

# 1. Crystal Physics

Lattice - Unit cell - Bravais lattice - Lattice planes - Miller indices -  $d$  spacing in cubic lattice - Calculation of number of atoms per unit cell - Atomic radius - Coordination number - Packing factor for SC, BCC, FCC and HCP structures - Diamond and graphite structure (qualitative treatment) - crystal growth techniques - solution, melt Bridgman and Czochralski and vapour growth techniques (qualitative).

## Introduction

Materials differ from one another in their properties. 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 non-conductors of heat and electricity, some are magnetic, some are non-magnetic and so on.

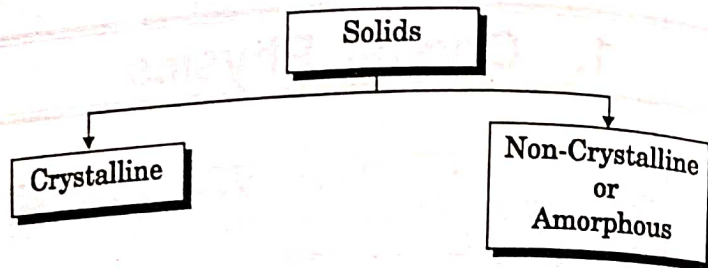
The differences in the properties of the solids are due to their structures. The behaviour of a solid material is closely related to its crystal structure.

## Classification of Solids

From the crystal structure point of view, solid-state materials are broadly classified as

- (i) **Crystalline materials** and
- (ii) **Non-Crystalline or Amorphous materials**





### (i) Crystalline Materials or Crystals

(The materials in which the atoms are arranged in a systematic pattern (regular pattern) are known as crystalline materials.)

(In these materials, the arrangement of atoms is in a periodically repeating pattern.)

The crystalline solid can be either a **single crystal** or **poly-crystalline**. In the single crystal, the entire solid consists of only one crystal.

In poly-crystalline material, a collection of many small crystals are separated by well-defined boundaries.

The atomic arrangements of the single crystal and the poly-crystal are shown in fig 1.1 (a) and (b).

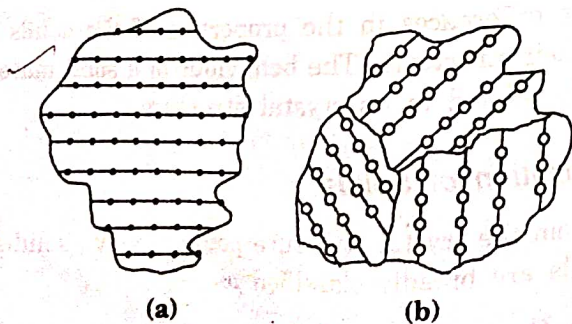


Fig. 1.1 Atomic arrangement (a) single crystal solid  
(b) poly-crystalline solid

The crystalline solids are made up of either metallic crystals or non-metallic crystals.

### Example

#### Metallic crystals

Copper, silver, aluminium, tungsten, etc.

#### Non-metallic crystals

Crystalline carbon, germanium, silicon, crystallized polymers, etc.

### Amorphous Materials

(Amorphous means without form.)

The materials in which atoms are arranged in an irregular (random) fashion are known as **amorphous materials** or **non-crystalline materials**.

### Example

(Glass, rubber and plastics.)

The arrangement of atoms in amorphous materials in two dimensions is shown in fig. 1.2.

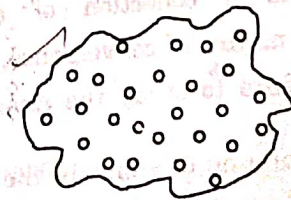


Fig. 1.2 Amorphous material

### Crystallographic terms

Let us study some of the important crystallographic terms.

#### Crystal

A crystal is a three-dimensional solid which consists of a periodic arrangement of atoms.

#### Crystal structure

The arrangement of atoms in a crystal is known as crystal structure. It is the basis for understanding the properties of materials.

#### Crystallography

The branch of physics which deals with internal structure, properties, external or internal symmetries in a crystal is called as crystallography.

### 1.1 LATTICE

A crystal is a collection of atoms in three dimensions. As a matter of convenience, these atoms are considered as points to study the crystal structure.

The representation of atoms in the crystal as points in three dimensions is known as **space lattice** or **simple lattice**.

Lattice is an imaginary geometrical concept. It is a large assembly of points in which each point represents the position of an atom in a crystal.

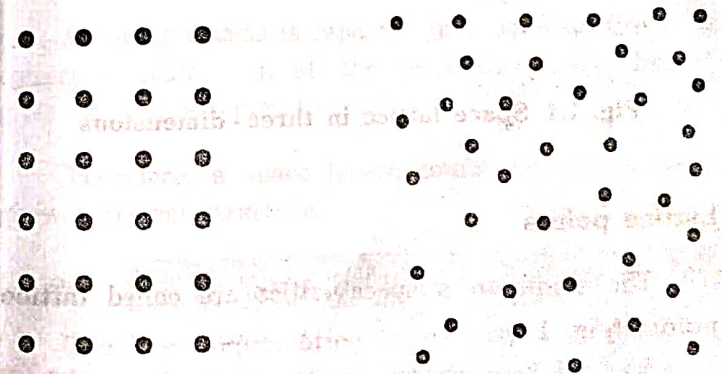
#### Definition

It is an array of points in space in which the environment about each point is the same i.e., every point has identical surroundings to that of every other point in the array.

#### Explanation

The collection of points in two dimensions is shown in fig. 1.3 (a) and (b)

It is found that in fig 1.3 (a) the environment about any two points is same. Hence, it is a space lattice.



(a) Two-dimensional space lattice

(b) Two-dimensional collection of points but not a space lattice

Fig. 1.3



On the other hand, in fig. 1.3 (b) the environment about any two points is not the same. So, it is not a space lattice.

The similar argument is extended to a three-dimensional space lattice.

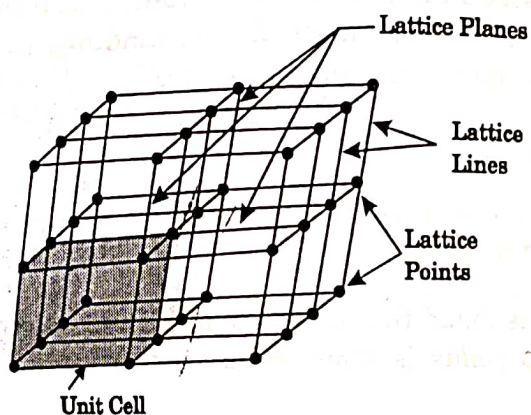


Fig. 1.4 Space lattice in three - dimensions

### Lattice points

The points in a space lattice are called lattice points (Fig. 1.4).

### Lattice lines

The lattice points are joined with lines as shown in fig. 1.4. These lines are known as lattice lines.

### Lattice plane:

A plane containing lattice points is known as a lattice plane.

### Basis

#### Definition

The crystal structure is obtained by adding a unit assembly of atoms to each lattice point. This unit assembly is called as basis.

#### Explanation

A basis may be a single atom or assembly of atoms which is identical in composition, arrangement and orientation.

When the basis is repeated in a space lattice with correct periodicity in all the three directions, then it gives the actual crystal structure.

Therefore, a space lattice combined with a basis gives a crystal structure.

ie.,  $\text{Space lattice} + \text{Basis} \rightarrow \text{Crystal structure}$

The basis representing lattice points is shown in fig 1.5 in which two atoms (represented by circles of smaller and large radii) are added to one lattice point (represented by a black dot).

For many metals, the number of atoms in basis is one (aluminium and barium crystals).



