dimensional lattice

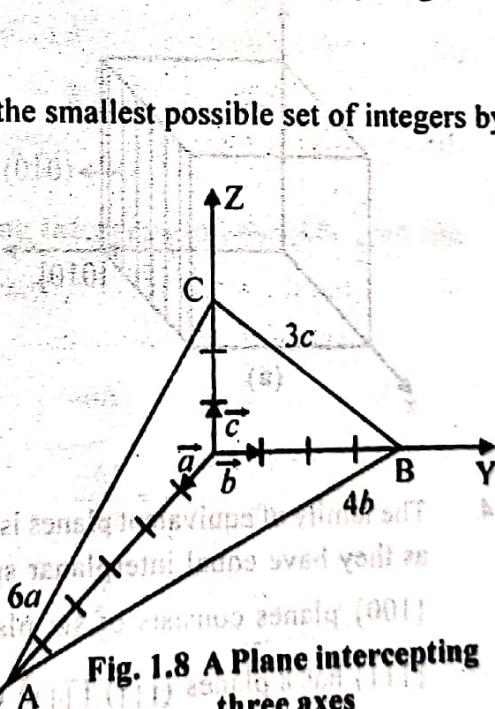


Fig. 1.8 A Plane intercepting three axes

Remarks:

1. If an intercept is at infinity i.e. plane is parallel to one of the axes and the corresponding index is zero.
2. If a plane cuts an axis on negative side of the origin, the corresponding index is negative and is indicated by placing a bar above that index. For example $(\bar{h}\bar{k}\bar{l})$ i.e. plane cuts Y-axis on negative side of the origin.

1.7 SALIENT FEATURES OF MILLER INDICES

1. The angle θ between two directions $[hkl]$ and $[h'k'l']$ is expressed as

$$\cos \theta = \frac{hh' + kk' + ll'}{(h^2 + k^2 + l^2)^{1/2} (h'^2 + k'^2 + l'^2)^{1/2}}$$

2. All equally spaced parallel planes have same miller indices i.e. Miller indices do not define a particular plane but a set of parallel planes. For example (642), (963), (321) have the miller indices (321) i.e. it is ratio of indices which is important.
3. The normal to the plane (hkl) is the direction $[hkl]$. It means, normal to a plane is a direction with the same indices. For example (Fig. 1.9).

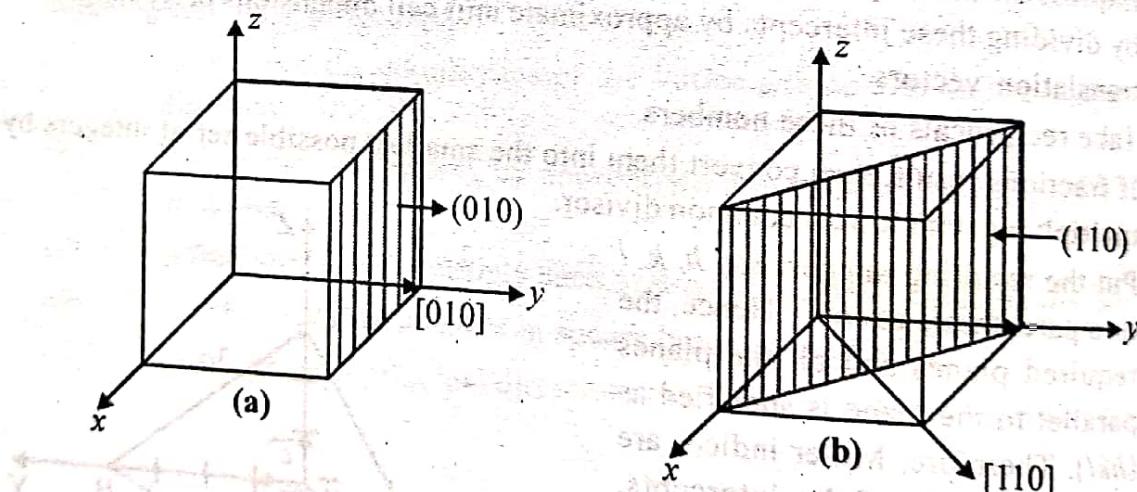


Fig. 1.9

4. The family of equivalent planes is denoted by $\{ hkl \}$. These are said to be equivalent as they have equal interplanar spacing and equal density of atoms. For example $\{100\}$ planes consists of six planes $(100), (\bar{1}00), (010), (0\bar{1}0), (001), (00\bar{1})$ and $\{111\}$ has 8 planes $(111), (\bar{1}11), (1\bar{1}1), (\bar{1}\bar{1}1), (\bar{1}\bar{1}\bar{1}), (\bar{1}\bar{1}1), (\bar{1}1\bar{1}), (1\bar{1}\bar{1})$.
5. The distance 'd' between adjacent parallel planes of a set of parallel planes (hkl) is given by

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

where 'a' is the cube edge of the cubic unit cell or lattice constant of the cell.

Example 1. Determine the miller indices of a plane which is parallel to x-axis and cuts intercepts of $2b$ and $c/2$ respectively along y and z-axis.

Solution: Following the procedure to find Miller indices, we get

Intercepts:

$$\begin{array}{ccc} \infty & 2b & \frac{c}{2} \\ \frac{\infty}{a} = \infty & \frac{2b}{b} = 2 & \frac{c}{2} \left(\frac{1}{c} \right) = \frac{1}{2} \\ \frac{1}{\infty} & \frac{1}{2} & 2 \end{array}$$

Reciprocals:

$$\begin{array}{ccc} \infty & \frac{1}{2} & 2 \\ 0 & 1 & 4 \end{array}$$

Clear fractions:

\Rightarrow The required Miller indices of the plane are (014).

Example 2. Determine the Miller Indices of a plane that makes intercepts of $2A^\circ$, $3A^\circ$, $4A^\circ$ on the coordinate axes of an orthorhombic crystal with $a:b:c = 4:3:2$.

Solution. Here, the primitives can be considered as (keeping the given ratio)

$$a = 4A^\circ,$$

$$b = 3A^\circ$$

and

$$c = 2A^\circ$$

Following the same procedure as above, we have

(i) Intercepts:

$$\begin{array}{ccc} 2A^\circ & 3A^\circ & 4A^\circ \end{array}$$

(ii) Multiples (division by primitives): $\frac{2A^\circ}{4A^\circ} = \frac{1}{2}$ $\frac{3A^\circ}{3A^\circ} = 1$ $\frac{4A^\circ}{2A^\circ} = 2$

(iii) Reciprocals

$$\begin{array}{ccc} 2 & 1 & \frac{1}{2} \end{array}$$

(iv) After removing fractions

$$\begin{array}{ccc} 4 & 2 & 1 \end{array}$$

The required Miller Indices of the plane are (421)

Example 3. Find Miller indices of a plane making intercepts of ∞ , $-6b$, $\frac{c}{2}$ on the respective axes where a, b, c are lattice parameters.

Solution.

(i) Intercepts:

$$\begin{array}{ccc} \infty & -6b & \frac{c}{2} \end{array}$$

(ii) Multiples (division by primitives): $\frac{\infty}{a} = \infty$ $\frac{-6b}{b} = -6$ $\frac{\frac{c}{2}}{c} = \frac{1}{2}$

(iii) Reciprocals

$$\begin{array}{ccc} 0 & -\frac{1}{6} & 2 \end{array}$$

(iv) After removing fractions

$$\begin{array}{ccc} 0 & -1 & 12 \end{array}$$

The required Miller Indices of the plane are (0 $\bar{1}$ 12)

1.8

REPRESENTATION OF PLANES OF KNOWN MILLER INDICES

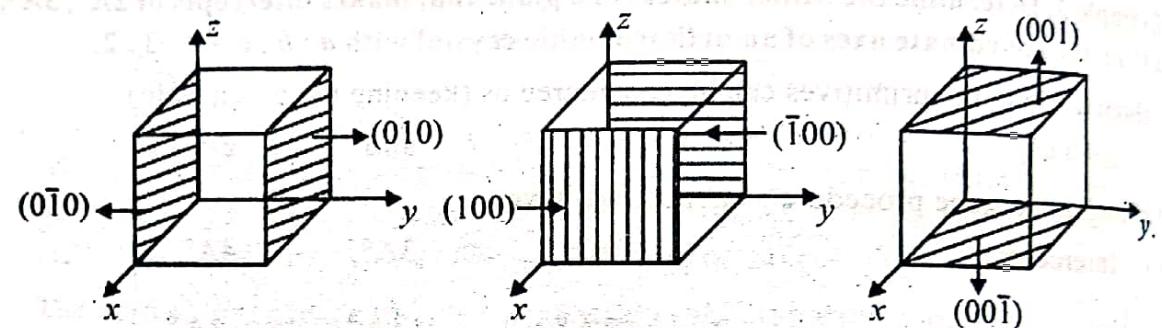
We know the procedure to find miller indices of a plane when intercepts made by it on three crystallographic axes are known. Now, to represent a given plane of known indices into an unit cell, the following procedure is adopted.

- (i) Take the reciprocals of the given miller indices.
- (ii) Represent these fractions or numbers in terms of axial units by multiplying respective primitive lengths.
- (iii) Indicate the length of the intercepts on the respective coordinate axes.
- (iv) Join the above end points, the resulting sketch will represent the required plane.

Note: A lattice point is chosen as origin conveniently so that we can represent the intercepts on the coordinate axes in the unit cells.

Example 4. Name and represent planes of six faces of a cube.

Solution. Six faces are (100) , $(\bar{1}00)$, (010) , $(0\bar{1}0)$, (001) , $(00\bar{1})$.

