

3.1 INTRODUCTION

The matter in this wonderful world is found to exist in three states, solids, liquids and gases.

We know that some solids are brittle, some are ductile, some are malleable, some are strong, some are weak, some are good conductors of heat and electricity, some are bad conductors of heat and electricity, some are magnetic, some are non-magnetic and so on, but all these materials are composed of atoms and molecules.

The constituent particles, i.e., atoms (or) molecules of matter are held together by the forces of attraction. *The attractive forces which hold the constituent particles of a substance together are called bonds.*

The reason for these different properties of the solids are due to their structure. i.e., the behaviour of the solid materials is closely related to the structure of the material. In this chapter we are going to discuss about the different crystal structures and their properties.

3.2 CLASSIFICATION OF SOLIDS

If we examine the solid materials with which we daily come across, we shall find that most of them do not have any characteristic difference in their outward appearance. But if we examine them under a microscope we shall find these materials to have different internal atomic structures.

Based on the internal atomic structure, the solids can be classified into two categories namely (i) Crystalline and (ii) Non-crystalline (or) Amorphous solids.

3.3 CRYSTALLINE SOLIDS (OR) CRYSTALS

Crystalline solids (or) crystals are those in which the constituent atoms (or) molecules are arranged in an orderly fashion throughout, in a three dimensional pattern.

Each atom (or) molecule is fixed at a definite point in space, at a definite distance from each other and in a definite angular orientation to all other atoms (or) molecules surrounding it. Therefore, crystalline solids have well defined geometrical form (pattern). i.e., they have well defined faces and angles between them.

As a practical example we can say that in a crystal, the atoms are arranged like soldiers on a parade ground in a well defined columns and rows.

Further when crystal breaks, all the broken pieces will have a regular shape. The crystalline solids have directional properties and therefore they are called anisotropic substances.

A crystalline material will be in two forms viz

(i) **Single crystal**, in which the solid contains only one crystal. These single crystals are produced artificially from their vapour (or) liquid state.

(ii) **Poly crystal**, which has an aggregate of many small crystals (or) grains separated by well defined grain boundaries. These crystals will have a sharp melting point.

Examples for crystalline solids: Diamond, Copper, Platinum, Silver, Polonium, Gold, Aluminium, Molybdenum, Nickel, Cadmium, Iron etc.

Crystallography: *The study of the geometric form and other physical properties of crystalline solids, using X-rays (or) electron beam (or) neutron beam etc., is termed as the science of crystallography.*

Note: Grains: The crystals are also known as grains.

Grain boundary: The boundary separating the two adjacent grains is called grain boundary.

Whiskers: Whiskers are nothing but artificially produced crystals. They are produced under some special conditions so that, they do not have any structural defects.

3.4 AMORPHOUS SOLIDS (OR) NON-CRYSTALLINE SOLIDS

"Amorphous" means "without form".

In amorphous solids the constituent particles i.e., atoms (or) molecules are not arranged in an orderly fashion. In other way we can say that in amorphous solids the same atomic groups are arranged randomly in all directions.

These solids have no directional properties and therefore they are called isotropic substances. These amorphous solids do not have a sharp melting point.

Examples for amorphous solids: Plastics, Rubber and Glass.

Note: Supercooled liquids

The materials such as glass, which exhibit some of the properties of a solid (like hardness, definite shape etc.) but are not crystalline, are known as supercooled liquids.

3.5 DIFFERENCES BETWEEN CRYSTALLINE AND NON-CRYSTALLINE MATERIAL

S. No.	Crystalline material	Non-crystalline material
1.	They have a definite and regular geometrical shapes which extend throughout the crystal.	They do not have definite geometrical shape.
2.	They are anisotropic.	They are isotropic.
3.	They are most stable.	They are less stable.
4.	They have sharp melting point.	They do not have sharp melting point.
5.	Examples: Diamond, NaCl, KCl, Copper, Iron, etc.	Examples: Glasses, Plastics, Rubber etc.

3.6 FUNDAMENTALS OF CRYSTALS AND ITS STRUCTURE

Crystal: Crystal is a regular polyhedral form bounded by smooth surfaces, which is formed by chemical compound under the action of its interatomic forces, when passing from the state of liquid (or) gas to that of a solid, under suitable conditions.

The phase change from liquid (or) gas to solid is called crystallization.

The crystal structure gives the arrangement of atoms within a crystal. Determination of crystal structure with the help of X-ray is known as X-ray crystallography.

X-rays are most widely used to study the crystal structure because, the wavelength of X-rays (10^{-12} to 10^{-10} m) are almost equal to that of the inter atomic distances and hence diffraction can easily occur, when they are are passed through the crystals.

Fundamental crystallographic terms (definitions)

1. Lattice

Lattice is defined as an array of points which are imaginarily kept to represent the position of atoms in the crystal such that every lattice point has got the same environment as that of the other and hence one lattice point cannot be distinguished from the other lattice point.

It is an imaginary concept.

2. Space lattice (or) crystal lattice

A three dimensional collection of points in space are called space lattice (or) crystal lattice. The environment about any particular point is in everyway the same.

(or)



Fig 3.6 (a)



Fig 3.6 (b)



Fig 3.6 (c)



Fig 3.6 (d)



Fig 3.6 (e)

Fig. 3.6

7. Unit cell

Definition

The **unit cell** is defined as the smallest geometric figure, the translational repetition of which in all over the three dimensions gives the actual crystal structure.

(or)

The unit cell may also be defined as the fundamental elementary pattern with minimum number of atoms, molecules (or) groups of molecules which represents the total characteristics of the crystal.

Explanation

Let us consider, a two dimensional crystal lattice as shown in fig. (3.7)

Let us consider a parallelogram $ABCD$ of side $AB = \vec{a}$ and $AD = \vec{b}$. When the parallelogram $ABCD$ is rotated repeatedly by any integral multiple of vectors \vec{a} and \vec{b} then, corresponding to AB and AD the whole pattern (or) array may be obtained. i.e., the whole crystal may thus be reproduced.

This region $ABCD$ is called a unit cell and \vec{a}, \vec{b} are called **basis vectors**.

The choice of a unit cell is **not unique**. It can be constructed in many number of ways like $A_1 B_1 C_1 D_1$ (or) $A_2 B_2 C_2 D_2$ etc., without affecting the symmetry of the crystal as shown in fig 3.7.

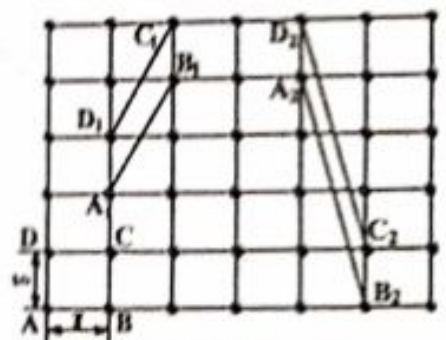


Fig 3.7

We can extend the same procedure for three dimensional case also. The fig. 3.8 shows the unit cell (shaded portion) in the three dimension, which on repetition over all the three directions viz x , y and z , we can get the total crystal structure.



Fig. 3.8

As a practical example, the unit cell may be considered as the brick of a wall. Here the wall represents the crystal. We know that the shape of the wall will depend upon the shape of the brick. Similarly the shape of the crystal will depend upon the shape of the unit cell.

Note: Other terms used to represent a unit cell:

The unit cell is also known as basic cell (or) basic unit or fundamental unit (or) fundamental elementary pattern (or) building block (or) lattice unit.

8. Lattice parameters (or) Unit cell parameters

The fig. 3.9 shows a unit cell of a three dimensional crystal lattice.

The lines drawn parallel to the lines of intersection of any three faces of the unit cell which do not lie in the same plane are called crystallographic axes.

The intercepts a , b and c are nothing but the edges of the unit cell, (i.e., the distance between two lattice points) which defines the dimensions of an unit cell. These intercepts are known as its primitives (or) characteristic intercepts on the axes.

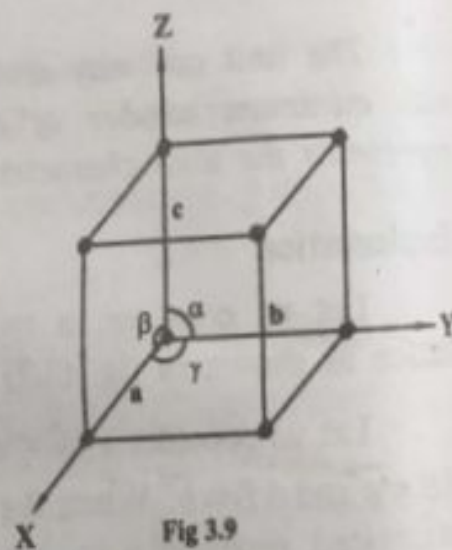


Fig. 3.9

Fig. 3.9 Lattice parameters

These three quantities a , b and c are also called the *fundamental translational vectors (or) axial lengths*. The angles between (a, b) , (b, c) and (c, a) are denoted by γ , α and β respectively. These three angles (α , β and γ) are called *interfacial angles*.