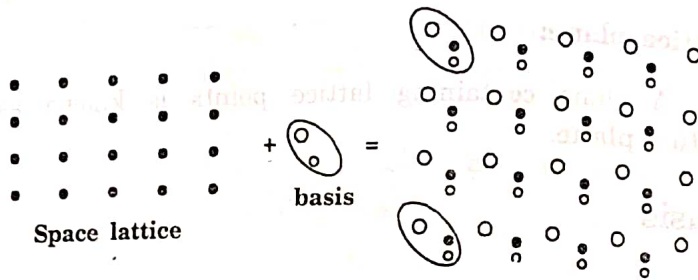


Fig. 1.5 Crystal structure is obtained when a basis is added to each lattice point

For NaCl and KCl, each basis has two atoms and for CaF<sub>2</sub>, it has three atoms. But, for many complicated structures, the basis exceeds more than 1000 atoms.

**Note:**

A space lattice refers to the geometry of a set of points in space whereas a crystal structure refers to the actual order or alignment of atoms in space.

**1.2 UNIT CELL**

Consider a two-dimensional space lattice as shown in fig. 1.6.

It is found that when a parallelogram ABCD is rotated repeatedly by an integral multiple of vectors  $\vec{a}$  and  $\vec{b}$  corresponding to AB and AD, the whole pattern or array is obtained.

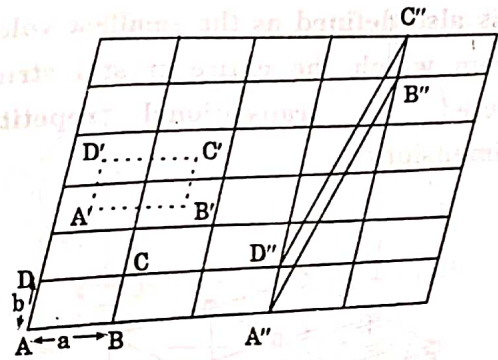


Fig. 1.6 Unit cell in two-dimension

The region ABCD is known as unit cell and  $\vec{a}$  and  $\vec{b}$  are basis vectors.

The choice of a unit cell is not unique. But, it can be constructed in a number of ways like A'B'C'D' or A''B''C''D''; without affecting the symmetry of the crystal (fig. 1.6).

**Definition**

A unit cell is defined as the smallest geometric figure which is repeated to derive the actual crystal structure.

The unit cell fully represents the characteristics of the entire crystal.

This same principle is extended for a three-dimensional case. A unit cell in three-dimensions is shown fig. 1.7.



It is also defined as the smallest volume of a solid from which the entire crystal structure is constructed by translational repetition in three-dimensions.

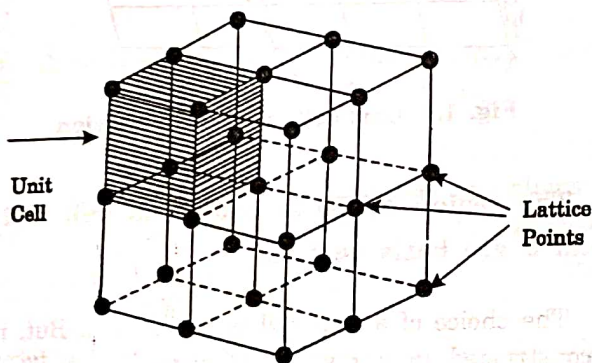


Fig. 1.7 Unit cell in three-dimensions

### Lattice parameters of the unit cell

A unit cell is constructed if the distance between two neighbouring lattice points along three directions and angles between them are known.

The distance between two neighbouring lattice points is nothing but the edges of the unit cell. The lengths  $OA$ ,  $OB$ ,  $OC$  in three axes  $OX$ ,  $OY$  and  $OZ$  are the axial lengths or intercepts. (Fig. 1.8).

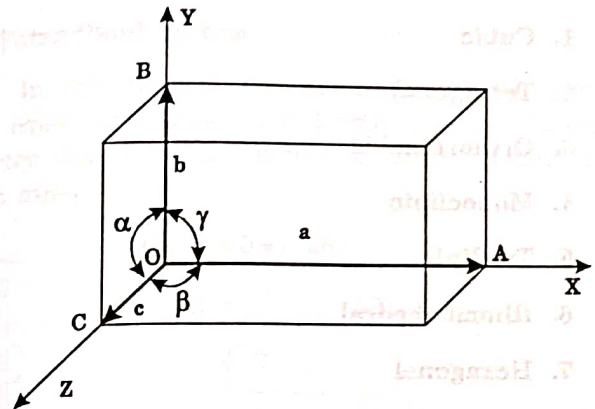


Fig. 1.8 Lattice parameters of the unit cell

In fig 1.8, the axial lengths  $OA = a$ ,  $OB = b$  and  $OC = c$  are known as intercepts  $a$ ,  $b$  and  $c$  along three axes.

### Interfacial angles

The angles between three intercepts ( $\alpha$ ,  $\beta$  and  $\gamma$ ) are called interfacial angles.

Both intercepts and interfacial angles are the lattice parameters of the unit cell. They determine the actual shape and size of the unit cell.

### Crystal systems

There are '7' types of crystal systems. They are



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

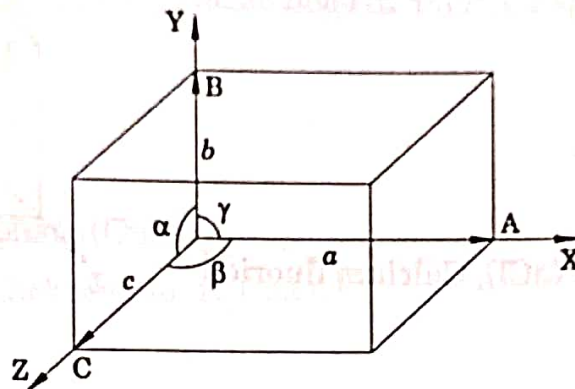


Fig. 5.7 Lattice parameters of a unit cell

### Primitive cell

It is defined as unit cell which contains lattice points at corner only. (or) It is the simplest type of unit cell contains only one lattice point per unit cell.

Example : Simple cubic (SC)

### Non-primitive cell

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

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

## 5.6 CRYSTAL SYSTEMS

Crystals are classified into seven crystal systems on the basis of lattice parameters. The seven basic crystal systems are

- i. Cubic system
- ii. Tetragonal system
- iii. Orthorhombic system
- iv. Monoclinic system
- v. Triclinic system
- vi. Rhombohedral (or) Trigonal system
- vii. Hexagonal system

The seven crystal systems are discussed briefly one by one as follows.



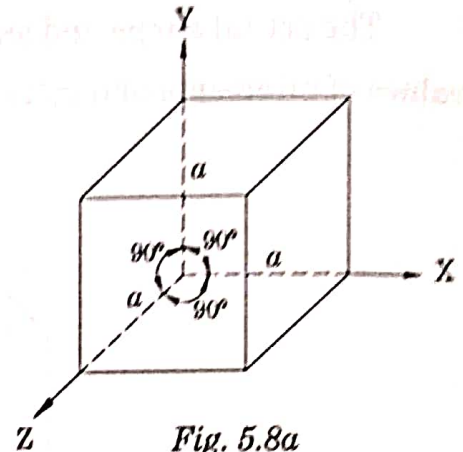
**(i) Cubic system**

This is a crystal system with three axes of equal lengths perpendicular to each other. (Fig. 5.8a.)

$$\text{i.e., } a = b = c \text{ and} \\ \alpha = \beta = \gamma = 90^\circ$$

**Example**

Sodium chloride (NaCl), Calcium fluoride (CaF<sub>2</sub>).

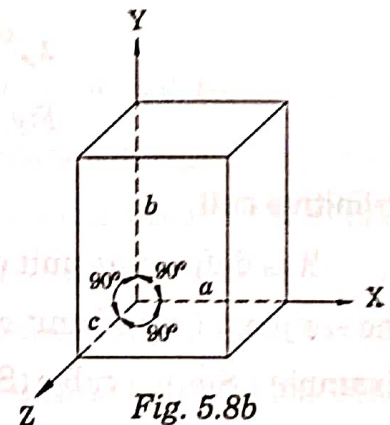
**(ii) Tetragonal system**

In this system, there are three axes perpendicular to each other. Two axes are equal in length and third axis is either longer or shorter. (Fig. 5.8b).

$$\text{i.e., } a = b \neq c \\ \alpha = \beta = \gamma = 90^\circ$$

**Example**

Ordinary white tin, indium.