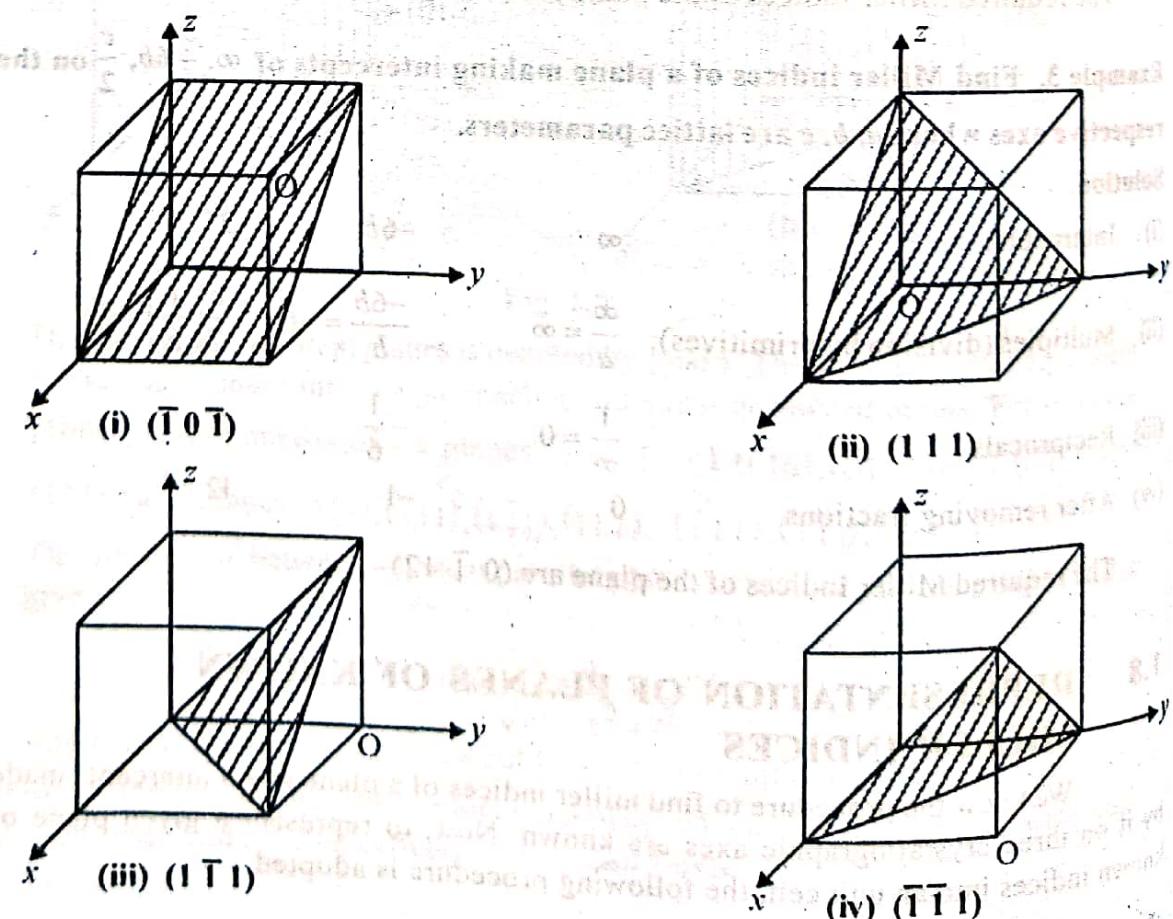


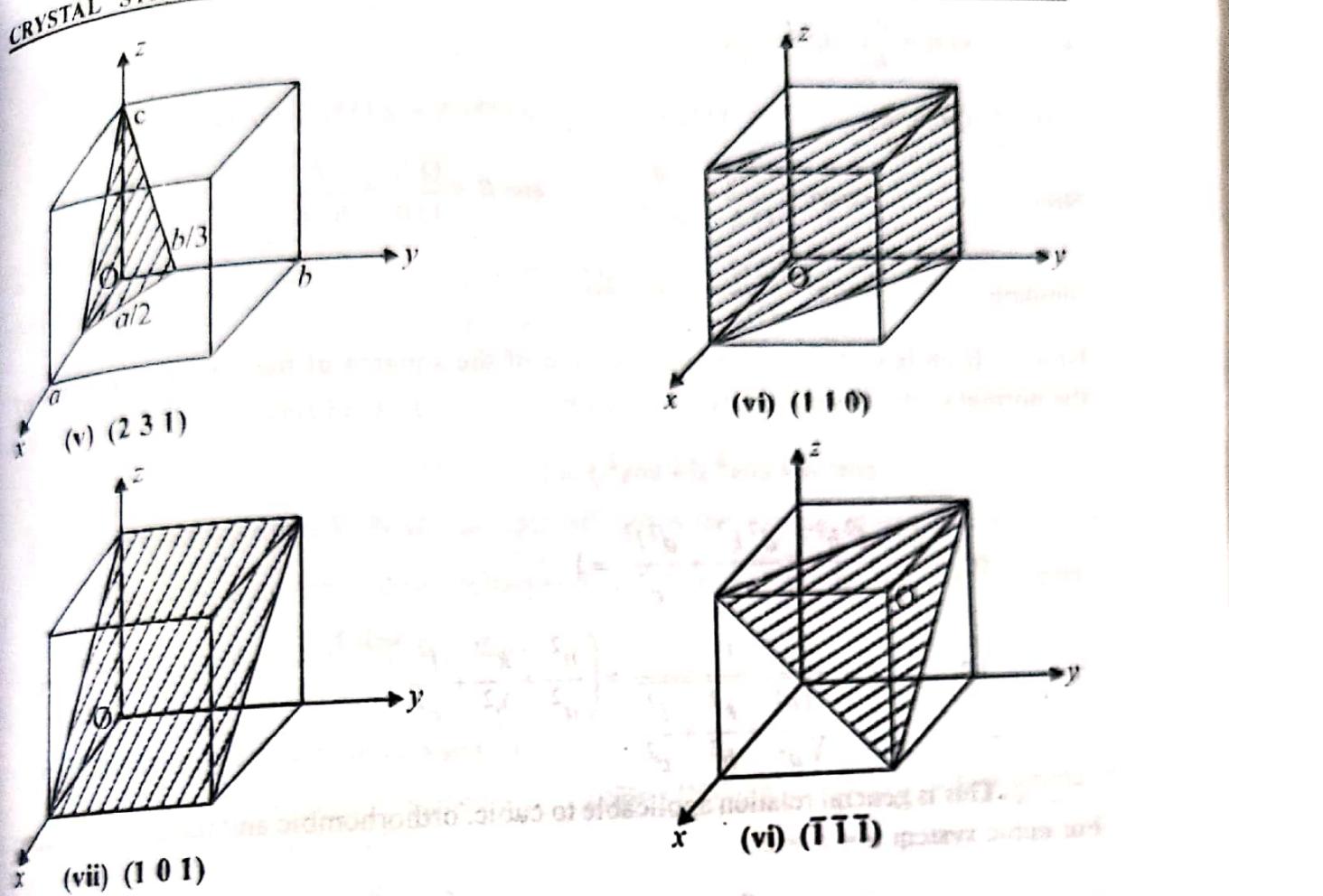
Example 5. Draw following planes inside the unit cell of a cubic crystal

(i) $(\bar{1}0\bar{1})$ (ii) (111) (iii) $(1\bar{1}\bar{1})$ (iv) $(\bar{1}\bar{1}1)$

(v) (231) (vi) (110) (vii) (101) (viii) $(\bar{1}\bar{1}\bar{1})$

Solution. Choose the conventional axes and construct a cubic unit cell with different origins in each case. In each case the lattice point 'O' represents as origin $(0, 0, 0)$.





1.9 INTERPLANAR SPACING

Consider a family of parallel planes $\{ hkl \}$. Take any lattice point of any of these planes as origin. Draw coordinate axes in direction of primitives $\vec{a}, \vec{b}, \vec{c}$. The interplanar spacing 'd' is the perpendicular distance between this origin and the plane (hkl) which is nearest to the origin 'O'. The plane (hkl) will make intercepts $\frac{a}{h}, \frac{b}{k}, \frac{c}{l}$ on X, Y, Z axes respectively.

Here, $\vec{a}, \vec{b}, \vec{c}$ are primitive vectors or lattice parameters. Draw normal on the (nearest) plane (hkl) from the origin. So, $ON = d$. Let α, β, γ are the angles between normal ON and the respective coordinate axes. Therefore,

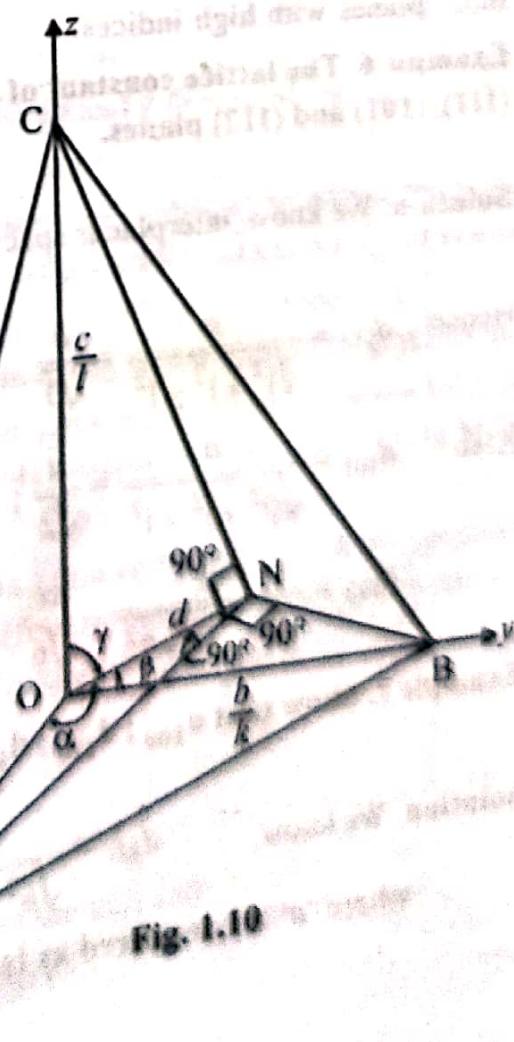


Fig. 1.10

and $OA = \frac{a}{h}; OB = \frac{b}{k};$

$$OC = \frac{c}{l}, \quad ON = d; \quad \angle ONA = \angle ONB = \angle ONC = 90^\circ$$

Now, $\cos \alpha = \frac{ON}{OA} = \frac{d}{a/h}; \quad \cos \beta = \frac{ON}{OB} = \frac{d}{b/k}$

Similarly $\cos \gamma = \frac{ON}{OC} = \frac{d}{c/l} = \frac{dl}{c}$

Now, from law of direction cosines, sum of the squares of the direction cosines of the normal to the plane is unity i.e. one i.e.

$$\cos^2 \alpha + \cos^2 \beta + \cos^2 \gamma = 1$$

or $\frac{d^2 h^2}{a^2} + \frac{d^2 k^2}{b^2} + \frac{d^2 l^2}{c^2} = 1$

i.e. $d = \sqrt{\frac{1}{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}} = \left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right)^{-1/2}$

This is general relation applicable to cubic, orthorhombic and tetragonal lattices.
For cubic system $a = b = c$.

Hence, $d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$

Clearly, planes with low indices have larger interplanar spacing compared with those planes with high indices.

Example 6. The lattice constant of a cubic lattice is 'a'. Calculate spacing between (111), (101) and (112) planes.

Solution. We know, interplanar spacing $d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$

Hence $d_{111} = \frac{a}{\sqrt{1^2 + 1^2 + 1^2}} = \frac{a}{\sqrt{3}}$

Also $d_{101} = \frac{a}{\sqrt{0^2 + 1^2 + 1^2}} = \frac{a}{\sqrt{2}}$

$$d_{112} = \frac{a}{\sqrt{1^2 + 1^2 + 2^2}} = \frac{a}{\sqrt{6}}$$

$$d_{101} = \frac{a}{\sqrt{2}}$$

Example 7. Show that $d_{100} : d_{110} : d_{111} = \sqrt{6} : \sqrt{3} : \sqrt{2}$.