Both, the intercepts (a, b, c) and interfacial angles (α, β, γ) constitutes the *lattice parameters (or) cell parameters of the unit cell*.

The actual size of the unit cell can be determined by knowing the values of intercepts and interfacial angles.

9. Primitive cell

A primitive cell is the simplest type of unit cell which contains only one lattice point per unit cell (contains lattice points at its corner only).

Example: Simple Cubic (SC)

10. Non-primitive Cell

If there are more than one lattice point in an unit cell, it is called a non-primitive cell.

Example: BCC and FCC contains more than one lattice point per unit cell.

If the number of lattice points per unit cell is two (BCC), three and four (FCC), then the unit cell is called doubly primitive, triply primitive and quadruply primitive respectively

3.7 THE CRYSTAL SYSTEMS

Crystals are classified into 7 crystal systems on the basis of lattice parameters viz (i) axial lengths a, b, c and (ii) interfacial (axial) angles α, β, γ .

The 7 basic crystal systems are

1. Triclinic
2. Monoclinic
3. Orthorhombic
4. Tetragonal
5. Hexagonal
6. Trigonal (or) Rhombohedral
7. Cubic.

The 7 crystal systems are discussed briefly one by one as follows

1. Triclinic crystal system

In triclinic crystal system, all the three crystal axes are not perpendicular to each other. The axial lengths are also not equal (different) along the three axes, as shown in fig. 3.10.

Lattice parameters are $\left[\begin{array}{l} a \neq b \neq c \\ \alpha \neq \beta \neq \gamma \neq 90^\circ \end{array} \right]$

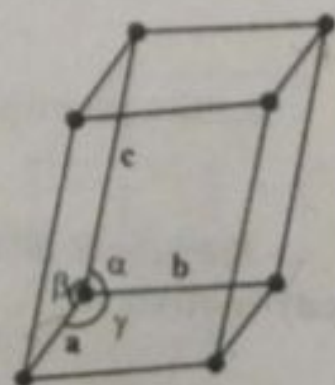


Fig 3.10

Triclinic lattice has only one form i.e., Simple.

2. Monoclinic crystal system

In monoclinic crystal system, two of the crystal axes are perpendicular to each other, but the third is obliquely inclined. The three axial lengths are different along the axes as shown in fig. 3.11.

$$\text{Lattice parameters are } \left[\begin{array}{l} a \neq b \neq c \\ \alpha = \gamma = 90^\circ \neq \beta \end{array} \right]$$

Monoclinic lattices may be in any one of these two forms viz. simple (or) base centred.

3. Orthorhombic crystal system

In orthorhombic crystal system, the three crystal axes are perpendicular to each other. In this system, all the three axial lengths are of unequal lengths (different), as shown in fig. 3.12.

$$\text{Lattice parameters are } \left[\begin{array}{l} a \neq b \neq c \\ \alpha = \beta = \gamma = 90^\circ \end{array} \right]$$

Orthorhombic lattice may be in any one of these four forms i.e., simple (or) base centred (or) body-centred (or) face centred.

4. Tetragonal crystal system

In tetragonal system, the three crystal axes are perpendicular to each other. Two of the three axial lengths are the same, but the third axial length is different, as shown in fig. 3.13

$$\text{Lattice parameters are } \left[\begin{array}{l} a = b \neq c \\ \alpha = \beta = \gamma = 90^\circ \end{array} \right]$$

Tetragonal lattices may be in any one of these two forms viz., Simple (or) Body-centred.

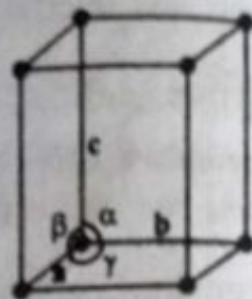


Fig 3.11

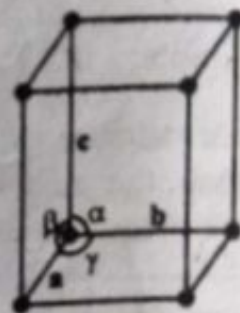


Fig 3.12

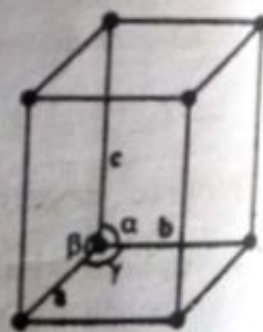


Fig 3.13

5. Hexagonal crystal system

In hexagonal crystal system, two of the crystal axes are 120° apart. While the third is perpendicular to both of them.

The axial lengths are the same along the axes that are 120° apart, but the axial length along the third axis is different, as shown in fig. 3.14.

Lattice parameters are $\Rightarrow \left[\begin{array}{l} a = b \neq c \\ \alpha = \beta = 90^\circ \text{ and } \gamma = 120^\circ \end{array} \right]$

Hexagonal lattice has only one form i.e., Simple

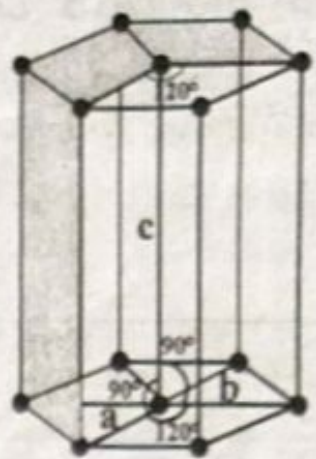


Fig 3.14

Note: From fig. 3.14 if we neglect the shaded portion, we can view the unit cell of HCP similar to other crystal systems.

6. Trigonal (or) Rhombohedral crystal system

In trigonal crystal system, the three axes are inclined to each other at an angle other than 90° . The three axial lengths are equal along the axes, as shown in fig. 3.15.

Lattice parameters are $\Rightarrow \left[\begin{array}{l} a = b = c \\ \alpha = \beta = \gamma \neq 90^\circ \end{array} \right]$

Trigonal lattice has only one form i.e., simple.

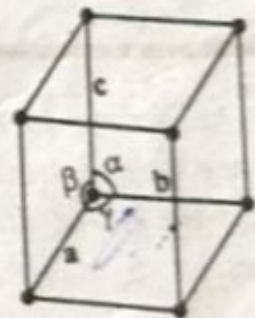


Fig 3.15

7. Cubic crystal system

In cubic crystal system, the three crystal axes are perpendicular to each other and the axial lengths is the same along all the three axis as shown fig. 3.16

Lattice parameters are $\Rightarrow \left[\begin{array}{l} a = b = c \\ \alpha = \beta = \gamma = 90^\circ \end{array} \right]$

Cubic lattices may be in any one of these three forms viz Simple Cubic (SC) (or) Body-Centred Cubic (BCC) (or) Face Centred Cubic (FCC)

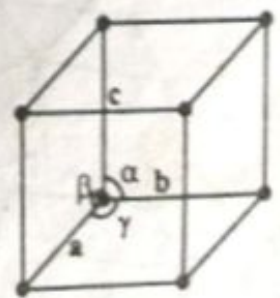


Fig 3.16

3.8 BRAVAIS LATTICES

Bravais in 1880 showed that there are 14 possible types of space lattices in the 7 crystal systems as shown in Table 3.1.

Table 3.1

S.No.	System	No. of Bravais lattices	Bravais Lattice
1.	Triclinic	1	Simple (or) Primitive
2.	Monoclinic	2	Simple (or) Primitive, Base Centred
3.	Orthorhombic	4	Simple (or) Primitive, Body Centred, Face Centred and Base Centred
4.	Tetragonal	2	Simple (or) Primitive and Body Centred
5.	Hexagonal	1	Simple (or) Primitive
6.	Trigonal	1	Simple (or) Primitive
7.	Cubic	3	SC (or) Primitive (P), BCC and FCC
	Total	14	

According to Bravais, there are only 14 possible ways of arranging points in space lattice from the 7 crystal systems such that, all the lattice points have exactly the same surroundings. These 14 space lattices are called the Bravais lattices.

Table 3.2 shows the seven crystal systems, which are divided into 14 Bravais lattices along with the unit cell parameters and examples.