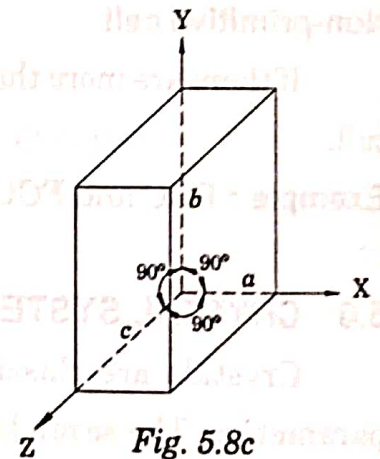
**(iii) Orthorhombic system**

In this system, there are three axes perpendicular to each other. These axes are all of different lengths. (Fig. 5.8c).

$$\text{i.e., } a \neq b \neq c \\ \alpha = \beta = \gamma = 90^\circ$$

**Example**

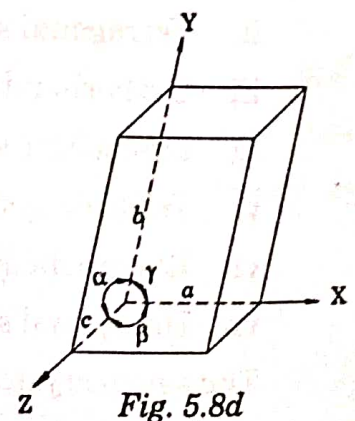
Sulphur, Topaz.

**(iv) Monoclinic system**

In this system, there are three axes of different lengths. Two axes are perpendicular to each other and third is obliquely inclined. (Fig. 5.8d).

$$a \neq b \neq c \text{ and} \\ \text{i.e., } \alpha = \beta = 90^\circ; \gamma \neq 90^\circ$$

**Example :** Na<sub>2</sub>SO<sub>3</sub>, FeSO<sub>4</sub>.



**(v) Triclinic system**

In this system, there are three axes of unequal lengths, all oblique to each other. (Fig.5.8e).

$$a \neq b \neq c \text{ and}$$

$$\alpha \neq \beta \neq \gamma \neq 90^\circ$$

**Example**

Copper sulphate ( $\text{CuSO}_4$ ).

Potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ )

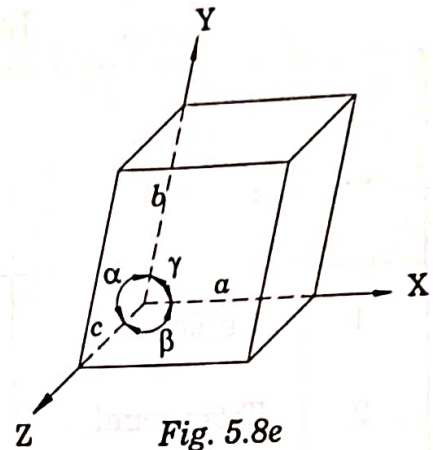


Fig. 5.8e

**(vi) Rhombohedral system**

In this system, there are three axes equal in lengths and are equally inclined to each other at an angle other than  $90^\circ$ . (Fig.5.8f).

$$a = b = c \text{ and}$$

$$\alpha = \beta = \gamma \neq 90^\circ$$

**Example**

Calcite.

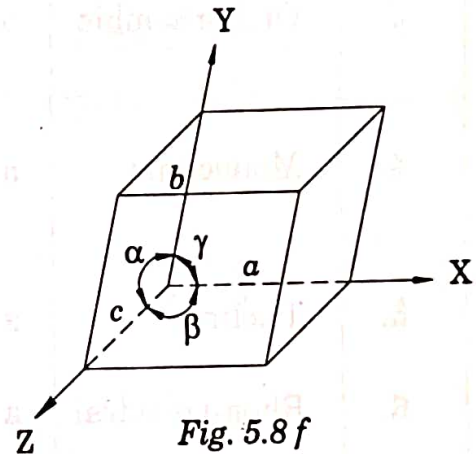


Fig. 5.8 f

**(vii) Hexagonal system**

In this system, two axes (say horizontal) are equal in one plane at  $120^\circ$  with each other. The third axis (say vertical) is different (ie., either longer or shorter than the other three axes) and perpendicular to this plane. (Fig.5.8g).

$$\text{ie., } a = b \neq c \text{ and}$$

$$\alpha = \beta = 90^\circ; \quad \gamma = 120^\circ$$

**Example**

Quartz, tourmaline.

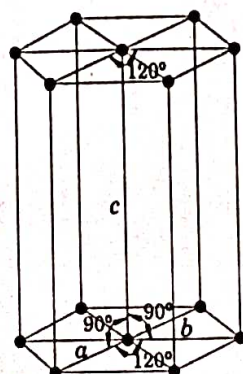


Fig. 5.8 g



Table 5.2 Seven crystal systems

Sl. No.	Crystal system	Axial length (a, b, c)	Interaxial angles ( $\alpha, \beta, \gamma$ )	Example
1.	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	NaCl, $\text{CaF}_2$ , Au, Cu
2.	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Ordinary white, tin, indium, $\text{SnO}_2$
3.	Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Sulphur, Topaz, $\text{BaSO}_4$ , $\text{KNO}_3$
4.	Monoclinic	$a \neq b \neq c$	$\alpha = \beta = 90^\circ$ ; $\gamma \neq 90^\circ$	$\text{Na}_2\text{SO}_4$ , $\text{FeSO}_4$ , Gypsum
5.	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	$\text{CuSO}_4$ , $\text{K}_2\text{Cr}_2\text{O}_7$
6.	Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	Calcite, Sb, Bi.
7.	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ$ ; $\gamma = 120^\circ$	Quartz, Zn, Mg.

### 5.7 BRAVAIS LATTICES

Bravais in 1880 showed that there are 14 possible types of space lattices in the 7 crystal systems as shown in table 5.3.

Table 5.3 Bravais lattice occurrences

S.No.	Crystal systems	No. of possible types	Bravais lattice
1.	Cubic	3	Simple, Body centred, Face centred
2.	Tetragonal	2	Simple, body centred
3.	Orthorhombic	4	Simple, Body centred, Face centred, Base centred.

4.	Monoclinic	2	Simple, Base centred
5.	Triclinic	1	Simple
6.	Rhombohedral	1	Simple
7.	Hexagonal	1	Simple
	<b>Total</b>	<b>14</b>	

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*.

The 14 possible Bravais lattices drawn from the 7 crystal systems are shown in Fig.(5.9).