Solution. We know, $d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$

where 'a' is considered as lattice constant.

$$\text{Hence, } d_{100} = \frac{a}{\sqrt{1^2 + 0^2 + 0^2}} = a, \quad d_{110} = \frac{a}{\sqrt{1^2 + 1^2 + 0^2}} = \frac{a}{\sqrt{2}}$$

$$\text{and } d_{111} = \frac{a}{\sqrt{1^2 + 1^2 + 1^2}} = \frac{a}{\sqrt{3}}$$

$$\text{Hence } d_{100} : d_{110} : d_{111} = a : \frac{a}{\sqrt{2}} : \frac{a}{\sqrt{3}} = \sqrt{6} : \sqrt{3} : \sqrt{2}$$

1.10 MORE ABOUT UNIT CELL

A unit cell is characterised by following characteristics:

- (i) **Unit Cell Volume, V:** If $\alpha = \beta = \gamma = 90^\circ$, then the volume of unit cell is $V = abc$, where a, b, c are primitive vectors and α, β and γ are the interfacial angles.

Further, when $a = b = c$, as in the case of cubic cells

then $V = a^3$.

- (ii) **Effective number of points per unit cell**

The following equation is used to calculate effective number of lattice points ' n ' belonging to a cubic cell.

$$n = N_b + \frac{N_f}{2} + \frac{N_c}{8}$$

where N_b = Atoms in the body of the unit cell, N_f = atoms at the centre of face of unit cell.

N_c = atoms at the corners of the unit cell

Hence, there is one atom in simple cubic cell and 2 in case of bcc cell and 4 in case of fcc lattice.

- (iii) **Coordination Number:** It is the number of nearest equidistant neighbouring atoms that a given atom has in a crystal. It is 6 for simple cubic lattice, 8 for bcc system and 12 for face centered cubic unit cell.

- (iv) **Atomic Packing factor (APP):** The fraction of the space occupied by atoms in a unit cell is known as packing efficiency or packing fraction. It is the ratio of volume occupied by atoms in a cell to the total volume of unit cell relating to the structure.

- (v) **Density of unit cell and lattice constant:** As a unit cell possesses all the structural properties of a crystal, the density of unit cell must be same as that of crystal. Let lattice constant of cubic lattice is ' a ', then volume of unit cell is $V = a^3$.

Let density of the crystal or unit cell is ρ . Then

$$\text{Density, } \rho = \frac{\text{Mass}}{\text{Volume}} = \frac{nm}{V} = \frac{nm}{a^3} \quad \dots(1)$$

where n = effective number of atoms in the unit cell

m = mass of each atom in the unit cell.

$$\text{or } m = \frac{M}{N_A}$$

where M is molecular weight of the material and N_A is Avogadro number.

$$\text{Hence, Density, } \rho = \frac{n M / N_A}{a^3}$$

$$\text{or Lattice constant } 'a' = \left(\frac{n M / N_A}{\rho} \right)^{1/3} \quad \dots(2)$$

Example 8. Polonium belongs to sc lattice. If lattice constant is 3.36\AA , Calculate its density. Atomic mass of polonium is 209.

Solution. Lattice constant $a = 3.36 \times 10^{-10} \text{ m}$, $n = 1$ for sc lattice

$$\rho = \frac{n M / N_A}{a^3} = \frac{1(209)}{6.02 \times 10^{26} \times (3.36 \times 10^{-10} \text{ m})^3} = 9150 \text{ kg/m}^3$$

Example 9. NaCl crystallizes in FCC structure. Its density is 2180 kg/m^3 . The atomic weight of sodium is 23 and of chlorine 35.5. Find lattice constant 'a' of the structure.

Solution. Density of sodium chloride = 2180 kg/m^3

Effective number in a FCC cell, $n = 4$ molecules

$$\begin{aligned} \text{Molecular weight of sodium chloride, } M &= (23 + 35.5) \text{ kg/k. mole} \\ &= 58.5 \text{ kg/k. mole} \end{aligned}$$

Avogadro Number = 6.026×10^{26} molecules/k. mole

$$\text{Now, volume, } a^3 = \frac{n(M)}{N_A \rho} = \frac{(4 \text{ atoms})(58.5 \text{ kg/k. mole})}{(6.026 \times 10^{26} \text{ atoms/k. mole})(2180 \text{ kg/m}^3)}$$

$$\text{Hence, lattice constant } a = (178.63 \times 10^{-30})^{1/3} = 5.63 \times 10^{-10} \text{ m}$$

Example 10. The unit cell of aluminium is face centred cubic with lattice constant $a = 4.05\text{\AA}$.

(a) How many unit cells are there in an aluminium foil 0.005 cm thick and side 25 cm square?

(b) It weighs 0.0085 kilogram . How many atoms are present?

(c) How many atoms are in each unit cell?

Solution. (a) Given : Lattice constant, $a = 4.05 \times 10^{-8} \text{ m}$

$$\text{Hence, volume of the unit cell} = V = a^3 = (4.05 \times 10^{-8})^3 \text{ m}^3$$

So, $[0.005 \times 10^{-2} \times (25 \times 10^{-2})^2] \text{ m}^3$ aluminium foil will have

$$= \frac{0.005 \times 10^{-2} \times (25 \times 10^{-2})^2}{(4.05)^3 \times 10^{-24}} = 4.8 \times 10^{22} \text{ unit cells}$$

(b) Atomic weight of aluminium is 27 kilogram

So, 27 kilogram contains 6.02×10^{26} atoms

Hence, 0.0085 kg will contain $\frac{6.02 \times 10^{26} \times 0.0085}{27}$ atoms
 $= 1.89 \times 10^{23}$ atoms

(c) We have to find number of atoms in each unit cell i.e. $n = ?$

Now, we know that volume, $V = a^3 = \frac{n M}{N_A \times \rho}$

$$\therefore n = \frac{a^3 (N_A) \rho}{M}$$

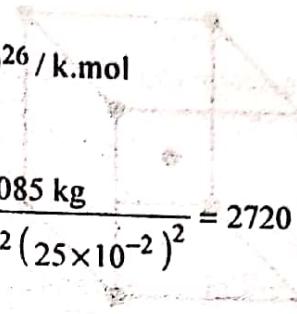
where $a^3 = (4.05 \times 10^{-8} \text{ m})^3$ given

N_A = Avogadro Number $= 6.02 \times 10^{26} / \text{k.mol}$

M = Atomic weight $= 27 \text{ kg}$

and $\rho = \text{density} = \frac{\text{Mass}}{\text{Volume}} = \frac{0.0085 \text{ kg}}{0.005 \times 10^{-2} (25 \times 10^{-2})^2} = 2720 \text{ kg/m}^3$

Hence $n = \frac{(4.05 \times 10^{-8})^3 (6.02 \times 10^{26}) (2720)}{27.0} \approx 4$



1.11 SIMPLE CUBIC STRUCTURE

1.11.1 Packing efficiency simple cubic structure

The unit cell of simple cubic structure is sketched in Fig. 1.11. The particles are located only at each corner in this cell. So, effective number of atoms in this cell is one. This cell is, therefore, primitive. Only one element, polonium, exhibits this structure below 75°C .

In a simple cubic cell atoms are in contact along the edges of the cube, as shown in Fig. 1.12. If ' r ' is atomic radius and the edge of cube, as shown in Fig. 1.12. If ' r ' is atomic radius and the edge of cube is ' a ', then from the Fig. 1.12, it is clear that $2r = a$

Now, let v = volume occupied by all the atoms in a unit cell

$$\Rightarrow v = n \times \text{volume of one atom}$$

$$= 1 \times \frac{4}{3} \pi r^3 = \frac{4}{3} \pi r^3 \quad \dots(1)$$

Hence and n is effective number of atoms in the unit cell.

V = volume of the unit cell

$$= a^3 = (2r)^3 = 8r^3 \quad \dots(2)$$

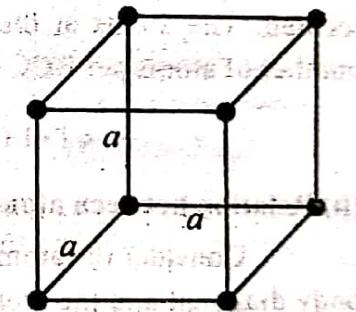


Fig. 1.11 Simple cubic structure

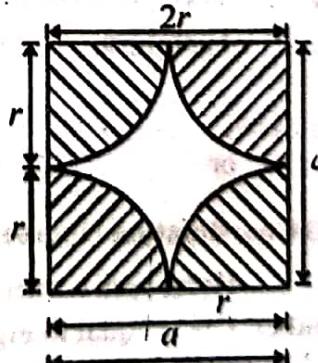


Fig. 1.12 One face of the cube of simple cubic structure

$$\text{Hence, Packing fraction} = \frac{V}{V} = \frac{\frac{4}{3}\pi r^3}{\frac{8r^3}{6}} = \frac{\pi}{6} = 0.52$$

Hence, packing efficiency of simple cubic structure is 52%.

1.11.2 Body Centered Cubic (BCC) Structure

The alkali and many of the alkaline earth metals crystallize in the b.c.c. structure. There is one atom at the body center besides the atoms at each corner of the unit cell of bcc structure as shown in Fig. 1.13 (a).

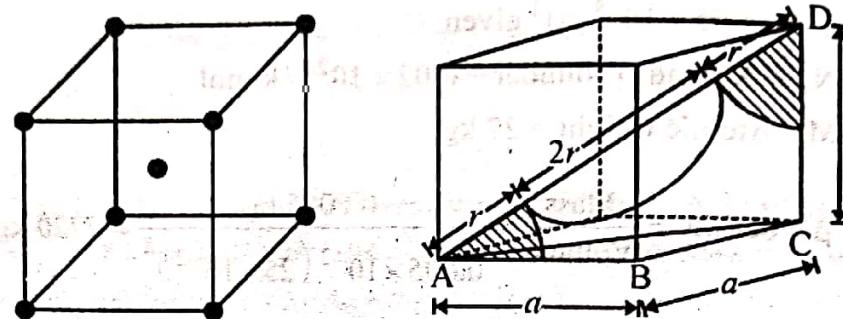


Fig. 1.13 (a) BCC unit cell

Fig. 1.13 (b) Determination of atomic radius in BCC cell

(i) Effective number of atoms per unit cell

The atoms at the center of the body of the cell cannot be shared by the adjacent cells and therefore contributes fully its volume and mass to the unit cell in which it is located. The atoms at the corners contribute each 1/8th share. Therefore, effective number of atoms per BCC cell is

$$n = 1 + 8 \times \frac{1}{8} = 1 + 1 = 2 \text{ atoms per unit cell.} \quad \dots(1)$$

(ii) Relation between atomic radius and cube, 'a'

Consider the atoms as hard spheres of radius 'r'. Here, they will meet along the body diagonal and the atoms along the corner do not touch each other. In a BCC cell, atoms are in contact along the body diagonal as shown in Fig. 1.13 (b). Hence from the Fig. 1.13 (b), it is clear that $a \neq 2r$ and length of the body diagonal $AD = 4r$.

Therefore,

$$(AD)^2 = (AC)^2 + (CD)^2 = (AB^2 + BC^2) + (CD)^2$$

$$(4r)^2 = (a^2 + a^2) + a^2 = 3a^2$$

or

$$4r = \sqrt{3}a$$

$$r = \frac{\sqrt{3}}{4}a \quad \dots(2)$$

(iii) Coordination Number

Here, each corner atoms is in contact with body center atom. Hence coordination number, CN is equal to eight.