Table 3.2
The Seven Crystals Systems, divided into 14 Bravais lattices

S.No.	Crystal System	Bravais lattice	Unit cell Parameters	Examples
1.	Triclinic	Simple	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$	$\text{CuSO}_4, \text{K}_2\text{Cr}_2\text{O}_7$
2.	Monoclinic	Simple	$a \neq b \neq c$ $\alpha = \beta = 90^\circ \neq \gamma$	$\text{Na}_2\text{SO}_4, \text{FeSO}_4$
		Base-centred		NO_2, SO_3
3.	Orthorhombic	Simple		$\text{KNO}_3, \text{BaSO}_4, \text{MgSO}_4$
		Base-centred	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	Sulphur, Topaz
		Body-centred		
		Face-centred		
4.	Tetragonal	Simple	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	$\text{NiSO}_4, \text{SnO}_2$, Indium, white tin
		Body-centred		
5.	Hexagonal	Simple	$a = b \neq c$ $\alpha = \beta = 90^\circ, \gamma = 120^\circ$	Tourmaline, Quartz
6.	Trigonal (Rhombohedral)	Simple	$a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$	$\text{CaSO}_4, \text{Bi}, \text{Sb}, \text{Calcite}$
7.	Cubic	Simple		$\text{NaCl}, \text{CaF}_2, \text{NaClO}_3$
		Body-centred	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	
		Face-centred		

3.18 MILLER INDICES

Introduction

We know, crystals are made up of large number of parallel equidistant planes, passing through the lattice points called *lattice planes*. The different ways (1, 2, 3, 4, 5, 6) in which the lattice planes can be chosen is as shown in fig. 3.39.

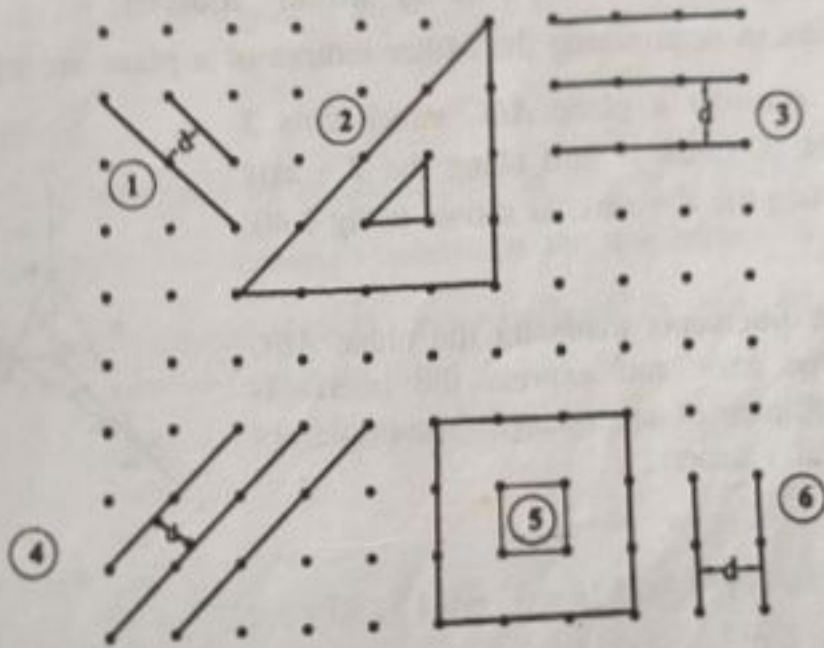


Fig. 3.39

The perpendicular distance between any two adjacent planes is called *Interplanar distance (d)*

Thus in a crystal, there exists different direction and different planes, each having its characteristic interplanar spacing.

Therefore, it is necessary to locate these directions and planes for a crystal. To identify the direction and to designate (to choose) a plane in a crystal, Miller, a scientist suggested a method as discussed below.

Miller indices

Miller introduced a set of three numbers to ^{choose} designate a plane in a crystal. This set of three numbers are known as Miller indices of the concerned plane.

Definition

Miller indices is defined as the reciprocal of the intercepts made by a plane on the crystallographic axes which are reduced to smallest numbers.

(or)

Miller indices are the three smallest possible integers, which have the same ratio as the reciprocals of the intercepts of the plane concerned along the 3 axes.

Procedure (or) Steps for finding Miller indices

The steps in determining the Miller indices of a plane are illustrated below.

Let us consider a plane ABC which cuts 3 units along the X-axis, 1 unit along the Y-axis and 2 units along the Z-axis, as shown in fig 3.40.

Step 1:

Find the intercepts made by the plane ABC along the three axes and express the intercepts in terms of multiples of axial lengths (multiples of the fundamental vectors) i.e.,

$$OA : OB : OC = pa : qb : rc$$

In this case Fig. 3.40 [$p = 3$, $q = 1$, and $r = 2$].

\therefore The intercepts are $3a : 1b : 2c$

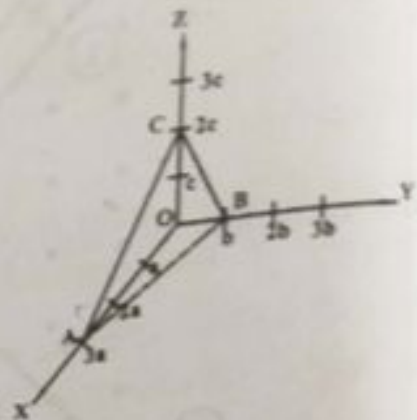


Fig. 3.40

Step 2:

Find the coefficients of the intercepts i.e., 3, 1, 2

Step 3:

Find the reciprocal of these numbers $\frac{1}{p} : \frac{1}{q} : \frac{1}{r}$ i.e., $\frac{1}{3} : \frac{1}{1} : \frac{1}{2}$

Step 4:

Convert these reciprocals into whole numbers by multiplying each and every reciprocal with their least common multiplier (LCM).

Since 6 is the LCM in this case, we get $6 \times \frac{1}{3} \quad 6 \times \frac{1}{1} \quad 6 \times \frac{1}{2}$

\therefore We have = 2 6 3

Step 5:

Enclose these numbers in a bracket like this $\rightarrow ()$ i.e., (2 6 3). This represents the indices of the given plane and is called the Miller indices of the plane.

Miller indices is generally denoted by (hkl) . Thus, we can write

$$h : k : l = \frac{a}{p} : \frac{b}{q} : \frac{c}{r} \text{ for any system and } h : k : l = \frac{a}{p} : \frac{a}{q} : \frac{a}{r} \text{ for cubic system.}$$

Points to Ponder

- » The Miller indices should be enclosed only in this bracket i.e., $\rightarrow ()$.
- » There should not be any comma's inbetween the numbers.
- » If the Miller indices is say (2 6 3) means it should be read as two six three, and not as two hundred and sixty three.
- » The direction of plane can be represented by enclosing the Miller indices in a square bracket (e.g) [2 6 3]

Note: 1. To represent the family of planes we can use this bracket i.e., $\rightarrow \{ \}$

2. Negative Miller indices can be represented by putting a bar over the numbers (e.g.) $(\bar{2} 6 \bar{3})$ represents the plane with intercepts on negative X axis, positive Y axis and negative Z axis.

another at the centre of bottom hexagonal face. Along with these atoms there are 3 more atoms in the middle layer, situated inbetween the top and bottom hexagonal face of the cell, in alternative vertical faces as shown in Fig. 3.21.

Examples: Magnesium, Osmium, Cobalt, titanium, etc.,



Fig. 3.21

3.10 PARAMETERS DETERMINING THE CRYSTAL STRUCTURE OF MATERIALS

Let us discuss some of the important parameters which are used to describe the crystal structure.

1. Number of atoms per unit cell (or) Effective number

The total number of atoms present in (or) shared by an unit cell is known as number of atoms per unit cell.

2. Atomic radius

Atomic radius is defined as half of the distance between any two nearest neighbour atoms which have direct contact with each other, in a crystal of a pure element.

It is usually expressed in terms of cube edge a .

3. Co-ordination number

Co-ordination number is the number of nearest neighbouring atoms to a particular atom.

(or)

Co-ordination number is the number of nearest neighbours directly surrounding a given atom.