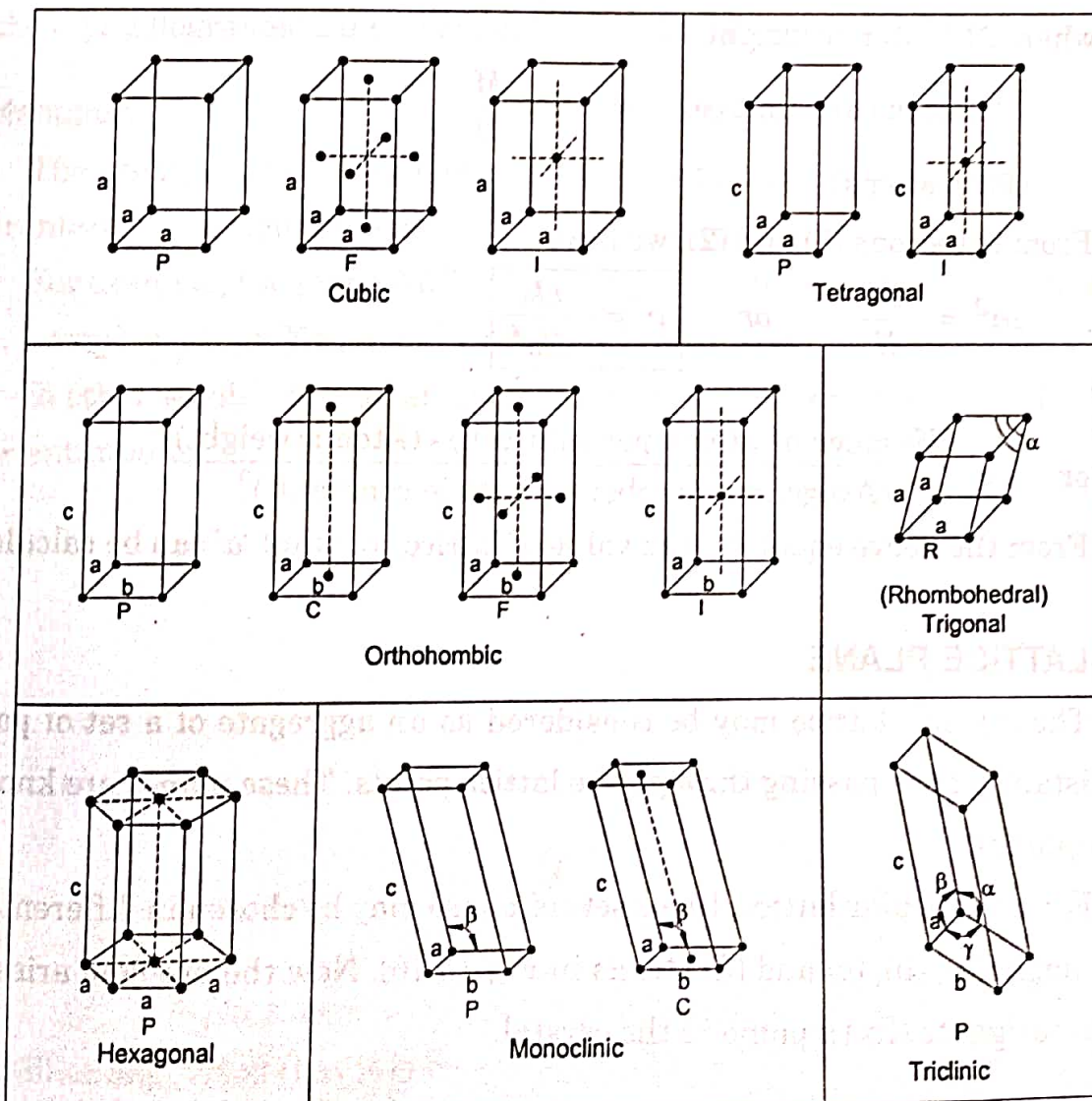


Fig. 5.9 Three dimensional 14 Bravais lattices



## 5.8 RELATION BETWEEN LATTICE CONSTANT AND DENSITY

Consider a cubic crystal of lattice constant 'a'.

$$\text{The density of the crystal} = \rho$$

$$\text{Volume of the unit cell} = a^3$$

$$\therefore \text{Mass in each unit cell} = \rho a^3 \quad \dots\dots(1)$$

$$\left( \because \text{density} = \frac{\text{Mass}}{\text{volume}} \right)$$

$$\text{The number of atoms per unit cell} = n$$

$$\text{The atomic weight of the material} = M$$

$$\text{Avogadro's number} = N$$

(i.e., Number of molecules per kg mole of the substance)

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

where  $M$  is atomic weight

$$\text{Mass in each unit cell} = n \times \frac{M}{N} \quad \dots\dots(2)$$

(for  $n$  atoms)

From equations (1) and (2), we have

$$\rho a^3 = \frac{nM}{N} \quad \text{or} \quad \boxed{\rho = \frac{nM}{Na^3}}$$

$$\text{or } \rho = \frac{(\text{Number of atoms per unit cell}) \times (\text{Atomic weight})}{(\text{Avogadro's number}) \times (\text{Lattice constant})^3}$$

From the above equation, the value of lattice constant 'a' can be calculated.

## 5.9 LATTICE PLANE

The crystal lattice may be considered as an aggregate of a set of parallel equidistant planes passing through the lattice points. These planes are known as *lattice planes*.

For a particular lattice, these sets of planes may be chosen in different ways, for example (a), (b), (c) and (d) etc. as in Fig. (5.10). Now the problem arises that how to designate (fix) a plane in the crystal.

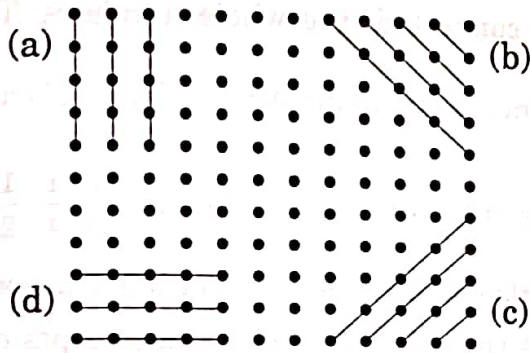


Fig. 5.10 Different lattice planes

### 5.10 MILLER INDICES

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

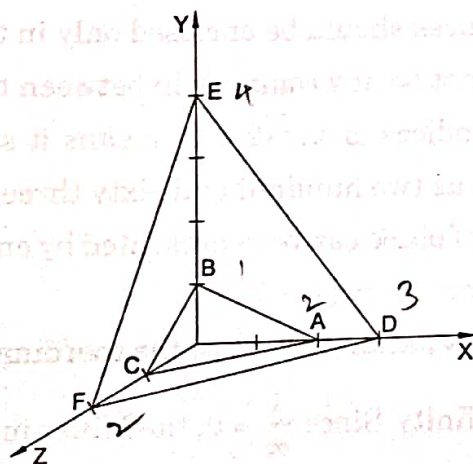
Miller indices is defined as the reciprocal of the intercepts made by the plane on the crystallographic axes which are reduced to smallest numbers.

#### Explanation

The orientation of planes or faces in a crystal may be described in terms of their intercepts on the three axes.

For example, the plane ABC of Fig.(5.11) has intercepts of 2 axial units on X-axis, 1 axial units on Y-axis and 1 axial units on Z-axis.

In other words, the numerical parameters of the faces are 2, 1 and 1. Hence its orientation is (2 1 1)



Handwritten notes showing calculations for Miller indices:

$(2, 1, 1)$   
 $\frac{1}{2}, \frac{1}{1}, \frac{1}{1}$   
 $(1, 2, 2)$

Another set of calculations:  
 $(3, 4, 2)$   
 $\frac{1}{3}, \frac{1}{4}, \frac{1}{2}$   
 $(4, 3, 6)$

Fig. 5.11 Different planes cutting crystallographic axes

Miller suggested that it is more useful to describe the orientation of a plane by the reciprocal of its numerical parameters rather than by its linear parameters.



These reciprocals are converted into whole numbers. They are called Miller indices. Hence Miller indices of a plane ABC of Fig.(5.11) are  $\left(\frac{1}{2} \frac{1}{1} \frac{1}{1}\right)$  or simply

(1 2 2). Similarly Miller indices of a plane DEF are  $\left(\frac{1}{3} \frac{1}{4} \frac{1}{2}\right)$  or simply (4 3 6)

Miller indices is also defined as 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 for finding Miller indices

To find the Miller indices for a given plane, the following steps are to be followed.

- i. The intercepts made by the plane along X, Y and Z axes are noted.
- ii. The co-efficients of the intercepts are noted separately.
- iii. Inverse is to be taken.
- iv. The fractions are multiplied by LCM so that all the fractions become integers.
- v. Write the integers within the parentheses.

### Points to remember

While finding the Miller indices of a plane, following points should be kept in mind.

- i. The Miller indices should be enclosed only in this bracket (i.e.,) ( )
- ii. There should not be any comma's in between the numbers.
- iii. 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.
- iv. The direction of plane can be represented by enclosing the Miller indices in a square bracket eg. [2 6 3].
- v. When a plane is parallel to one of the coordinate axes, it is said to meet that axis at infinity. Since  $\frac{1}{\infty} = 0$ , the Miller indices for that axis is zero.
- vi. When the intercept of a plane is on the negative part of any axis, the Miller indices is distinguished by a bar put directly over it. Eg. (h  $\bar{k}$  l).