(iv) Atomic Packing factor, APP

For BCC structure, $n = 2$ atoms/ unit cell

$$a = \frac{4r}{\sqrt{3}}$$

Hence, volume of the unit cell, $V = a^3 = \frac{64r^3}{3\sqrt{3}}$ (3)

Now volume of the cell occupied by atoms:

$$v = n \times \text{volume of one atom}$$

$$\Rightarrow v = 2 \times \frac{4}{3} \pi r^3 = \frac{8}{3} \pi r^3 \quad \dots(4)$$

$$\text{Hence, A.P.F.} = \frac{v}{V} = \frac{\frac{8}{3} \pi r^3}{\frac{64r^3}{3\sqrt{3}}} = \frac{\pi \sqrt{3}}{8} = 0.68$$

So, packing efficiency of bcc structure is 68% and empty space is 32%.

1.11.3 Face Centered Cubic (FCC) Cell

A unit cell of this FCC structure is shown in Fig. 1.14 (a). There are four effective number of atoms per unit cell in fcc lattice. If the atoms in Fig. 1.14 (b) are drawn on the scale as that of the inter-atomic distance, then we will observe that these atoms would touch each other along the face diagonal directions.

Let 'a' is lattice constant, 'r' is atomic radius. Nearest neighbour distance = $2r$. But, here $a \neq 2r$ as atoms along cube edge do not touch each other.

Relation between 'a' and 'r'

From Fig. 1.14 (b): $AC^2 = AD^2 + DC^2$

$$\text{or } (4r)^2 = a^2 + a^2$$

$$\text{or } a = 2\sqrt{2}r \quad \dots(1)$$

Hence, volume of fcc unit cell; $V = a^3 = (2\sqrt{2}r)^3 = 16\sqrt{2}r^3$

Now, $n = \text{number of atoms per unit cell} = 4$

$$v = \text{volume occupied by atoms in the unit cell} = 4 \times \frac{4}{3} \pi r^3$$

$$\text{Atomic Packing Factor} = \frac{v}{V} = \frac{\frac{16}{3} \pi r^3}{16\sqrt{2}r^3} = \frac{\pi}{3\sqrt{2}} = 0.74 \text{ (or 74%)}$$

Hence, it is closed packed structure. The best example of this is sodium chloride structure.

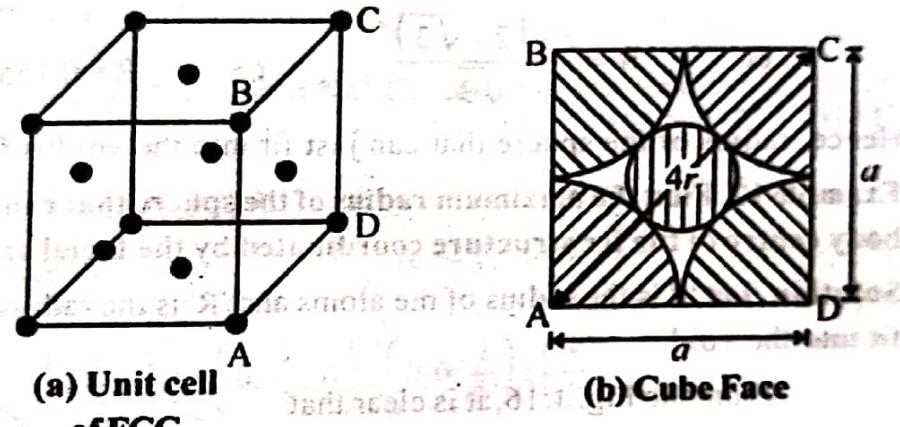


Fig. 1.14 Unit cell and Cube Face of FCC structure

Example 11. Find the maximum radius of interstitial sphere that can just fit into the void in between the body centered atoms of bcc structure.

Solution. Let ' r ' be the radius of the atoms and ' R ' is the radius of the sphere that can just fit into the void.

From the Fig. 1.15, it is clear that

$$r + R = \frac{a}{2}$$

$$\text{or } R = \frac{a}{2} - r \quad \dots(1)$$

where a = cube edge.

Also, for bcc structure

$$a = \frac{4r}{\sqrt{3}} \quad \dots(2)$$

Therefore, from equations (1) and (2), we get

$$R = \frac{4r}{(2)(\sqrt{3})} - r$$

$$\text{or } R = \frac{2r}{\sqrt{3}} - r$$

$$\text{or } R = \frac{r(2 - \sqrt{3})}{\sqrt{3}}$$

$$\text{i.e. } R = 0.155r$$

Hence, radius of the sphere that can just fit into the void is $0.155r$.

Example 12. Find the maximum radius of the sphere that can just fit into the void at the body centre of the fcc structure coordinated by the facial atoms.

Solution. Let ' r ' is the radius of the atoms and ' R ' is the radius of the sphere that can just fit into the void.

From the Fig. 1.16, it is clear that

$$r + R = \frac{a}{2}$$

$$\text{or } R = \frac{a}{2} - r \quad \dots(1)$$

For fcc structure, we know that the relation between a and r is

$$a = \frac{4r}{\sqrt{2}}$$

Therefore, from equations (1) and (2), we get

$$R = \frac{4r}{(2)(\sqrt{2})} - r$$

$$\text{or } R = \frac{2r}{\sqrt{2}} - r$$

$$\text{or } R = r[\sqrt{2} - 1]$$

Hence, radius of the sphere that can just fit into the void is $R = 0.414r$.

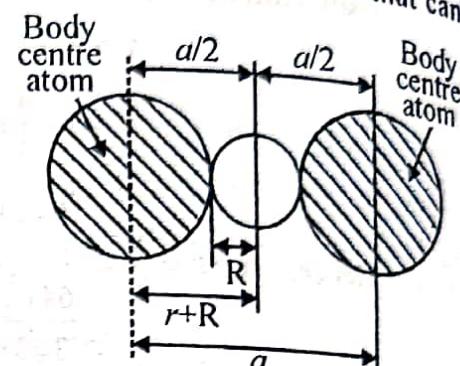


Fig. 1.15 Body centre atoms of adjacent unit cells

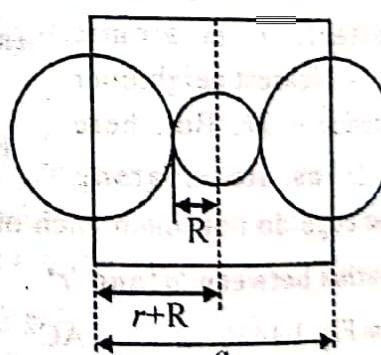


Fig. 1.16 Opposite face centre atoms of same unit cells

1.11.4 NaCl Structure

It has a fcc structure. Its basis consists of Na^+ ion and one Cl^- ion separated by one half of the edge of a unit cell of sodium chloride structure. The unit cell of NaCl structure is shown in Fig. 1.17.

NaCl structure can be considered as interpenetration of two fcc sublattices – one of entirely Na^+ ions having its origin at the point $(0, 0, 0)$ and other entirely of Cl^- ions having its origin midway along a cube

edge say at point $\left(\frac{a}{2}, 0, 0\right)$.

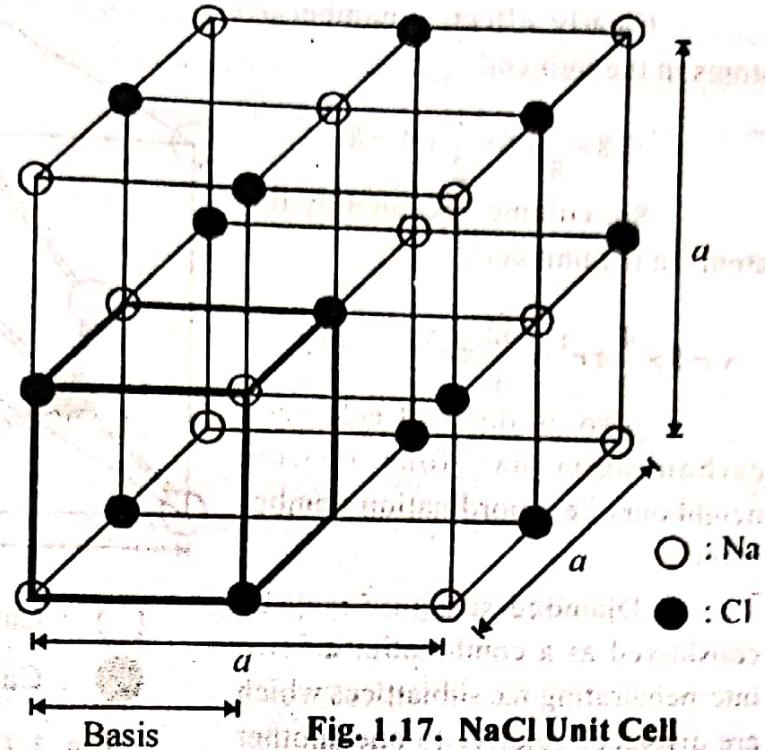


Fig. 1.17. NaCl Unit Cell

Hence, there are four molecules of NaCl (or 4 Na^+ Cl^- ion pairs) in each cubic unit cell with different ions in positions:

$$\text{Na}^+: (0, 0, 0); \left(\frac{1}{2}, \frac{1}{2}, 0\right); \left(\frac{1}{2}, 0, \frac{1}{2}\right); \left(0, \frac{1}{2}, \frac{1}{2}\right)$$

$$\text{Cl}^-: \left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right); \left(0, \frac{1}{2}, 0\right); \left(0, 0, \frac{1}{2}\right); \left(\frac{1}{2}, 0, 0\right)$$

These are eight corner points of a simple cube in the NaCl unit cell.

NaCl structure may also be considered as composed of two types of ions arranged alternatively at the lattice points of a simple cubic lattice. The lattice is simple cubic if difference between Na^+ and Cl^- ions is ignored. In this NaCl crystal lattice, each ion is surrounded by six nearest neighbours of opposite kind i.e. here coordination number is 6; and nearest neighbouring distance is $a/2$.

While for same kinds of ions, coordination number is 12 and nearest neighbouring distance is $\frac{a}{2}$. Its lattice constant is 6.29 \AA . Crystals having NaCl structure: KBr, KCl, PbI, PbS, AgBr, MgO, MnO, BaO etc.

1.12 DIAMOND CUBIC STRUCTURE

This structure is derived from fcc structure. The basic unit cell of diamond cubic structure has carbon atoms at all the fcc positions and in addition also at the alternate tetrahedral void sites along the body diagonals. So, it has carbon atoms at fcc positions and four more atoms inside the body of diamond cubic unit cell as shown in Fig. 1.18.