4. Atomic packing factor (or) packing density (or) density of packing

Atomic packing factor is defined as the ratio between the volume occupied by the total number of atoms per unit cell (v) to the total volume of the unit cell (V).

$$\text{i.e., APF} = \frac{\text{Volume occupied by the total number of atoms per unit cell}}{\text{Total volume of the unit cell}} = \frac{(v)}{(V)}$$

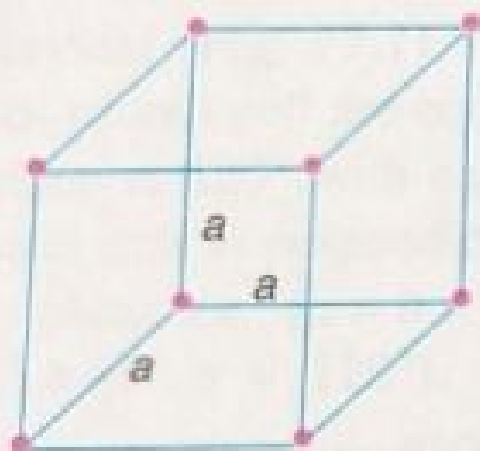


$$\text{(or) APF} = \frac{\text{Total Number of atoms per unit cell} \times \text{Volume of one atom}}{\text{Total volume of the unit cell}}$$

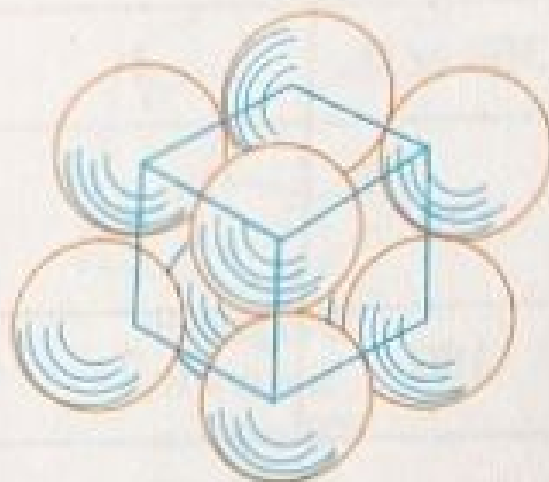
Let us discuss all the above parameters one by one for a simple cubic structure.

77.4 Simple Cubic (SC) Structure

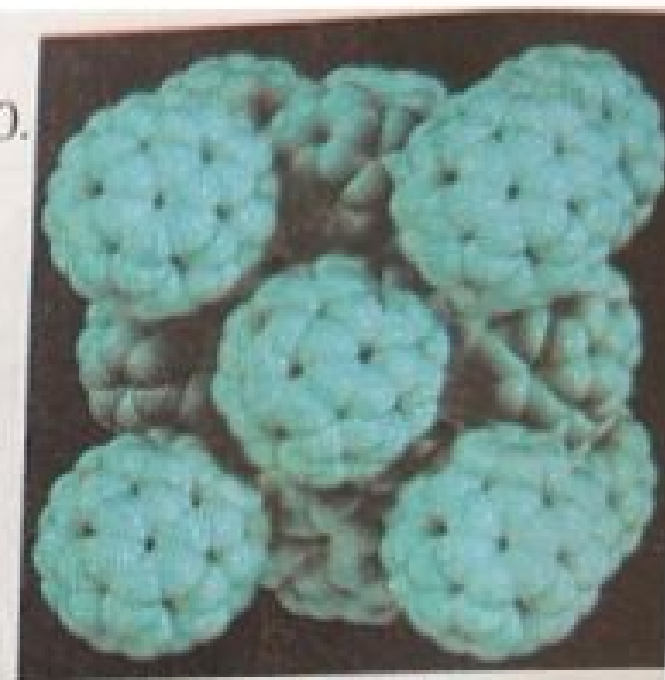
The cubic unit cell for simple cubic lattice is shown in Fig. 77.10.



(a) atomic-site model



(b) hard sphere model



Simple Cubic Structure.

Fig. 77.10

(i) **Number of atoms per unit cell**

There are 8 atoms at the 8 corners of the cell.
 Each corner atom is shared by 8 unit cells that adjoin at each corner.
 The share of each corner atom to a unit cell is $1/8$ of an atom.

Total number of atoms per unit cell is $8 \times \frac{1}{8} = 1$.

(ii) **Atomic radius, r**

In a SC cell the atoms are in contact along the edges of the cube (Fig. 77.11).

a is length of side of cubic cell.
 The atoms touch along cube edges.

Nearest neighbour distance,

$$2r = a$$

$$\therefore r = a/2.$$

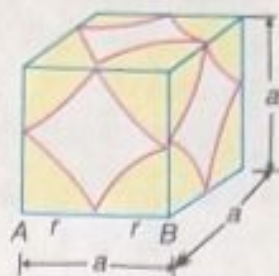


Fig. 77.11

(iii) **Coordination number, CN**

Each corner atom touches four atoms in its horizontal plane, and two atoms, one vertically above it and one vertically below it. So there are six equally spaced nearest neighbour atoms each at a distance ' a ' from that atom. Therefore, the coordination number is six.

$$CN = 6.$$

(iv) **Packing Factor**

$$\begin{aligned} \text{Packing factor} &= \frac{\text{Volume of all atoms in the unit cell}}{\text{Volume of the unit cell}} \\ &= \frac{\text{No. of atoms in unit cell} \times \text{Volume of one atom}}{\text{Volume of the unit cell}} \\ &= \frac{1 \times \frac{4}{3} \pi r^3}{(a)^3} = \frac{4\pi r^3}{3(2r)^3} \quad (\because a = 2r) \\ &= \frac{\pi}{6} = 0.52. \end{aligned}$$

\therefore Packing factor = 52%

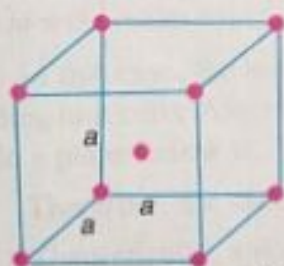
Simple cubic structure is a loosely packed structure.
 Polonium is the only element which exhibits this structure.

77.5 Body Centred Cubic (BCC) Structure

Fig. 77.12 (a) shows the arrangement of lattice points in a BCC cell.
 Fig. 77.12 (b) shows the arrangement of atoms represented as hard spheres.
 Fig. 77.12 (c) shows the BCC repeating structure.



Body Centred Cubic Structure.



(a) atomic site model



(b) hard sphere model



(c) repeating structure in a crystal

Fig. 77.12

Let us now compute the characteristics of a BCC cell.

(i) Number of atoms per unit cell

There are 8 atoms at the 8 corners, each shared by 8 unit cells and one atom at the body centre. The atom at the centre of the body of the cell wholly belongs to the unit cell.

Thus, the total number of atoms per unit cell is $8 \times \frac{1}{8} + 1 = 2$.

(ii) Atomic radius, r

In this case, atoms touch each other along the diagonal of the cube (Fig. 77.13).

The length of the body diagonal = $4r$.

$$AG^2 = AC^2 + CG^2 = (AB^2 + BC^2) + CG^2$$

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

$$\text{Atomic radius } r = \frac{\sqrt{3}a}{4}$$

$$\text{Lattice constant } a = \frac{4}{\sqrt{3}}r.$$

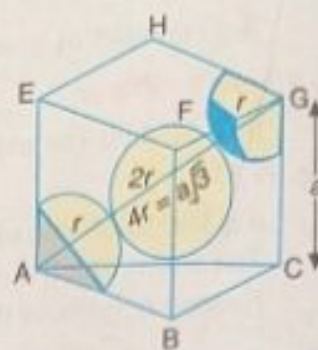


Fig. 77.13

(iii) Coordination number, CN

The unit cell contains one atom at each of the eight corners of the unit cell and one atom at the body centre. The nearest atom to the corner atom is the body centred atom and not the other corner atoms. The number of nearest neighbours is eight (Fig. 77.14).

The body centre atom is in contact with all the eight corner atoms. Therefore, the coordination number is eight.

$$CN = 8.$$

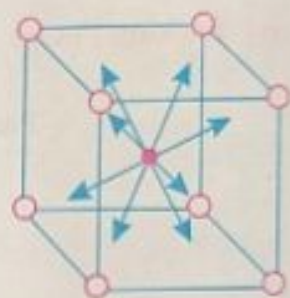


Fig. 77.14

(iv) Packing Factor

$$\text{Packing factor} = \frac{\text{Volume of all atoms in the unit cell}}{\text{Volume of the unit cell}}$$

$$= \frac{\text{No. of atoms in unit cell} \times \text{Volume of one atom}}{\text{Volume of the unit cell}}$$

$$= \frac{2 \times (4/3)\pi r^3}{a^3} = \frac{8\pi r^3}{3a^3}$$

$$= \frac{8\pi \left(\frac{\sqrt{3}a}{4}\right)^3}{3a^3}$$

$$\left(\because r = \frac{\sqrt{3}a}{4} \right)$$

$$= \frac{\sqrt{3}\pi}{8} = 0.68.$$

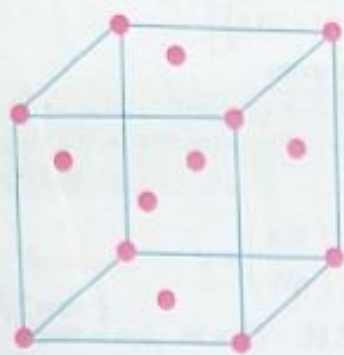
\therefore Packing factor = 68%.