Important features of Miller indices

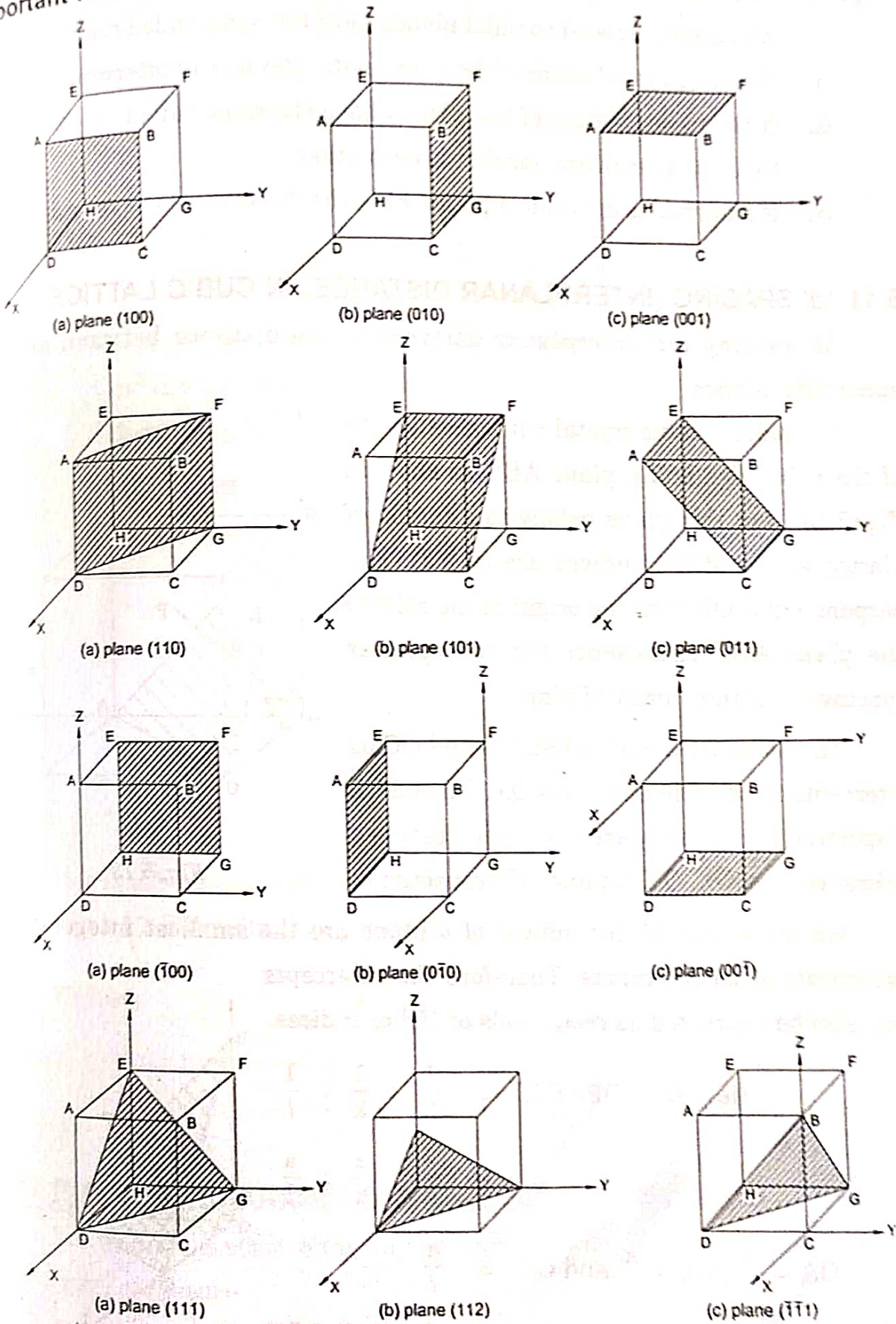


Fig. 5.12 Miller indices for some crystal planes



Important features of the Miller indices, are as follows

- i. All equally, spaced parallel planes have the same index numbers  $(hkl)$
- ii. A plane parallel to one of the co-ordinate axes has an intercept of infinity.
- iii. If the miller indices of two planes have the same ratio (i.e. 422 or 211), then the planes are parallel to each other.
- iv. If a normal is drawn to a plane  $(hkl)$ , the direction of the normal is  $[hkl]$

### 5.11 'd' SPACING (INTERPLANAR DISTANCE) IN CUBIC LATTICE

'd' spacing (or) interplanar distance is the distance between any two successive planes.

Consider a cubic crystal with 'a' as length of the cube edge and a plane ABC as show in Fig.(5.13). Let this plane belong to a family of planes whose Miller indices are  $(h k l)$ . The perpendicular OP from the origin of the cube to the plane ABC represents the interplanar spacing (d) of this family of plane.

The plane ABC makes OA, OB and OC as intercepts on the reference axes OX, OY and OZ respectively.  $\alpha$ ,  $\beta$  and  $\gamma$  are the angles between reference axes OX, OY, OZ and OP respectively.

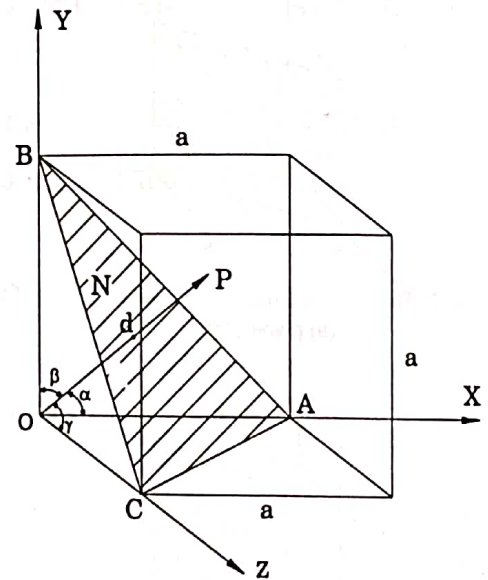


Fig. 5.13

We know that Miller indices of a plane are the smallest integers of the reciprocals of its intercepts. Therefore the intercepts may also be expressed as reciprocals of Miller indices.

$$\begin{aligned} \text{(ie) } OA : OB : OC &= \frac{1}{h} : \frac{1}{k} : \frac{1}{l} \\ &= \frac{a}{h} : \frac{a}{k} : \frac{a}{l} \end{aligned}$$

$$\therefore OA = \frac{a}{h}; OB = \frac{a}{k} \text{ and } OC = \frac{a}{l}$$

From the geometry of the right angles OAP, OBP and OCP (Fig.5.14).

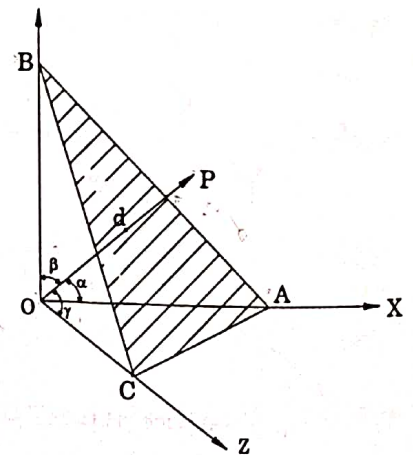


Fig. 5.14

We have, 
$$\cos \alpha = \frac{OP}{OA} = \frac{d}{a} = \frac{dh}{a}$$

$$\cos \beta = \frac{OP}{OB} = \frac{d}{a} = \frac{dk}{a}$$

$$\cos \gamma = \frac{OP}{OC} = \frac{d}{a} = \frac{dl}{a}$$

We know that, the law of direction cosines is

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

Substituting the values, we have,

$$\left(\frac{dh}{a}\right)^2 + \left(\frac{dk}{a}\right)^2 + \left(\frac{dl}{a}\right)^2 = 1$$

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

$$\therefore d^2 = \frac{a^2}{(h^2 + k^2 + l^2)}$$

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

This is the relation between interplanar spacing 'd', cube edge 'a' and Miller indices (h k l). Extending the planes to cut at 2a, 3a, ..... so on

We have 
$$d_2 = \frac{2a}{\sqrt{h^2 + k^2 + l^2}}$$

$$d_3 = \frac{3a}{\sqrt{h^2 + k^2 + l^2}}$$

## 5.12 IMPORTANT PARAMETERS IN CRYSTAL STRUCTURE

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

### i. Number of atoms per unit cell

The number of atoms possessed by a unit cell is known as number of atoms



per unit cell. The distribution of atoms is different for different lattice structure. This can be determined if the arrangement of atoms inside the unit cell is known.