Clearly, effective number of atoms in the unit cell

$$= 8 \times \frac{1}{8} + 6 \times \frac{1}{2} + 4 = 8$$

So, volume occupied by the atoms in the unit cell,

$$v = 8 \times \frac{4}{3} \pi r^3 = \frac{32}{3} \pi r^3 \quad \dots(1)$$

Also, in this unit cell, each carbon atom has four nearest neighbours i.e. coordination number is four.

Diamond structure may be considered as a combination of two interpenetrating fcc sublattices which are displaced relative to one another along the body diagonal of the cube by one quarter of its length. If one sublattice has its origin at $(0, 0, 0)$, the other sublattice has its origin at a

position $\left(\frac{a}{4}, \frac{a}{4}, \frac{a}{4}\right)$ along the body

diagonal. Here ' a ' is cube edge. Hence, nearest neighbouring distance, $2r$ is equal to

$$\text{or } 2r = \sqrt{\frac{a^2}{16} + \frac{a^2}{16} + \frac{a^2}{16}}$$

$$\text{or } 2r = \sqrt{3} a/4$$

$$\text{or } a = \frac{8r}{\sqrt{3}} \quad \dots(2)$$

Hence, volume of the unit cell,

$$V = a^3 = \left(\frac{8r}{\sqrt{3}}\right)^3 = \frac{512r^3}{3\sqrt{3}} \quad \dots(3)$$

From (1) and (3), we get, packing fraction

$$\text{or } \text{APPF} = \frac{v}{V} = \frac{\frac{32}{3} \pi r^3}{\frac{512}{3\sqrt{3}} r^3} = \frac{\pi \sqrt{3}}{16} = 0.34 \text{ or } 34\%$$

Hence, diamond cubic structure is loosely packed structure. Here, two fcc sublattices interpenetrate each other such that four atoms of one sublattice take the

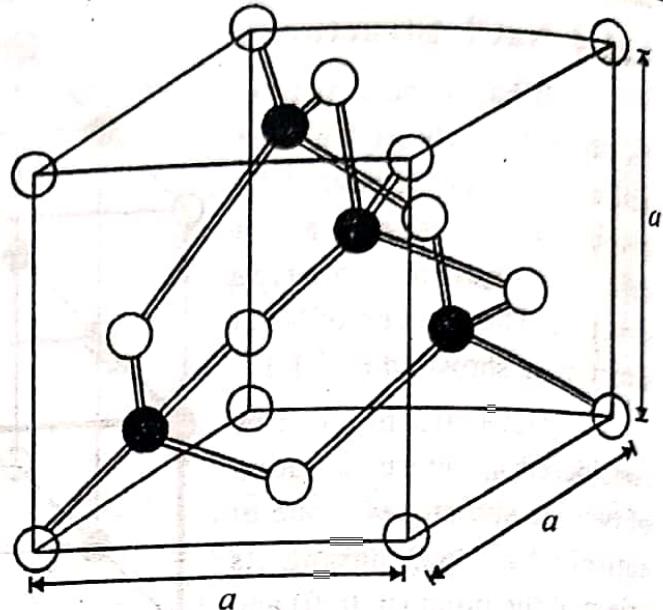


Fig. 1.18 Diamond cubic unit cell
 : Carbon atoms at FCC position
 : Carbon atoms at tetrahedral sites

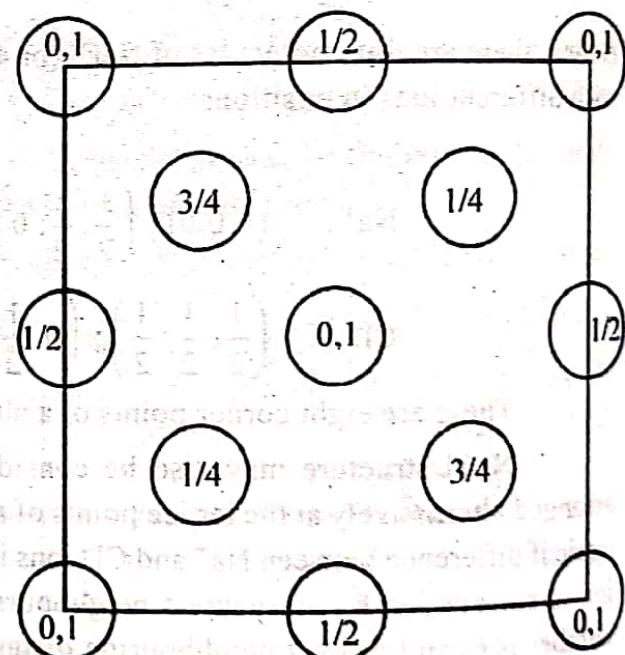


Fig. 1.19 Plan view showing carbon positions in diamond cubic cell

[Heights of atoms are written in circles]

alternate positions of tetrahedral void sites along the body diagonals. The additional carbon atoms, which occupy these alternate tetrahedral void sites in the fcc arrangement, open up the closed packed fcc arrangement which decreases the packing efficiency considerably.

Note: The points $(0, 1)$ and $1/2$ are on the fcc lattice and those at $1/4$ and $3/4$ are on similar lattice displaced along the body diagonal by $1/4$ of the cube edge.

1.12.1 Zinc Blende (ZnS) structure

Its structure is similar to the diamond structure. Only difference is that there are different kinds of atoms at tetrahedral sites and fcc positions. It means, if sulphide (s^{2-}) ions occupy fcc positions, then Zn^{2+} ions occupy tetrahedral void positions and vice versa. Other examples: CuCl, GaAs etc. are similar compounds.

1.13 HEXAGONAL CLOSE - PACKED STRUCTURE

Consider a layer of similar atoms with each atom surrounded by six atoms in one plane as shown in Fig. 1.18. Another similar layer B can be placed on top of layer A such that the atoms of layer B occupy the alternate depressions formed by the atoms of layer A.

When a third layer of atoms is placed on the top of the B-layer in such a way that the atoms of third layer exactly overlap the atoms of 'A' layer and this type of stacking is repeated successively, the following layered arrangement of atoms is obtained:ABABAB.....

This type of stacking is called hcp stacking and such structures are known as hexagonal closed - packed structures. The name corresponds to the shape of the conventional unit cell which is shown in Fig. 1.21. There are twelve atoms located at the corners, two at the centres of the hexagonal planes, and three completely inside the hexagon forming a part of B-layer. The effective number of atoms in this unit cell is equal to

$$n = 12 \text{ corner atoms} \times \frac{1}{6} + 2 \text{ atoms at the centre of each hexagonal face} \times \frac{1}{2} \\ + 3 \text{ body atoms in the hexagonal unit cell} \times 1$$

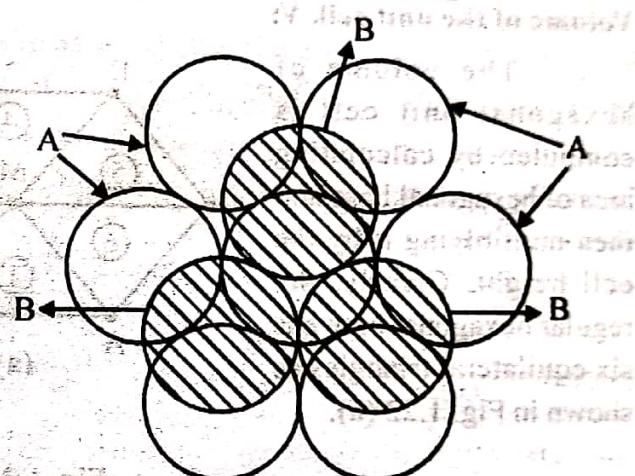


Fig. 1.20 Arrangement of atoms in Hexagonal Base and three atoms lying above them

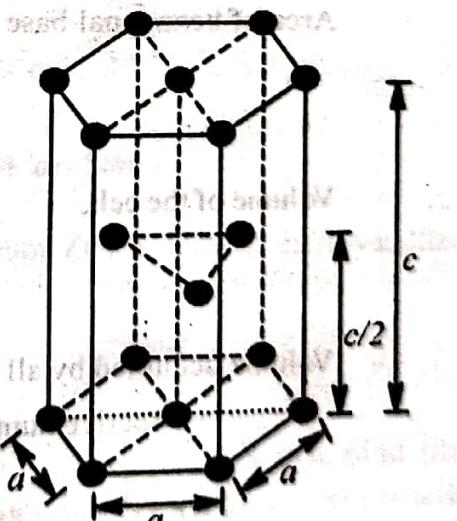


Fig. 1.21 Conventional unit cell of hexagonal closed packed structure

$$\Rightarrow n = 12 \times \frac{1}{6} + 2 \times \frac{1}{2} + 3 \times 1 \\ = 2 + 1 + 3 = 6 \text{ atoms/unit cell} \quad \dots(1)$$

In case of hexagonal close-packed structure, each atom is surrounded by 12 similar nearest neighbours. Out of these 12 neighbours, six lie in one plane and three each in adjacent parallel planes above and below this plane forming B-layers. Hence, coordination number is 12.

The atoms are in contact along the edges of the hexagon as shown in Fig. 1.20. The atoms in the base forms a regular hexagon. Let 'a' be the edge of the hexagon and 'c' is the height of unit cell and let 'r' is the radius of each atom, then, we can write

$$a = 2r \quad \dots(2)$$

where $2r$ is nearest neighbour distance.

Volume of the unit cell, V:

The volume of hexagonal unit cell is computed by calculating area of hexagonal base and then multiplying it by the cell height. Clearly, the regular hexagonal base has six equilateral triangles as shown in Fig. 1.22 (a).

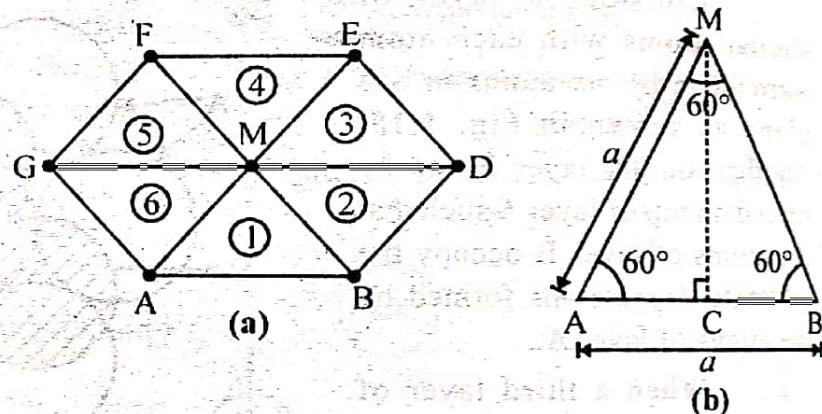


Fig. 1.22 Determination of area of the hexagonal base of HCP cell

$$\text{Area of hexagonal base} = 6 \times \text{area of } \triangle MAB$$

$$= 6 \left(\frac{1}{2} AB \times MC \right) = 6 \times \frac{1}{2} a \times a \sin 60^\circ = \frac{3\sqrt{3}}{2} a^2$$

\therefore Volume of the cell,

$$V = \text{Area of hexagonal base} \times \text{height of the cell}$$

$$V = \frac{3\sqrt{3} a^2}{2} \times c = \frac{3\sqrt{3} a^2 c}{2} \quad \dots(3)$$

Volume occupied by all the atoms in the cell

= effective number of atoms in the cell \times volume of each atom

$$v = 6 \times \frac{4}{3} \pi r^3 = 8\pi r^3 = 8\pi \left(\frac{a}{2} \right)^3 = \pi a^3 \quad \dots(4)$$

Calculation of c/a ratio:

The Fig. 1.23 shows an equilateral triangle with atoms at its corners touching each other and one atom at the centroid upon these three atoms. The three body atoms lie in a horizontal plane at a height $c/2$ from the centroids of alternate equilateral triangles in the base. If A, B and M are the three atoms which form equilateral triangle, then, the

body atom Z will be placed on these three atoms and this atom will attain a height equal to $c/2$ as shown in Fig. 1.23.