Thus the packing factor is equal to 68%. So it is not a closely packed structure.

Tungsten, sodium, iron and chromium have this type of structure.

77.6 Face Centred Cubic (FCC) Structure

The unit cell of this structure is shown in Fig. 77.15.

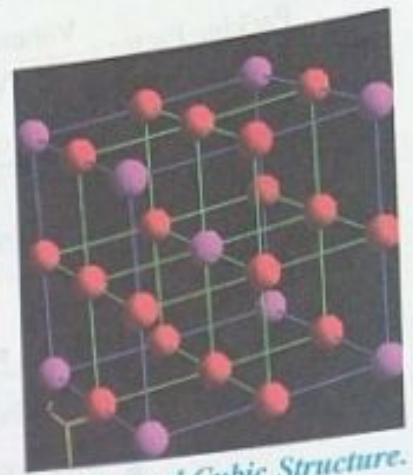


(a) atomic site model



(b) hard sphere model

Fig. 77.15



Face Centred Cubic Structure.

The face centred cubic unit cell is a nonprimitive cell.

It has six atoms at the centres of six faces and eight atoms at the eight corners of the cube.

We shall now determine the characteristics of the FCC cell.

(i) Number of atoms per unit cell

There are 8 atoms, each shared by 8 unit cells at 8 corners and 6 face-centred atoms, each shared by 2 cells.

The total number of atoms per unit cell = contribution due to 8 corner atoms + contribution due to 6 face centred atoms

$$= \left(\frac{1}{8} \times 8\right) + \left(\frac{1}{2} \times 6\right) = 1 + 3 = 4$$

Thus the total number of atoms per unit cell is 4.

(ii) Atomic radius, r

In a FCC cell, atoms are in contact along the face diagonal of the cube (Fig. 77.16).

Length of the face diagonal, $AF = 4r$.

$$AF^2 = AB^2 + BF^2$$

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

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

$$\therefore \text{Atomic radius, } r = \frac{a}{2\sqrt{2}}$$

$$\text{Lattice constant } a = 2\sqrt{2}r.$$

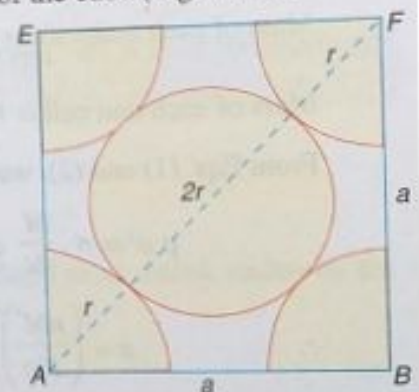


Fig. 77.16

(iii) Coordination number CN

In this case, the nearest neighbours of any corner atom are the face centred atoms of the surrounding unit cells. Any corner atom has four such atoms in its own plane, four in a plane above it and four in a plane below it.

Therefore, the coordination number $CN = 12$.

Theoretically, a sphere can touch simultaneously 12 identical spheres at the maximum in a three dimensional structure. Thus, an FCC cell has the maximum value for the coordination number.

(iv) Packing Factor

$$\begin{aligned}
 \text{Packing Factor} &= \frac{\text{Volume of all atoms in the unit cell}}{\text{Volume of the unit cell}} \\
 &= \frac{\text{No. of atoms in unit cell} \times \text{Volume of one atom}}{\text{Volume of unit cell}} \\
 &= \frac{4 \times \frac{4}{3} \pi r^3}{a^3} \\
 &= \frac{16}{3} \cdot \frac{\pi r^3}{(2\sqrt{2}r)^3} \quad (\because a = 2\sqrt{2}r) \\
 &= \frac{\pi}{3\sqrt{2}} = 0.74
 \end{aligned}$$

\therefore Packing factor = 74%

When compared with *SC* and *BCC*, this has the highest packing factor.

Most of the metals like copper, aluminium, lead and silver have this structure.

77.7 Calculation of Lattice Constant

Consider a cubic lattice of lattice constant a .

Let ρ be the density of the crystal.

Volume of the unit cell = a^3

\therefore Mass in each unit cell = ρa^3 ... (1)

Let n = No. of molecules (lattice points) per unit cell,

M = molecular weight and

N = Avogadro number (*i.e.*, number of molecules per kg mole of the substance).

Mass of each molecule = $\frac{M}{N}$

Mass of each unit cell = $n \times \frac{M}{N}$... (2)

From Eqs. (1) and (2), we have

$$M = \rho a^3 N$$

$$\therefore \text{Volume occupied by one atom} = \frac{24.515 \times 10}{2} = 12.26 \times 10^{-30} \text{ m}^3.$$

(ii) In FCC, $a = 2\sqrt{2}r = 2\sqrt{2} \times 1.292 \text{ \AA}$

$$= 2\sqrt{2} \times (1.292 \times 10^{-10}) \text{ m} = 3.654 \times 10^{-10} \text{ m}.$$

$$\text{Volume of unit cell} = a^3 = (3.654 \times 10^{-10})^3 = 48.787 \times 10^{-30} \text{ m}^3.$$

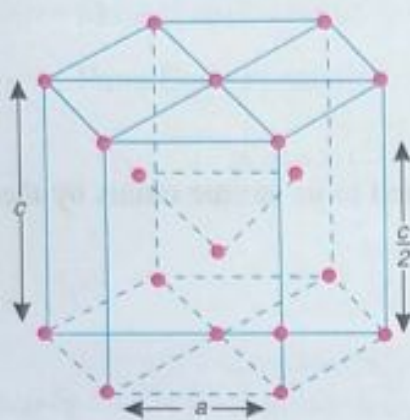
$$\text{Number of atoms per unit cell} = 4$$

$$\text{Volume occupied by one atom} = \frac{48.787 \times 10^{-30}}{4} = 12.2 \times 10^{-30} \text{ m}^3$$

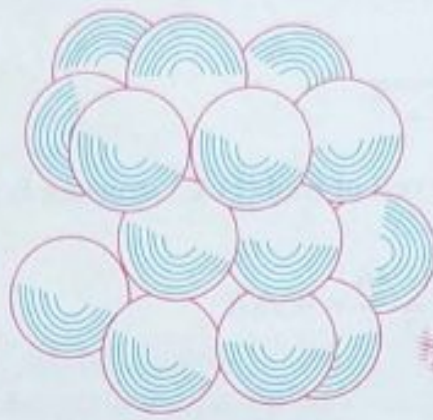
$$\therefore \text{Volume change in \%} = \frac{12.26 - 12.2}{12.26} \times 100 = 0.489.$$

77.8 Hexagonal Close Packed (HCP) Structure

The conventional unit cell for hexagonal close packed structure is shown in Fig. 77.17.



(a) atomic site model



(b) hard sphere model



Hexagonal Close Packed (HCP) Structure.

Fig. 77.17

There are three layers of atoms in the unit cell.

- (i) At the bottom layer, central atom has six nearest neighbour atoms in the same plane.
- (ii) Top layer has the same atomic arrangement as the bottom layer.

(iii) At $c/2$ distance from the bottom layer there is a middle layer containing three atoms.
Let us now compute the characteristics of HCP cell.

(i) **Number of atoms per unit cell**

The top layer contains 6 atoms at the corners and one atom at the centre.

The corner atoms are shared between 6 unit cells. Hence 6 atoms contribute only 1 atom to the unit cell.

The central atom is shared between 2 unit cells and therefore contributes $\frac{1}{2}$ atom to unit cell.

Hence the top layer contributes $1 + \frac{1}{2} = \frac{3}{2}$ atoms to the unit cell.

Similarly, the bottom layer contributes $\frac{3}{2}$ atoms to the unit cell.

The three atoms of the middle layer lie within the volume of the unit cell and hence fully (3 atoms) contribute to the cell.