## ii. Coordination number

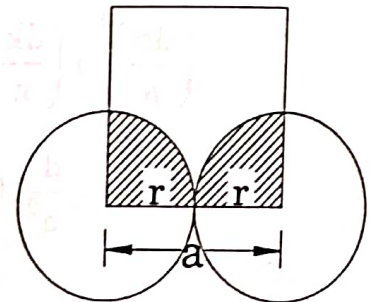
The coordination number of an atom in a crystal is the number of nearest atoms directly surrounding with that atom. If the coordination number is high, then the structure will be more closely packed. It signifies the tightness of packing of atoms in the crystal.

## iii. Atomic radius

Atomic radius is defined as half of the distance between any two nearest neighbour atoms which have direct contact with each other. It is usually expressed in terms of cube edge 'a'. (Lattice parameter).

$$2r = a$$

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



## iv. Atomic packing factor (or) Packing density

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 ( $V$ ).

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

$$\text{APF} = \frac{v}{V}$$

### 5.12.1 Simple cubic (SC) structure

A simple cubic (SC) unit cell consists of eight corner atoms as shown in Fig.(5.16). Let us determine the characteristics of the SC structure.

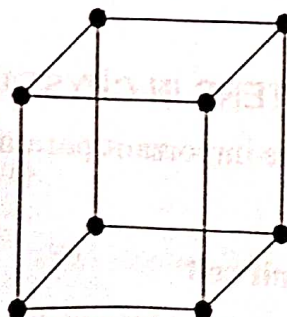


Fig. 5.16 Simple cube

**i. Number of atoms per unit cell**

In actual crystal each and every corner atoms is shared by eight adjacent unit cells. Therefore, each and every corner atoms contributes  $\frac{1}{8}$ <sup>th</sup> of its part to one unit cell.

The total number of atoms present in a unit cell

$$= \frac{1}{8} \times \text{total number of corner atoms}$$

$$= \frac{1}{8} \times 8 = 1 \text{ atom.}$$

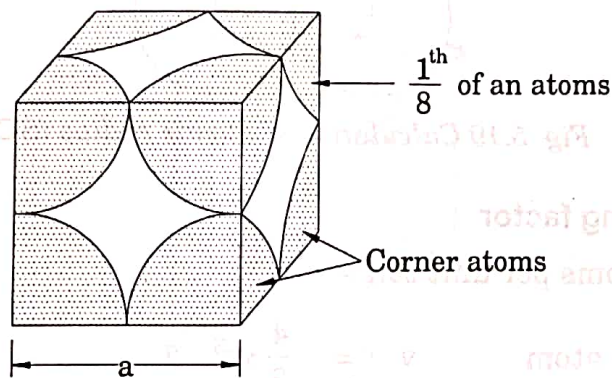


Fig. 5.17 Arrangement of atoms in SC unit cell

**ii. Co-ordination number**

Let us consider any corner atom, there are four nearest neighbours in its own plane. There is another nearest neighbour in a plane which lies just above this atom and another just below this atom. Therefore, the total number of nearest neighbours is six and hence the co-ordination number is 6.

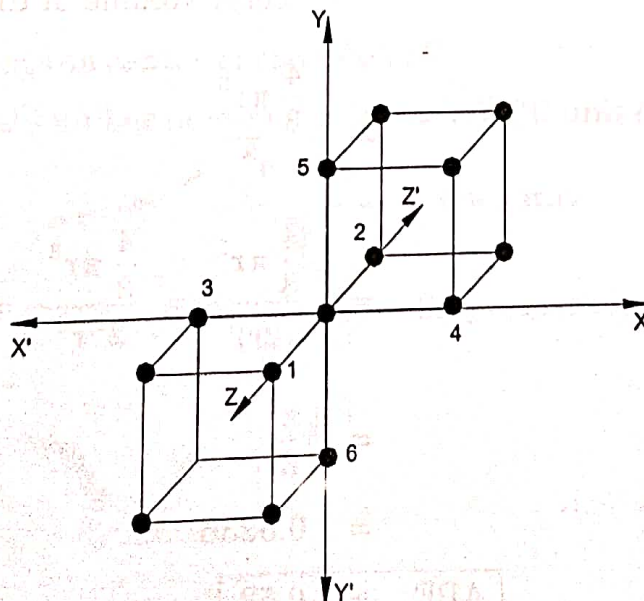


Fig. 5.18 Co-ordination number



**iii. Atomic radius**

For a simple cubic unit cell, the atomic radius is given by,  $r = \frac{a}{2}$

Where 'a' is the side of the unit cell and is equal to the distance between centres of the two nearest atoms.

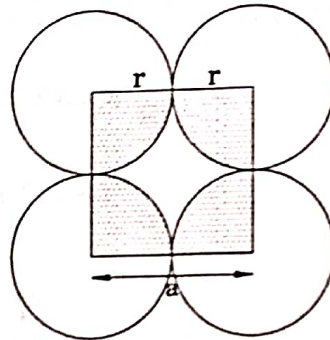


Fig. 5.19 Calculation of atomic radius (SC)

**iv. Atomic packing factor**

Number of atoms per unit cell = 1

Volume of one atom  $v = \frac{4}{3} \pi r^3$

Radius of atom in SC  $r = \frac{a}{2}$  [ $\because a = 2r$ ]

Volume of the unit cell  $V = a^3$

Atomic packing factor =  $\frac{\text{Volume occupied by the total number of atoms per unit cell (v)}}{\text{Total volume of the unit cell (V)}}$

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

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

$$= \frac{\pi}{6}$$

$$= 0.5236$$

$$\boxed{\text{APF} = 0.52}$$

Therefore, 52% of the volume is occupied by the atoms and remaining 48% volume is vacant in SC structure.

Thus, the packing density is 52%. Since the packing density is very low, SC has loosely packed structure.

**Example :** Polonium (Po)

### 5.12.2 Body centred cubic (BCC) structure

In body centered cubic structure, the unit cell has one atom at each corner of the cube and one at body center of the cube. Fig.(5.20) shows the arrangement of atoms in a BCC cell.

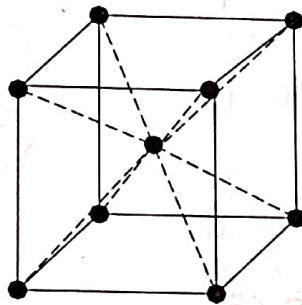


Fig. 5.20 BCC cell

#### i. Number of atoms per unit cell

In a body centered cubic structure, the atoms touch along the diagonal of the body. Each and every corner atoms are shared by eight adjacent unit cell.

∴ The total number of atoms contributed by the corner atoms

$$= \frac{1}{8} \times 8 = 1 \text{ atom.}$$

One full atom at the center of the unit cell.

Therefore, total number of atoms present in BCC unit cell = 2 atoms.