From $\triangle MAB$, the median AY divides $\angle MAB$ into two halves such that $\angle YAB = 30^\circ$.

Also $AM = MB = AB = a$

X is centroid, hence $AX = \frac{2}{3}AY$

$$\text{Now } AY = a \cos 30^\circ = \frac{\sqrt{3}}{2}a$$

$$\therefore AX = \frac{2}{3} \cdot \frac{\sqrt{3}}{2}a = \frac{a}{\sqrt{3}}$$

In $\triangle AXZ$, Z is an atom which rests on all the three atoms at the corners of $\triangle MAB$. It can be located at centroid X of $\triangle MAB$ and attain a height of $c/2$. Hence, $ZX = c/2$.

$$\text{In } \triangle AXZ; \quad AZ^2 = ZX^2 + AX^2$$

$$\text{or } a^2 = \left(\frac{c}{2}\right)^2 + \left(\frac{a}{\sqrt{3}}\right)^2$$

$$\text{or } c^2 = \frac{8a^2}{3}$$

$$\text{Hence, volume } V = \frac{3\sqrt{3}}{2}a^2c = \frac{3\sqrt{3}}{2}a^2\sqrt{\frac{8}{3}}a = 3\sqrt{2}a^3 \quad \dots(6)$$

$$\text{Hence, Atomic packing factor, } \text{APF} = \frac{V}{V} = \frac{\frac{\pi a^3}{3\sqrt{3}a^2c}}{\frac{3\sqrt{3}}{2}} = \frac{\pi a^3}{3\sqrt{2}a^3} \quad \dots(7)$$

$$\text{or } \text{APF} = \frac{\pi}{3\sqrt{2}} = 0.74 \text{ or } 74\%$$

Hence, it is closed packed structure. Magnesium, Zinc, Cadmium etc. crystallize in the hexagonal closed packed structure.

1.14 BONDING IN SOLIDS

The solids are classified depending on the types of forces that bind the component atoms or molecules. There are, both, attractive and repulsive forces which hold the atoms at a particular distance such that the opposite forces just balance each other. The process of holding the atoms together in a crystal is known as bonding. There are different types of bondings in different solids. A particular type of bonding within a crystal determines the physical, chemical and electrical properties of that crystal. Before studying types of bondings in crystals, we must have an idea about nature of forces among the atoms.

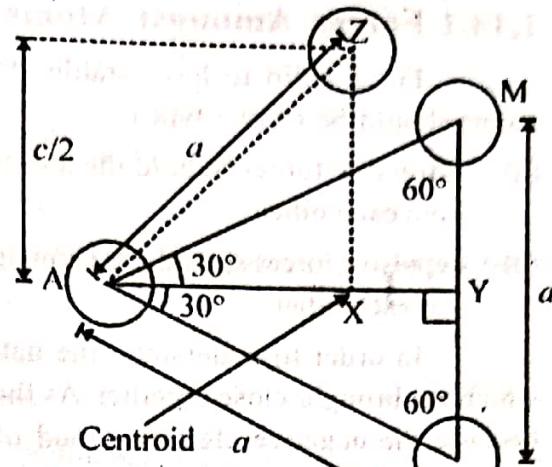


Fig. 1.23 Determination of c/a ratio for HCP cell

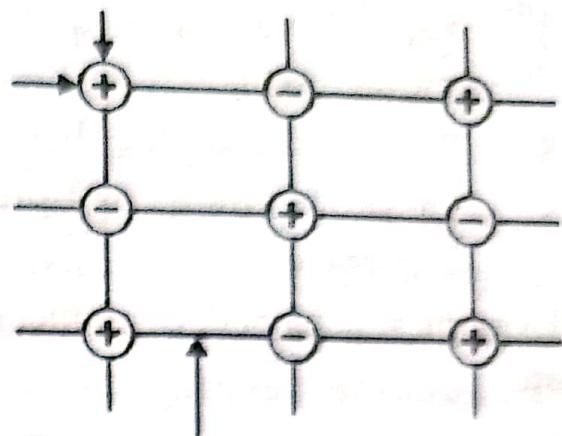
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1.15 TYPES OF BONDINGS IN SOLIDS

1.15.1 Ionic Bonds

An ionic bond is formed by the actual transfer of electrons from one atom to the other so that each atom acquires a stable electronic configuration of the nearest inert gas atoms. The atom which loses electrons becomes electropositive and atom which gains electrons becomes electronegative. The electropositive atoms are usually atoms like Na, K, Ca etc. While electronegative atoms are non-metallic atoms like O, F, Cl etc.

The sources of cohesive energy that binds crystal together is the coulombic electrostatic interaction between the ions. The magnitude of cohesive energy is about



Strong attractive forces between positive and negative ions

Fig. 1.25 Ionic Bonding

5–10 eV per molecule. The crystals resulting from ionic bonding are known as *ionic crystal*. The ionic bonding is shown in Fig. 1.25.

Examples: NaCl, CsCl, KBr etc. alkalihalides and alkaline oxides etc.

Properties:

1. Large binding energy about 5–10 eV/ molecule.
2. Strong binding of these molecules.
3. These are non-directional bonds.
4. These are good ionic conductors.
5. These have high melting point.
6. These are poor thermal conductors.
7. These have low electrical conductivity.
8. These are soluble in ionizing solvents like water.
9. These have intermediate close packed structure.

1.15.2 Covalent Crystals

A covalent bond is formed by an equal sharing of valence electrons between two neighbouring atoms, each having incomplete outermost shell. The atoms do so to acquire stable electronic configuration. The crystals resulting from this bonding are called covalent crystals. Here, there is no actual transfer of electrons from one atom to the other. Unlike ionic bond, it is directional, since bonding electron pair is concentrated along the line joining the atoms. The covalent bonding is shown in Fig. 1.26.

Properties

1. These crystals are strongly bound as binding energy in covalent bonds is about 8 eV.
2. These are hard and brittle crystals.
3. These have loosed packed structure.
4. Some crystals are semiconductors.
5. These have poor thermal conductivity.
6. These have intermediate density.
7. These have intermediate melting and boiling points.
8. These bonds are highly directional.
9. These become opaque at higher frequencies.

Examples: Diamond, Cl₂, Silicon, Germanium etc.

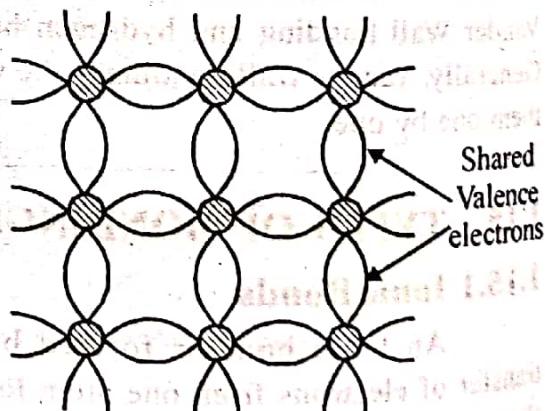


Fig. 1.26 Covalent Bonding

1.15.3 Metallic Bonding

These bonds are due to electrostatic attraction between the positive ion cores and the free electron gas. In metals, valence electrons of the component atoms are free to move through the crystal. They do not form any permanent bond between atoms.

Thus, metal, is a framework of the positive ions plus free electron gas. The crystal is held together by electrostatic attraction between the negative electron gas and the positive metal ions. Free electrons act like mobile glue to bind positive ion cores together through electrostatic attraction. The bond, so, formed is called *metallic bond*. The valence electrons change their positions with time and hence sharing of electrons is not localized. Due to delocalized nature of valence electrons, metallic bond is weaker and not directional. Metals prefer closed packed structure like fcc and hcp closed packed structure. The metallic bonding is shown in Fig. 1.27.

Examples: Metals like Iron, Nickel, Cobalt, Copper etc.

Properties

- These bonds are non directional.
- The metallic crystals prefer closed packed structure.
- It has moderate to strong bonding and bonding energy range from 1 – 100 eV per atom.
- These metallic bonds are of high density.
- These crystals have moderate to high melting point.
- These are good electric conductors.
- These are good thermal conductors and good heat conductors.
- These are highly ductile and malleable.
- These are opaque to electromagnetic radiations.
- There occurs alloy formation due to these bonds as there is no much difference between electrons of different elements.

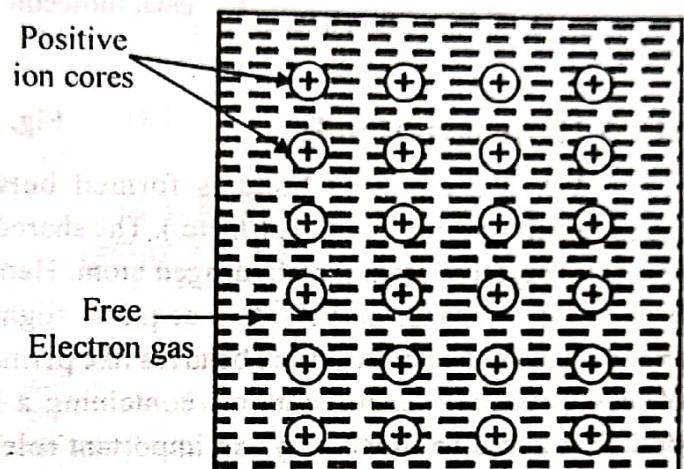


Fig. 1.27 Frame work of positive ion cores and free electrons

1.15.4 Molecular Crystals (Vander Wall Bonds)

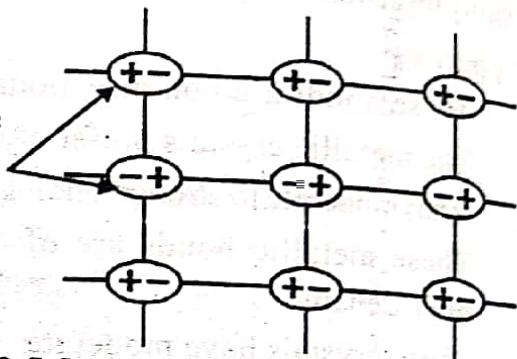
This type of bonding exists in atoms or molecules which have their outermost shell completely filled and hence, have no tendency to gain, lose or share valence electrons with other atoms or molecules. The crystals resulting from this bonding are called molecular crystals. This type of binding arises due to dipolar interaction between atoms of crystal. The electrons of adjacent atoms tend to repel each other and thus produce polarisation in the molecule by disturbing the symmetry of charge distribution. Due to disturbance in electron cloud of an atom, the positive and negative centers of charges do not coincide and electric dipoles are created. This type of dipoles induce dipole attractions in the neighbouring dipoles and also these bonds are called *Vander Wall Bonds*. The presence of this interaction is manifested by the fact that the inert gases can be liquified at very low temperatures. The molecular bonding is shown in Fig. 1.28.