Thus, the total number of atoms/unit cell.

$$= \frac{3}{2} + \frac{3}{2} + 3 = 6.$$

(ii) **Atomic radius, r**

The atoms are in contact along the edges of the hexagon

(Fig. 77.18)

$$\therefore 2r = a$$

$$\text{or } r = a/2.$$

(iii) **Coordination number, CN**

Consider the central atom at the top layer of HCP structure. It touches 6 atoms in its plane, 3 atoms in the plane just below it and 3 atoms in the plane just above it. Hence the coordination number is 12.

(iv) **Volume of the unit cell**

The volume of the unit cell is determined by computing the area of the base of the unit cell and then by multiplying it by the cell height. The area of the base of the unit cell is the area of the hexagon ABDEFG (Fig. 77.19). It is equal to the sum of the areas of the six equal-sized triangles.

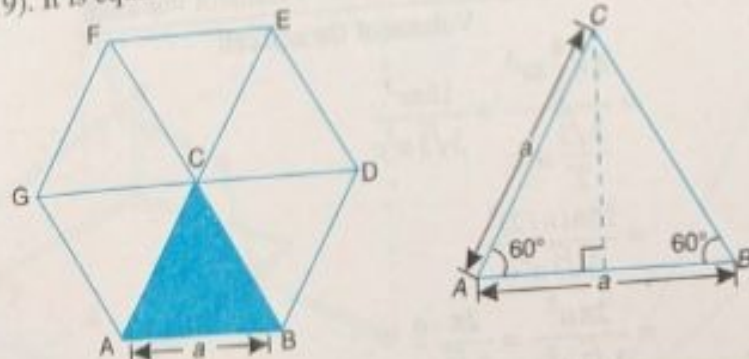


Fig. 77.18

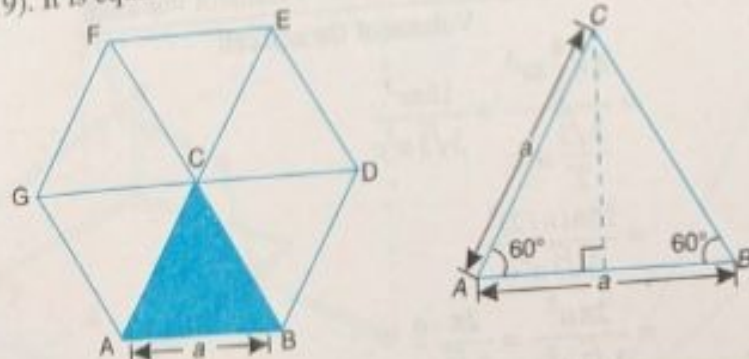


Fig. 77.19

$$\therefore \text{Area of hexagon } ABDEFG = 6 (\text{area of } \Delta ABC)$$

$$= 6 \times \left[\frac{1}{2} \times a \times (a \sin 60^\circ) \right]$$

$$= 3a^2 \left(\frac{\sqrt{3}}{2} \right) = \frac{3\sqrt{3}}{2} a^2.$$

∴ Volume of the unit cell, $V = (\text{area of the base}) \times (\text{Height of the cell})$

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

Calculation of c/a ratio

Let c be the height of the unit cell and a be its edge. Also $a = 2r$.

The three body atoms lie in a horizontal plane at a height $c/2$ from the orthocentres of alternate equilateral triangles in the base or at top of the hexagonal cell.

From Fig. 77.20,

$$(2r)^2 = x^2 + \left(\frac{c}{2} \right)^2$$

But, $x = \frac{2}{3} AN = \frac{2}{3} \left(a \frac{\sqrt{3}}{2} \right) = \frac{a}{\sqrt{3}}$

Also $2r = a$

$$\therefore a^2 = \left(\frac{a}{\sqrt{3}} \right)^2 + \left(\frac{c}{2} \right)^2 = \frac{a^2}{3} + \frac{c^2}{4}$$

$$\frac{c^2}{4} = a^2 - \frac{a^2}{3} = \frac{2a^2}{3}$$

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

$$\therefore \frac{c}{a} = \sqrt{\frac{8}{3}} = 1.633.$$

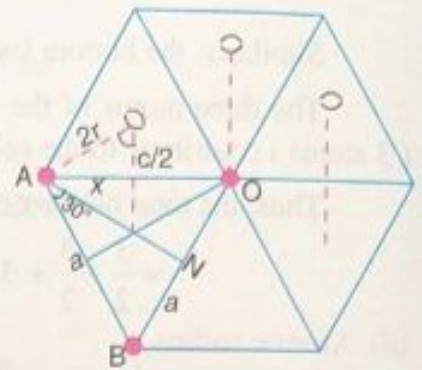


Fig. 77.20

(v) Calculation of packing factor

$$\text{Packing factor} = \frac{\text{Volume of all atoms in the unit cell}}{\text{Volume of the unit cell}}$$

$$= \frac{\text{No. of atoms in unit cell} \times \text{Volume of one atom}}{\text{Volume of the unit cell}}$$

$$= \frac{6 \times \frac{4}{3} \pi r^3}{\frac{3\sqrt{3}}{2} a^2 c} = \frac{16\pi r^3}{3\sqrt{3} a^2 c}$$

$$= \frac{16\pi (a/2)^3}{3\sqrt{3} a^2 c}$$

$$\left(\because r = \frac{a}{2} \right)$$

$$= \frac{2\pi a^3}{3\sqrt{3} a^2 c} = \frac{2\pi a}{3\sqrt{3} c}$$

$$= \frac{2\pi}{3\sqrt{3}} \sqrt{\frac{3}{8}}$$

$$\left(\because \frac{c}{a} = \sqrt{\frac{8}{3}} \right)$$

$$= \frac{\pi}{3\sqrt{2}} = 0.74$$

∴ Packing factor = 74%

Since the density of packing is 74%, it is a close packed structure. Magnesium, zinc and cadmium crystallize in this structure.

Example 1. Zinc has HCP structure. The height of the unit cell is 0.494 nm. The nearest neighbour distance is 0.27 nm. The atomic weight of zinc is 65.37. Calculate the volume of the unit cell and density of zinc.

Solution. Here, $a = 2r = 0.27 \times 10^{-9}$ m; $c = 0.494 \times 10^{-9}$ m.

Volume of the unit cell.

$$V = \frac{3\sqrt{3} a^2 c}{2} = \frac{3 \times \sqrt{3} \times (0.27 \times 10^{-9})^2 \times (0.494 \times 10^{-9})}{2}$$

$$= 9.356 \times 10^{-29} \text{ m}^3.$$

Let ρ = density of the crystal.

Mass of the unit cell = $\rho V = (9.356 \times 10^{-29})\rho$ kg.

The number of atoms belonging to a unit cell of HCP = 6.

If M is the atomic weight and N the Avogadro number, then

$$\text{mass per unit cell} = \frac{6M}{N} = \frac{6 \times 65.37}{6.02 \times 10^{26}}$$

3.16 COMPARISON CHART FOR SC, BCC, FCC, AND HCP STRUCTURES

The parameters determining the crystal structure of SC, BCC, FCC and HCP are given for comparison, in Table 3.3.

TABLE - 3.3

S. No	SYSTEM	SC	BCC	FCC	HCP
1.	Atoms per unit cell	1	2	4	6
2.	Atomic radius	$\frac{a}{2}$	$\frac{a\sqrt{3}}{4}$	$\frac{a\sqrt{2}}{4}$	$\frac{a}{2}$
3.	Coordination number	6	8	12	12
4.	Atomic packing factor	$\frac{\pi}{6} = 0.52$	$\frac{\pi\sqrt{3}}{8} = 0.68$	$\frac{\pi\sqrt{2}}{6} = 0.74$	$\frac{\pi}{3\sqrt{2}} = 0.74$
5.	Packing density	52%	68%	74%	74%
6.	Examples	Polonium	Cr, Fe, Na	Pb, Ni, Ag	Mg, CO, Ti

3.22 'd' SPACING (INTERPLANAR DISTANCE) IN CUBIC LATTICE

'd' Spacing or Interplanar distance: 'd' Spacing (or) Interplanar distance is the distance between any two successive planes.

Let us consider a cubic lattice with two planes ABC and $A'B'C'$ as shown in fig. 3.49. Let d_1 be the distance between the origin (O) and the first plane (ABC). Let d_2 be the distance between the origin and the second plane ($A'B'C'$). Let 'd' be the distance between the two planes ABC and $A'B'C'$.

To find, the distance between the origin and the first plane.

Let us consider the plane ABC as shown in fig. (3.49). The plane ABC belongs to a family of planes whose Miller indices are (hkl) . The perpendicular ON from the origin (O) to the plane represents the distance (' d_1 ') between origin and the first plane of this family of planes.