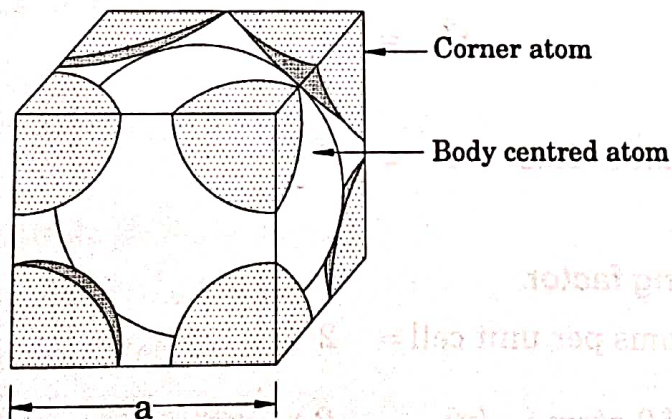


Fig. 5.21 Arrangement of atom in BCC cell



## ii. Co-ordination number

In this case, there are 8 corner atoms one at each corner of the unit cell and one atom at the body centre. For any corner atom of the unit cell, the nearest atoms are the body centred atoms. As such, each corner atom is surrounded by 8 unit cells having 8 body centred atoms. Hence coordination number is 8.

## iii. Atomic radius

Consider the atoms at A, G and at centre of the cell. These atoms lie in one straight line along the body diagonal AG of the cube.

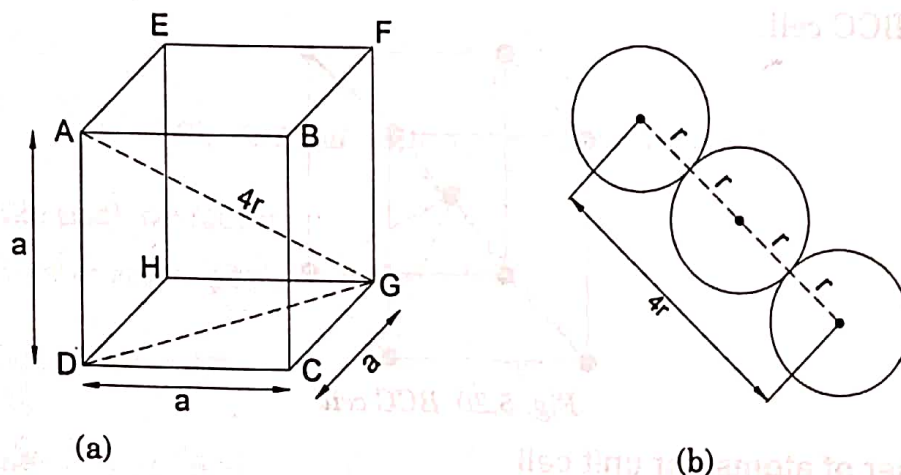


Fig. 5.22 Atomic radius in BCC

From the Fig. 5.22

$$AG^2 = AD^2 + DG^2$$

$$(4r)^2 = AD^2 + DC^2 + CG^2 \quad [\because DG^2 = DC^2 + CG^2]$$

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

$$16r^2 = 3a^2$$

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

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

## iv. Atomic packing factor

$$\text{Number of atoms per unit cell} = 2$$

$$\therefore \text{Volume of 2 atoms (v)} = 2 \times \frac{4}{3} \pi r^3$$

$$\text{Radius of atom in BCC (r)} = \frac{a\sqrt{3}}{4}$$

$$\text{Volume of the unit cell (V)} = a^3$$

$$\text{Atomic packing factor} = \frac{\text{Volume occupied by the total number of atoms per unit cell (v)}}{\text{Total volume of the unit cell (V)}}$$

$$= \frac{2 \times \frac{4}{3} \pi r^3}{a^3}$$

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

$$= \frac{\frac{8}{3} \pi r^3}{\frac{64 r^3}{\sqrt{3} \times 3}}$$

$$= \frac{8}{3} \times \frac{\sqrt{3} \times 3 \times \pi}{64} = \frac{\sqrt{3} \pi}{8}$$

$$\boxed{\text{APF} = 0.68}$$

Therefore, 68% of the volume is occupied by atoms and remaining 32% of the volume is vacant in BCC structure.

Thus the packing density is 68%. Since the packing density is greater than simple cubic, it has tightly packed structure when compared to SC.

**Examples :** Tungsten, Molybdenum, Chromium.

### 5.12.3 Face centred cubic (FCC) structure

A face centred cubic structure consists of eight corner atoms and six face centered atoms. The arrangement of atoms in face centered cubic unit cell is shown in Fig.(5.23).

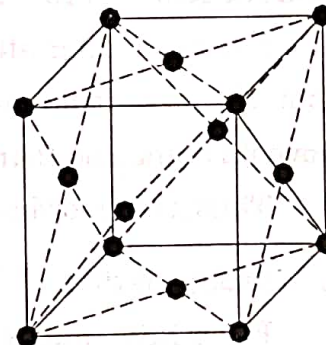


Fig. 5.23 FCC unit cell



i. **Number of atoms per unit cell**

An FCC unit cell consists of eight corner atoms and each and every corner atom is shared by eight adjacent unit cells. Therefore, each and every corner atom contributes  $\frac{1}{8}$ th of its part to one unit cell.

The total number of atoms by corner atom =  $\frac{1}{8} \times 8 = 1$  atom.

In addition, there are 6 atoms at the face centers of the cube. Each face centered atom is shared by two surround unit cells. Hence, the number of face centered atoms in unit cell,

$$= \frac{1}{2} \times 6 = 3 \text{ atoms.}$$

Therefore, total number of atoms in one unit cell =  $1 + 3 = 4$  atoms.

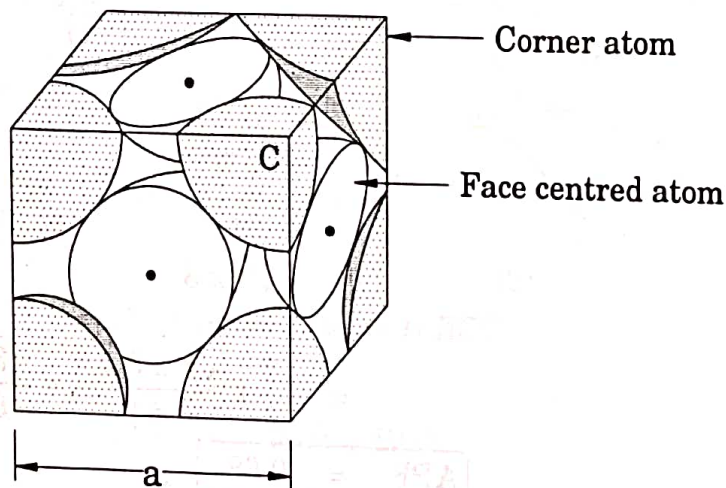


Fig. 5.24 Arrangement of atoms in FCC unit cell

ii. **Co-ordination number**

In this case, there are eight atoms at the eight corners of the unit cell and 6 atoms at center of the six faces.

For any corner atom of the unit cell, the nearest atom is the face centered atom. For any corner atom, there are four face center atoms in its plane and four above its plane and four below its plane.

Thus, the co-ordination number of this case =  $4 + 4 + 4 = 12$ .

iii. **Atomic radius**

For a FCC unit cell, the atomic radius can be calculated from Fig.(5.25) as follows:

$$DB^2 = DC^2 + CB^2$$

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

$$16r^2 = 2a^2$$

$$r^2 = \frac{2a^2}{16}$$

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

$$\therefore \text{Atomic radius } r = \frac{a\sqrt{2}}{4}$$

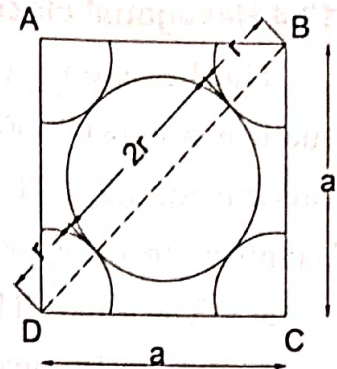


Fig. 5.25 Calculation of atomic radius in FCC

#### iv. Atomic packing factor

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

$$\text{Volume of 4 atoms (v)} = 4 \times \frac{4}{3} \pi r^3$$

$$\text{Radius of atom in FCC (r)} = \frac{a\sqrt{2}}{4}$$

$$\text{Volume of the unit cell (V)} = a^3$$

Volume occupied by the total

$$\text{Atomic packing factor} = \frac{\text{number of atoms per unit cell (v)}}{\text{Total volume of the unit cell (V)}}$$

$$= \frac{4 \times \frac{4}{3} \pi r^3}{\left(\frac{4r}{\sqrt{2}}\right)^3} = \frac{\frac{16}{3} \pi r^3}{\frac{4^3 r^3}{(\sqrt{2})^3}} = \frac{\frac{16}{3} \pi r^3}{\frac{64 r^3}{2\sqrt{2}}}$$

$$= \frac{16}{3} \times \frac{2\sqrt{2}}{64} \pi = \frac{\pi\sqrt{2}}{6}$$

$$\boxed{\text{APF} = 0.74}$$

Therefore, 74% of the volume is occupied by the atoms and remaining 26% of the volume is vacant in FCC structure.