Examples: Argon, Solid CO₂, Neon, Solid nitrogen etc.

Properties

1. These are due to Vander Wall forces of attraction between polarised atoms or molecules, after mutual polarisation of molecules due to each other.
2. These crystals are soft.
3. These have weak bonding.
4. Cleavage of these occurs easily.
5. Loose packed structures.
6. These have very low melting points.
7. These have low electrical and thermal conductivity.
8. These bonds are non-directional.
9. These are transparent.
10. These have low density.

Centres of +ve & -ve charges separated in each molecule



1.15.5 Hydrogen Bonds

Fig. 2.5 Molecular Bonding

When a covalent bond is formed between hydrogen atom and highly electronegative atom (like O, F, Cl, etc.). The shared electron pair gets attracted towards the electronegative atom than hydrogen atom. Hence, electronegative atom acquires a slight negative charge and H-atom acquires slight positive charge. The molecule so formed is said to be polarised and behaves like permanent dipole. This type of interaction between oppositely charged atoms containing a hydrogen atom is called hydrogen bond. The hydrogen bond plays an important role in formation of ice and water. The hydrogen bonding in ICE is shown in Fig. 1.29.

Properties

1. These bonds are moderate (not too weak as molecular crystals).
2. These are directional bonds in nature.
3. These have loose packed structures.
4. These have low electrical and thermal conductivity.
5. These have dielectric properties.
6. These substances have low density.
7. These have low melting points.
8. These have low binding energies and can be easily cleaved.

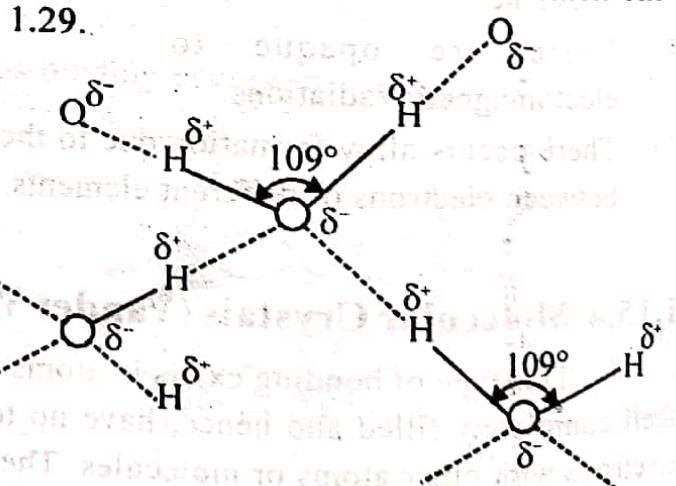


Fig. 1.29 Hydrogen bonding in ICE

2.12 POINT DEFECTS IN SOLIDS

An ideally perfect crystal is one in which atoms are arranged in perfectly regular manner without any deviation in all the directions of crystal. There is no lattice defect in an ideal crystal. However, ideal crystals never occurs in nature. Any deviation of crystal from perfect periodicity is called defect in the crystal. Real crystals always have some defects. All defects found in real crystals can be classified into three main categories. These are:

1. Point defects
2. Line defects
3. Surface defects

We shall confine our study to point defects only.

Point Defects

When the deviation from periodic regular arrangement is localised only around a few atoms, then such type of deviation in the crystal is called point imperfection or point defect. These defects produce a very localised interuption in the regularity of the lattice. The influence of point defect extends only through a few atoms. Point defect produces strain in a very small region of crystal around the defect but does not affect the regularity of distant regions. The point defects in the crystals may be in the form of either impurities or vacancies. The most common point defects in the crystals are described below:

1. Vacancies: A vacancy is simplest point defect in a crystal. This defect arises due to missing atom or vacant atomic site. A vacancy arises when an atom leaves its site. Such defects arise either due to imperfect packing during the original crystallisation or from thermal vibrations of the atoms at high temperatures. When the crystal is heated, the probability that the atoms will jump out of their position will increase. For most of the crystals, this thermal energy is of the order of 1 eV per vacancy. The vacancies may be single, double or more as shown in Fig. 2.21

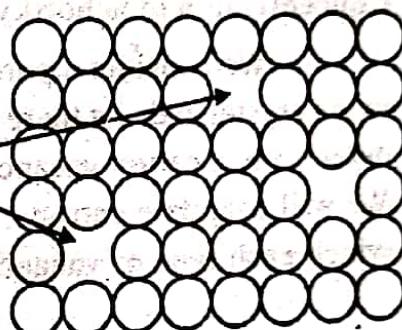


Fig. 2.21 Vacancies

2. Interstitialities: When atomic packing factor is low in a crystal structure, an extra atom may be introduced in the crystal structure. The extra atom can enter the interstitial space between the regularly arranged atoms only when it is smaller than the parent atoms of the crystal. Otherwise, it will

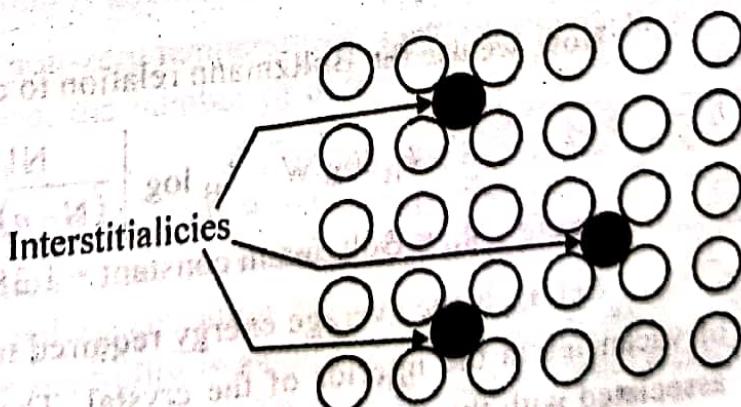


Fig. 2.22

produce atomic distortions. Hence a defect in which an extra atom enters in the interstitial space between regularly arranged atoms of loosely packed structure, is known as interstitial defect as shown in the Fig. 2.22. Interstitialities may also be single interstitial, di-interstitials etc. Clearly, vacancy and interstitials are opposite phenomena in nature.

3. Schottky Defects: Such type of defects are found commonly in ionic crystals. The Schottky defects are usually produced as a result of the thermal vibrations. As the temperature is increased, more and more Schottky defects can be produced in the crystal.

In this type of defect, vacancies are created in a crystal due to migration of ion pairs to the surface of the crystal. Such types of defects arise near the surface of the crystal. In this defect, the formation of vacancies involves a local readjustment of the charge in the crystal such that charge neutrality is maintained in the crystal as a whole. Thus, if in an ionic crystal, there is a vacancy in a positive ion site, the charge neutrality may be achieved by creating vacancy in neighbouring negative ion site. Such a pair of vacant sites is called Schottky defects as shown in Fig. 2.23.

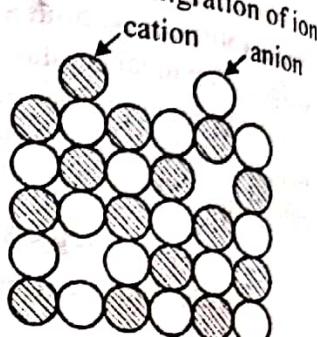


Fig. 2.23 Schottky defect

When crystals are prepared, vacancies always occur in all the crystals. As a result of thermal vibrations, vacancies are produced. Formally, such a defect might be produced by plucking interior ions out of its regular site and placing it on the surface. This process requires energy. Also the disorder increases entropy. In thermal equilibrium, a certain number of vacancies are always present which can be estimated as below:

Concentration of Schottky defects:

We consider a pure crystal composed of equal numbers of cation - anion pairs in the crystal and let there are total N cation-anion pairs in the crystal. Let ' n ' Schottky defects i.e. n cation vacancies and n anion vacancies are to be produced in the interior. We will calculate entropy, S , by using the result that the number of different ways in which each type of vacancies can be produced is given by

$$W = \frac{N!}{(N-n)!n!} \cdot \frac{N!}{(N-n)!n!} = \left[\frac{N!}{(N-n)!n!} \right]^2 \quad \dots(1)$$

The exponent 2 is because there are n cation vacancies as well as n anion vacancies out of N cation - anion pairs. So, total number of different ways of producing these vacancies will be compound probability which is given by the product of two probabilities.

Now, we use the Boltzmann relation to calculate entropy, S ,

$$S = k_B \log W = k_B \log \left[\frac{N!}{(N-n)!n!} \right]^2 \quad \dots(2)$$

where k_B = Boltzmann constant = 1.38×10^{-23} J/K

Let \bar{E}_s is the average energy required to produce a Schottky defect i.e. a pair of vacancies in the interior of the crystal. Then $n\bar{E}_s$ is the total change in energy associated with the generation of n Schottky defects. This change in internal energy produces a change in free energy, according to following relation:

$$F = E - TS$$

Here, $E = \text{change in internal energy due to production of } n \text{ schottky defects}$
Hence $E = n \bar{E}_s$
and S is the change in entropy.

Hence, $F = n \bar{E}_s - k_B T \log \left[\frac{N!}{(N-n)! n!} \right]^2 \quad \dots(3)$

The logarithmic term in equation (3) containing factorials can be simplified by using Stirling's approximation:

$$\log x! \approx x \log x - x$$

so that $\log \left[\frac{N!}{(N-n)! n!} \right]^2 \approx 2 [\log N! - \log (N-n)! - \log n!]$
 $\approx 2 [N \log N - N - (N-n) \log (N-n) + (N-n) - n \log n + n]$
 $= 2 [N \log N - (N-n) \log (N-n) - n \log n] \quad \dots(4)$

So, from (3), we have

$$F = n \bar{E}_s - 2k_B T [N \log N - (N-n) \log (N-n) - n \log n] \quad \dots(5)$$

At thermal equilibrium, the free energy is constant, hence

$$\frac{\partial F}{\partial n} \Big|_T = 0 = \bar{E}_s - 2k_B T \log \left(\frac{N-n}{n} \right)$$

or $\bar{E}_s = 2k_B T \log \left(\frac{N-n}{n} \right)$

or $\frac{N-n}{n} = e^{\bar{E}_s / 2k_B T} \quad \dots(6)$

As the number of vacancies in a crystal is much smaller than the number of ions, hence $n \ll N$ or $N-n \approx N$. Therefore, equation (6) can be approximated as

$$\frac{N-n}{n} = e^{\bar{E}_s / 2k_B T} \quad \text{or} \quad n = N \exp(-\bar{E}_s / 2k_B T) \quad \dots(7)$$

Using above equations, number of Schottky defects in the ionic crystals at ordinary temperature can be calculated. Hence, equation (7) gives concentration of Schottky defects when the equilibrium is attained at temperature T .