Let OX, OY and OZ represents the orthogonal (or) reference axis and let OA, OB and OC be the intercepts made by the plane on X, Y and Z axis respectively.

Let α, β, γ represents the angle between ON and the X, Y and Z axes respectively as shown in fig. 3.50. [It has to be noted that α, β, γ does not represent the interfacial angles.]

Then, the intercepts of the plane on the three axis are,

$$OA = \frac{a}{h}, \quad OB = \frac{a}{k}, \quad OC = \frac{a}{l} \quad \left[\text{since } p : q : r = \frac{a}{h} : \frac{a}{k} : \frac{a}{l} \right]$$

$$\therefore OA : OB : OC = \frac{a}{h} : \frac{a}{k} : \frac{a}{l}$$

where $a \rightarrow$ length of the cube edge.

From $\triangle ONA$ in fig. (3.50), we can write

$$\cos \alpha = \frac{ON}{OA} = \frac{d_1}{a/h} = \frac{d_1 h}{a}$$

From $\triangle ONB$ in fig 3.50 we can write

$$\cos \beta = \frac{ON}{OB} = \frac{d_1}{a/k} = \frac{d_1 k}{a}$$

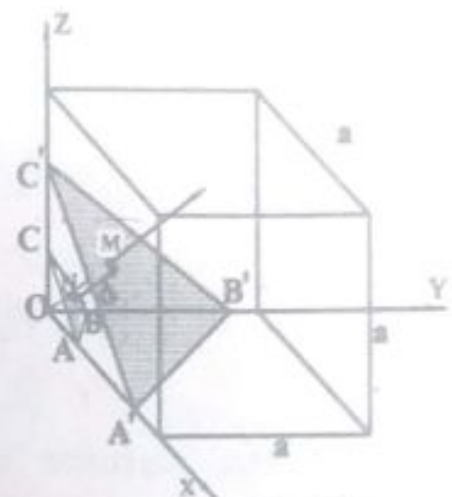


Fig. 3.49

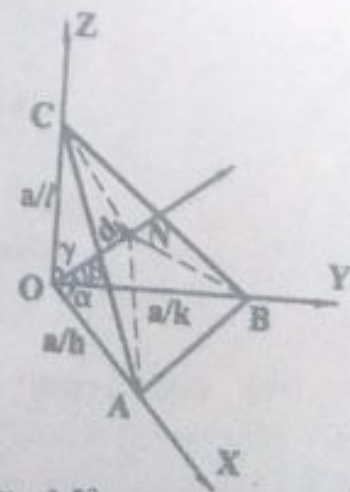


Fig. 3.50

From $\triangle ONC$ in fig. 3.50 we can write, $\cos \gamma = \frac{ON}{OC} = \frac{d_1}{a} = \frac{d_1 l}{a}$

$$\therefore \cos \alpha : \cos \beta : \cos \gamma = \frac{d_1 h}{a} : \frac{d_1 k}{a} : \frac{d_1 l}{a}$$

From the law of direction cosines we can write $\cos^2 \alpha + \cos^2 \beta + \cos^2 \gamma = 1$

$$\therefore \left(\frac{d_1 h}{a}\right)^2 + \left(\frac{d_1 k}{a}\right)^2 + \left(\frac{d_1 l}{a}\right)^2 = 1$$

$$\text{(or)} \quad \frac{d_1^2}{a^2} (h^2 + k^2 + l^2) = 1$$

$$\text{Therefore, } d_1^2 = \frac{a^2}{h^2 + k^2 + l^2}$$

$$\text{(or)} \quad d_1 = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

To find the distance between the origin and the second plane

Let us consider the second plane $A'B'C'$ parallel to the 1st plane ABC . Let d_2 be the perpendicular distance of the plane from the origin 'O' i.e., $OM = d_2$

By similar assumptions, from fig. 3.51 we can write

$$OA' : OB' : OC' = \frac{2a}{h} : \frac{2a}{k} : \frac{2a}{l}$$

Similarly from fig 3.51,

$$\text{We can write } \cos \alpha' = \frac{OM}{OA'} = \frac{d_2}{2a/h} = \frac{d_2 h}{2a}$$

$$\cos \beta' = \frac{OM}{OB'} = \frac{d_2}{2a/k} = \frac{d_2 k}{2a}$$

$$\cos \gamma' = \frac{OM}{OC'} = \frac{d_2}{2a/l} = \frac{d_2 l}{2a}$$

$$\text{(or)} \quad \cos \alpha' : \cos \beta' : \cos \gamma' = \frac{d_2 h}{2a} : \frac{d_2 k}{2a} : \frac{d_2 l}{2a}$$

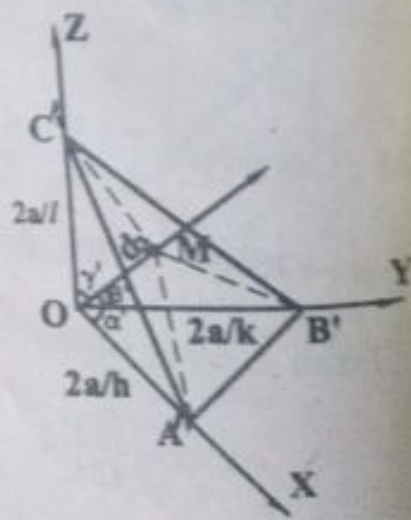


Fig. 3.51

From the law of direction cosines, we can write $\cos^2 \alpha' + \cos^2 \beta' + \cos^2 \gamma' = 1$

$$\therefore \left(\frac{d_2 h}{2a} \right)^2 + \left(\frac{d_2 k}{2a} \right)^2 + \left(\frac{d_2 l}{2a} \right)^2 = 1$$

$$\frac{d_2^2 h^2}{4a^2} + \frac{d_2^2 k^2}{4a^2} + \frac{d_2^2 l^2}{4a^2} = 1$$

$$\frac{d_2^2}{4a^2} (h^2 + k^2 + l^2) = 1$$

$$\text{(or)} \quad d_2^2 = \frac{4a^2}{(h^2 + k^2 + l^2)}$$

$$\text{(or)} \quad \boxed{d_2 = \frac{2a}{\sqrt{h^2 + k^2 + l^2}}} \quad \dots (2)$$

Interplanar distance (d)

We know interplanar distance is the distance between two successive planes. Since ' d ' is the distance between the two planes ABC and $A'B'C'$, we can write the interplanar distance (d) as

$$\boxed{d = d_2 - d_1} \quad \dots (3)$$

Substituting equations (1) and (2) in equation (3) we get

$$\text{Interplanar distance } d = \frac{2a}{[h^2 + k^2 + l^2]^{1/2}} - \frac{a}{[h^2 + k^2 + l^2]^{1/2}}$$

$$d = \frac{a}{[h^2 + k^2 + l^2]^{1/2}}$$

$$\text{(or)} \quad \boxed{d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}} \quad \dots (4)$$

Equation (4) represents the interplanar distance, which is same as that of the distance between the origin and the first plane, represented by equation (1).

∴ Packing factor = 74%

Since the density of packing is 74%, it is a close packed structure. Magnesium, zinc and cadmium crystallize in this structure.

Example 1. Zinc has HCP structure. The height of the unit cell is 0.494 nm. The nearest neighbour distance is 0.27 nm. The atomic weight of zinc is 65.37. Calculate the volume of the unit cell and density of zinc.

Solution. Here, $a = 2r = 0.27 \times 10^{-9}$ m; $c = 0.494 \times 10^{-9}$ m.

Volume of the unit cell.

$$V = \frac{3\sqrt{3}a^2c}{2} = \frac{3 \times \sqrt{3} \times (0.27 \times 10^{-9})^2 \times (0.494 \times 10^{-9})}{2}$$

$$= 9.356 \times 10^{-29} \text{ m}^3.$$

Let ρ = density of the crystal.

Mass of the unit cell = $\rho V = (9.356 \times 10^{-29})\rho$ kg.

The number of atoms belonging to a unit cell of HCP = 6.

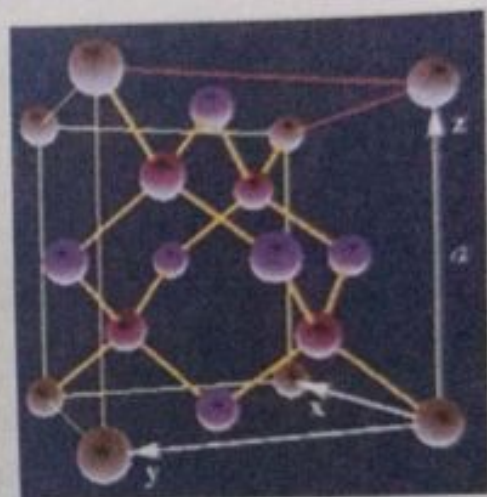
If M is the atomic weight and N the Avogadro number, then

$$\text{mass per unit cell} = \frac{6M}{N} = \frac{6 \times 65.37}{6.02 \times 10^{26}}$$

$$(9.356 \times 10^{-29}) \rho = \frac{6 \times 65.37}{6.02 \times 10^{26}}$$

$$\rho = \frac{6 \times 65.37}{6.02 \times 10^{26} \times (9.356 \times 10^{-29})}$$

$$\rho = 6964 \text{ kg m}^{-3}.$$



Diamond Cubic Structure.

77.9 Diamond Cubic Structure

The diamond structure is a combination of two interpenetrating face-centred cubic (FCC) sublattices.

The unit cell is sketched in Fig. 77.21 (a).

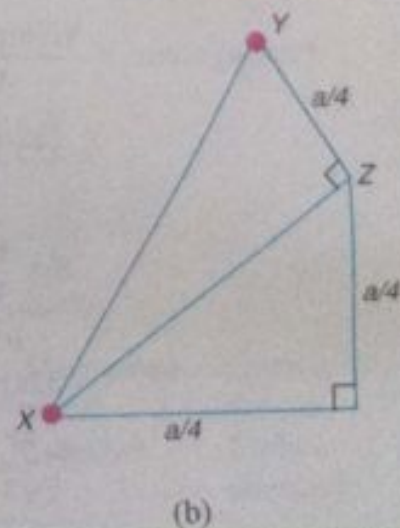
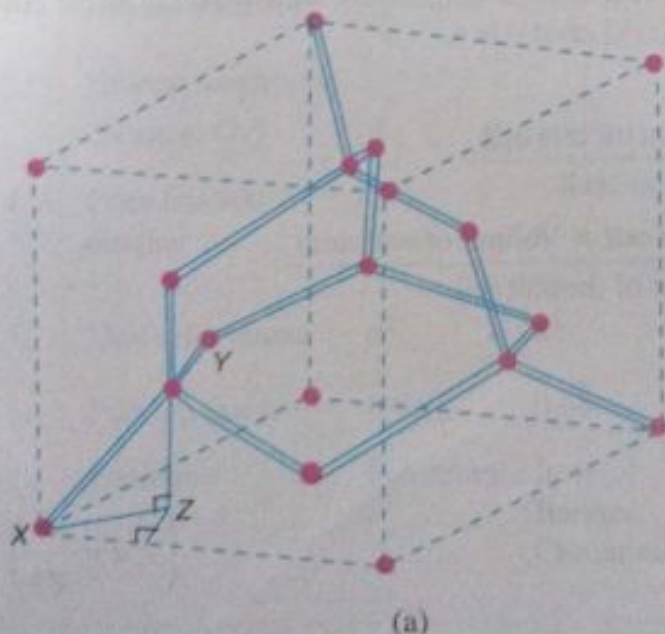


Fig. 77.21

One sublattice, say X , has its origin at $(0, 0, 0)$. The other sublattice, Y , has its origin quarter of the way along the body diagonal i.e., at the point $(a/4, a/4, a/4)$.

The diamond cubic structure is loosely packed, since each atom has only four nearest neighbours.

(i) **Number of atoms per unit cell**

In the unit cell, in addition to the eight corner atoms, there are six face centred atoms and four more atoms are located inside the unit cell. Each corner atom is shared by eight adjacent unit cells and each face centred atom is shared by two unit cells. Hence the total number of atoms per unit cell is,

$$\left(\frac{1}{8} \times 8\right) + \left(\frac{1}{2} \times 6\right) + 4 = 8.$$

(ii) **Atomic radius, r**

From Fig. 77.21 (b),

$$XZ^2 = \left(\frac{a}{4}\right)^2 + \left(\frac{a}{4}\right)^2 = \frac{a^2}{8}$$

Also $XY^2 = XZ^2 + YZ^2 = \frac{a^2}{8} + \frac{a^2}{16} = \frac{3a^2}{16}$.

But $XY = 2r$

$$\therefore (2r)^2 = \frac{3a^2}{16}$$

$$r = \frac{\sqrt{3}}{8} a$$

Lattice constant $a = \frac{8r}{\sqrt{3}}$.

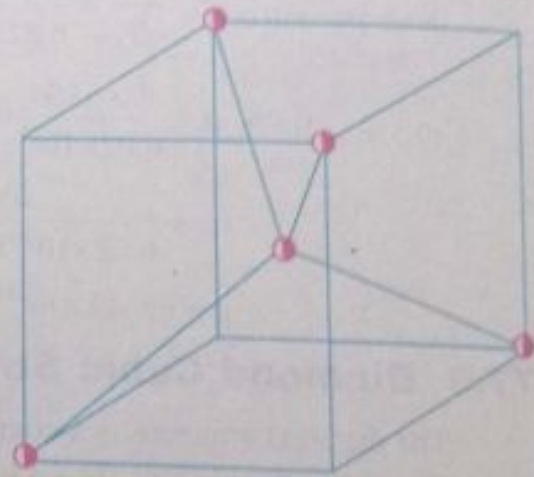


Fig. 77.22

(iii) **Coordination Number**

In a diamond crystal, the carbon atoms are linked by directional covalent bonds. Each carbon atom forms covalent bonds with four other carbon atoms that occupy four corners of a cube in a tetrahedral structure (Fig. 77.22).

In the diamond lattice, each atom has four nearest neighbours with which it forms covalent bonds. Thus the coordination number of diamond crystal is 4.

(iv) **Packing Factor**

$$\begin{aligned} \text{Packing factor} &= \frac{\text{Volume of all atoms in the unit cell}}{\text{Volume of the unit cell}} \\ &= \frac{\text{No. of atoms in unit cell} \times \text{Volume of one atom}}{\text{Volume of the unit cell}} \end{aligned}$$

$$= \frac{8 \times \frac{4}{3} \pi r^3}{a^3}$$

$$= \frac{32\pi r^3}{3 \left(\frac{8r}{\sqrt{3}}\right)^3}$$

$$\left(\because a = \frac{8r}{\sqrt{3}}\right)$$

$$= \frac{\pi\sqrt{3}}{16} = 0.34$$

∴ Packing factor = 34 %

Thus it is a loosely packed structure.

Carbon, silicon, germanium and grey tin crystallize in diamond structure.

Example 1. Silicon has the same structure as diamond and a bond length of 0.2351 nm. Estimate its density.

Solution. In the case of diamond cubic structure,

$$\text{Nearest neighbour distance } 2r = \frac{\sqrt{3}}{4} a$$

Number of atoms per unit cell = 8

$$a = \frac{4}{\sqrt{3}} (2r) = \frac{4}{\sqrt{3}} \times 0.2351 \text{ nm} = 0.543 \text{ nm} = 0.543 \times 10^{-9} \text{ m}$$

$$\rho = \frac{nM}{Na^3} = \frac{8 \times 28.09}{(6.02 \times 10^{26})(0.543 \times 10^{-9})^3} = 2331 \text{ kg m}^{-3}$$

77.10 Summary

The characteristics of the unit cells of simple cubic, BCC, FCC, HCP and diamond cube structures are summarized in Table 1.

TABLE 1

Sl. No.	Characteristic	(SC)	(BCC)	(FCC)	(HCP)	(DC)
1.	Number of atoms per unit cell	1	2	4	6	8
2.	Atomic radius, r	$\frac{a}{2}$	$\frac{a\sqrt{3}}{4}$	$\frac{a}{2\sqrt{2}}$	$\frac{a}{2}$	$\frac{a\sqrt{3}}{8}$
3.	Nearest neighbour distance, $(2r)$	a	$\frac{a\sqrt{3}}{2}$	$\frac{a}{\sqrt{2}}$	a	$\frac{a\sqrt{3}}{4}$
4.	Coordination number	6	8	12	12	4
5.	Unit cell volume	a^3	a^3	a^3	$\frac{3\sqrt{3}}{2} a^2 c$	a^3
6.	Packing factor	0.52	0.68	0.74	0.74	0.34
7.	Examples	Polonium	Iron, Barium, Chromium	Aluminium, Copper, Lead, Gold	Magnesium, zinc, cadmium	Germanium, Silicon, Carbon diamond