It can be concluded that at non-zero temperatures, a certain amount of defects is always present in the crystal. Also, the number of defects in the crystal increases exponentially as its temperature rises.

4. Frenkel Defects: In this type of defect, an atom or ion is transferred from its lattice position to an interstitial site, a position which is not occupied by any atom as shown in Fig. 2.24. Clearly, charge neutrality is again maintained by having an ion in the interstitial position. This pair of vacancy and interstitialcy is called a *Frenkel defect*.

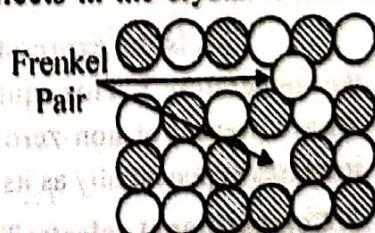


Fig. 2.24 Frenkel Defect

Concentration of frankel defects

We consider again a pure crystal composed of equal numbers of cations and anions. Let it contains N ion pairs and n Frenkel defects i.e. n cation or n anion vacancies and n interstitial ions have to be produced in the interior of the crystal. As before, to calculate its free energy change, we first calculate change in entropy S . Now, the number of different ways, W , in which n frenkel defects can be produced is given by

$$W = \frac{N!}{(N-n)!n!} \cdot \frac{N_i!}{(N_i-n)!n!} \quad \dots(1)$$

where N_i is the number of interstitial positions in the crystal.

Using Boltzmann relation, $S = k_B \log W$

$$\text{and hence, } S = k_B \log \left[\frac{N!}{(N-n)!n!} \cdot \frac{N_i!}{(N_i-n)!n!} \right] \quad \dots(2)$$

If E_i is the energy required to create a vacancy and the associated interstitial position, then total internal energy change, E , is expressed as

$$E = n E_i \quad \dots(3)$$

Hence, due to this disorder, the change in free energy, F , is expressed as

$$F = n E_i - k_B T \log \left[\frac{N!}{(N-n)!n!} \cdot \frac{N_i!}{(N_i-n)!n!} \right] \quad \dots(4)$$

Simplifying the factorial terms by using Stirling's formula ($\log x! \approx \log x - x$),

and then solving $\frac{\partial F}{\partial n} \Big|_T = 0$ at thermal equilibrium, we will get

$$\frac{\partial F}{\partial n} \Big|_T = 0 = E_i - k_B T \log \frac{(N-n)(N_i-n)}{n^2} \quad \dots(5)$$

Since $N \gg n$ and $N_i \gg n$, this gives

$$\frac{E_i}{k_B T} \approx \log \frac{N N_i}{n^2} = \log(N N_i) - 2 \log n$$

which after rearranging the terms becomes

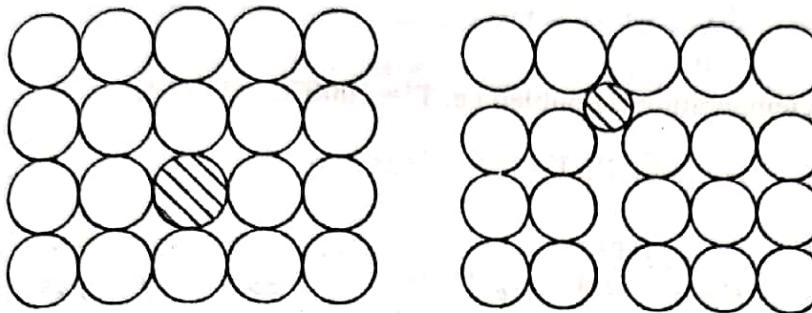
$$\log n = \frac{1}{2} \log(N N_i) - \frac{E_i}{2k_B T}$$

so that $n = (N N_i)^{1/2} e^{-E_i/2k_B T} \quad \dots(6)$

This is the expression for the equilibrium concentration of Frankel defects at the temperature T . This equation also predicts that certain amount of Frenkel defects is always present at non-zero temperatures, and number of defects present in the crystal increases exponentially as its temperature rises.

5. Compositional defects: These defects arise from impurity atoms during crystallization. An impurity atom or ion may enter the lattice substitutionally or interstitially. A

substitution impurity is created when a foreign atom replaces parent atom in the lattice Fig. 2.25 (a). The electronic configuration of impurity atom should be close to that of parent atom for the substitution. Alloys are the best examples of substitutional solids. The physical properties like electrical conductivity, are changed.



(a) Substitutional impurity

(b) Interstitial impurity

Fig. 2.25 Compositional defects

An interstitial impurity is small sized foreign atom occupying an interstitialcy or space between regularly arranged atoms Fig. 2.25 (b). Interstitial atoms or ions are relatively more mobile and reactive than those occupying the normal lattice positions. In photographic processes, the combination of free electrons with interstitial silver ions is believed to be one of the primary stages.

6. Electronic defects: The deviations from the charge distribution in crystals are known as electronic defects. We can also say that the errors in the normal regularity of charge distribution are electronic defects. For example, an impurity atom or ion may have a charge quite different from that of the parent atoms and hence there occurs disturbance in local electronic charge. A vacancy or interstitial can produce deviation or error in electronic charge distribution. These electronic defects in charge are necessary to explain electrical conductivity and related phenomenon in solids. The most important example of this, is the creation of positive and negative charge carriers which is responsible for the operation of p-n junction and transistors.

Example 4: The fraction of vacancy sites in a metal is 1×10^{-10} at 500°C . What will be the fraction of vacancy sites at double the temperature?

Solution. The fraction of vacancies in a crystal is given by

$$f = \frac{n}{N} = e^{-\bar{E}_s/2k_B T}$$

$$\text{or } \log_e f = -\frac{\bar{E}_s}{2k_B T} \log_e e = -\frac{\bar{E}_s}{2k_B T}$$

$$\text{Now, } f = 1 \times 10^{-10},$$

$$\text{Hence, } \log_e (1 \times 10^{-10}) = -\frac{\bar{E}_s}{2 k_B T}$$

$$\text{or } \log_e 1 - \log_e 10 = -\frac{\bar{E}_s}{2 k_B T}$$

or

$$\text{But } T = 500^\circ\text{C} = 773 \text{ K}$$

$$\text{So, } \frac{\bar{E}_s}{2 k_B} = 23.03 \times 773$$

when temperature is doubled i.e. $T' = 1000^\circ\text{C} = 1273 \text{ K}$.

$$\text{then } f' = e^{-\bar{E}_s/2k_B T'}$$

$$\text{or } f' = e^{-\frac{23.03 \times 773}{1273}} = e^{-13.984} \Rightarrow f' = 8.45 \times 10^{-7}$$

Hence, fraction of vacancies (at 1273 K) = 8.45×10^{-7} .

Example 5. The density of Schottky defects in a sample of sodium chloride is $5 \times 10^{11} \text{ m}^{-3}$ at 300K. If interionic separation is 2.82 \AA . What is the average energy required to create one Schottky defect?

Solution. Given: Interionic separation = $2.82 \text{ \AA} = 2.82 \times 10^{-10} \text{ m}$

Density of defects, $n = 5 \times 10^{11} \text{ m}^{-3}$ and $T = 300 \text{ K}$.

Since the unit cell of sodium chloride (without defect) contains four ion pairs, therefore, its volume will be

$$V = (2 \times 2.82 \times 10^{-10})^3 = 1.794 \times 10^{-28} \text{ m}^3$$

Consequently, 1 m^3 of an ideal crystal will contain

$$\frac{4}{1.794 \times 10^{-28}} = 2.23 \times 10^{28} \text{ ion pairs} = N$$

$$\text{Now, using the equation } \frac{n}{N} = \exp\left(-\frac{\bar{E}_s}{2k_B T}\right)$$

Substituting various values, we get

$$\bar{E}_s = 2k_B T \times \frac{1}{n} \left(\frac{2.23 \times 10^{28}}{5 \times 10^{11}} \right)$$

Here $k_B = 8.614 \times 10^{-5} \text{ eV/K}$.

$$\text{Hence, } \bar{E}_s = 2 \times 8.614 \times 10^{-5} \times 300 \times \ln(4.46 \times 10^{16}) = 1.98 \text{ eV Ans.}$$

Example 6. The energy required to remove a pair of Na^+ and Cl^- ions from NaCl is $\sim 2 \text{ eV}$. Calculate the approximate fraction of Schottky defects present in the NaCl crystal at room temperature?

Solution. Given: Temperature $T = 300 \text{ K}$

Energy required to remove a pair of ions = $\bar{E}_s = 2 \text{ eV}$

Therefore, using the expression fraction = $\frac{n}{N} = \exp\left(-\frac{\bar{E}_s}{2kT}\right)$

where $k = 8.614 \times 10^{-5} \text{ eV/K}$

$$\Rightarrow \frac{n}{N} = \exp\left(\frac{-2}{2 \times 8.614 \times 10^{-5} \times 300}\right) = e^{-38.7} = 1.56 \times 10^{-17} \text{ Ans.}$$

Example 7. The average energy required to create a Frenkel defect in an ionic crystal is 1.4 eV. Calculate the ratio of Frenkel defects at 300 K and 600 K in 1 g of the crystal?

Solution. Given: $E_i = 1.4 \text{ eV}$, $T_1 = 300 \text{ K}$, $T_2 = 600 \text{ K}$

Making use of the relation $n = (N N_i)^{1/2} \exp\left(-\frac{E_i}{2kT}\right)$,

where $k = \text{Boltzmann constant} = 8.614 \times 10^{-5} \text{ eV/K}$

$$\text{we obtain } n_{300} = (N N_i)^{1/2} \exp\left(-\frac{1.4}{600 k}\right)$$

$$\text{and } n_{600} = (N N_i)^{1/2} \exp\left(-\frac{1.4}{1200 k}\right)$$

$$\text{So that } \frac{n_{300}}{n_{600}} = \exp\left(-\frac{1.4}{k}\right) \left(\frac{1}{600} - \frac{1}{1200}\right) = 1.316 \times 10^{-6} \text{ Ans.}$$

Example 8. How can Schottky and Frenkel defects be related to vacancies and interstitialcies?

Solution. In nonmetallic crystals, the formation of vacancies involve readjustment of charge in the crystal such that the charge neutrality is maintained in the crystal. As we know, Schottky defect is produced by creating a pair of vacant sites in a positive ion site and in a negative ion site. Hence, we can say vacancies are created in the crystal, so, Schottky defects are closely related to vacancies.

Hence, expression for concentration of vacancies is

$$\frac{n}{N} = \exp\left(-\frac{\bar{E}_s}{2kT}\right)$$

While, in case of Frenkel defect, positive ion is at an interstitial position in the crystal instead of its parent position. So, Frenkel defect is closely related to interstitialcies. Hence, same expression for concentration of frenal defects can be used for interstitialcies concentration in the crystal:

$$n = (N N_i)^{1/2} \exp\left(-\frac{E_i}{2k_B T}\right)$$