Thus the packing density is 74%. Since the packing density is high the FCC structure has tightly packed structure.

Examples : Copper, Nickel, Gold, Lead and Platinum.



### 5.12.4 Hexagonal close packed structure

The hexagonal close packed (HCP) structure is shown in Fig.(5.26). In the HCP structure, an unit cell contains three types of atoms as three layers.

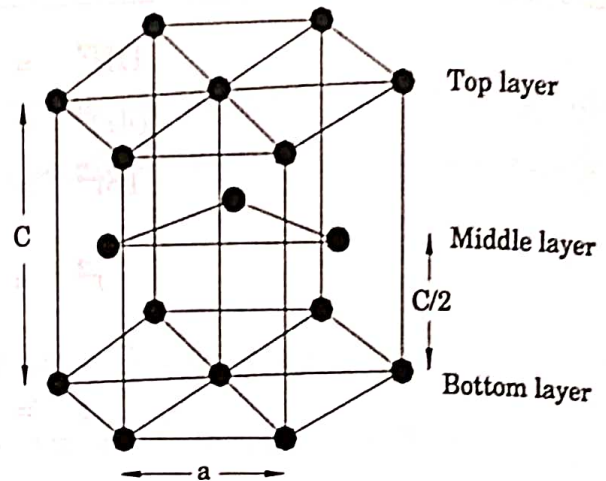


Fig. 5.26 HCP structure

- The unit cell has one atom at each of the 12 corners of the hexagonal structure.
- 2 base centered atom, one at the top face of the hexagon and another at the bottom face of the hexagon.
- In addition to corner and base atoms, 3 atoms are situated in between the top and bottom face of hexagon, in alternate vertical faces. Also note that these atoms are situated inside the faces. So that they can't be shared by other cells as shown in Fig.(5.26).

#### i. Number of atoms per unit cell

Each corner atom is shared by six other unit cell, (i.e) each corner atom gives  $\frac{1}{6}$ <sup>th</sup> of its share.

$$\therefore \text{Number of atoms in the upper hexagonal plane} = \frac{1}{6} \times 6 = 1$$

$$\therefore \text{Number of atoms in the lower hexagonal plane} = \frac{1}{6} \times 6 = 1$$

Each central atom is shared by two unit cells, which means upper and lower planes contain  $\frac{1}{2}$  atom each.

$$\text{Total number of central atoms in both upper and lower planes} = \frac{1}{2} \times 2 = 1$$

Finally, 3 atoms situated in the middle layer of the unit cell. They are not shared by any other adjacent unit cells.

$$\therefore \text{Total number of atoms in HCP crystal} = 1 + 1 + 1 + 3 = 6.$$

ii. Co-ordination number

If we consider the bottom layer, the central atom has 6 nearest neighbouring atoms in the same plane. Further at a distance  $\frac{C}{2}$  from the bottom layer, there are two layers, one is above and another is below the bottom layer containing 3 atoms in each layer.

$\therefore$  Total number of neighbouring atoms =  $6 + 3 + 3 = 12$  atoms.

$\therefore$  Co-ordination number = 12.

iii. Atomic radius

To find the atomic radius of the HCP structure. Consider any two corner atoms. It has to be noted that each and every corner atom touches each other, therefore they are the nearest neighbours.

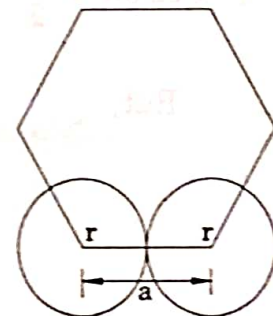


Fig. 5.27 Calculation of atomic radius in HCP

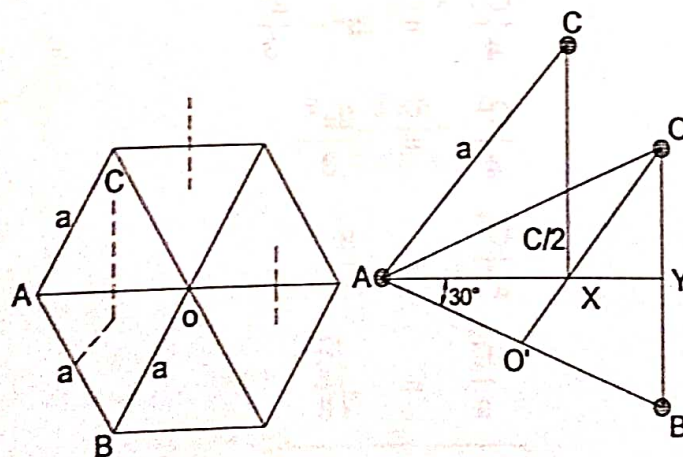
From Fig.(5.27), we can write,

$$a = 2r$$

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

iv. Relation between C and a [ $\frac{C}{a}$  ratio]

Let 'C' is the height of the unit cell and 'a' is the distance between two neighbouring atoms. Now consider the triangle ABO in the bottom layer of HCP structure.(Fig.5.28).



(a) Bottom layer of HCP structure (b) Triangle ABO  
Fig. 5.28



Here A, B and O are the lattice points and exactly above these at a perpendicular distance the next layer atom lies at C.

$$\text{In the triangle ABY, } \cos 30^\circ = \frac{AY}{AB}$$

$$\begin{aligned} AY &= AB \cos 30^\circ \\ &= \frac{a\sqrt{3}}{2} \quad [\because AB = a] \end{aligned}$$

$$[\because \cos 30^\circ = \frac{\sqrt{3}}{2}]$$

$$\begin{aligned} \text{But, } AX &= \frac{2}{3} AY \\ &= \frac{2}{3} \frac{a\sqrt{3}}{2} \\ &= \frac{a}{\sqrt{3}} \end{aligned}$$

In the triangle AXC,

$$AC^2 = AX^2 + CX^2$$

Substituting the values for  $AC^2$ ,  $AX^2$  and  $CX^2$  we have,

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

$$a^2 = \frac{a^2}{3} + \frac{C^2}{4}$$

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

$$\frac{C^2}{4} = \frac{2a^2}{3}$$

$$\frac{C^2}{a^2} = \frac{8}{3}$$

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

$$\boxed{\frac{C}{a} = 1.633}$$

## v. Atomic packing factor

Area of the base = 6 x Area of the triangle AOB.

$$\therefore \text{Area of the triangle AOB} = \left(\frac{1}{2}\right)(BO)(AO)$$

$$= \frac{1}{2}a \times \frac{a\sqrt{3}}{2}$$

$$\text{Thus, the area of the base} = 6 \times \frac{1}{2} \times \frac{a\sqrt{3}}{2}$$

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

Hence, the volume of the HCP unit cell (V) = Area x C (height)

$$V = \frac{3}{2}\sqrt{3}a^2C$$

Number of atoms present in a unit cell = 6

$$\therefore \text{Volume of the atoms present in unit cell (v)} = 6 \times \frac{4}{3}\pi r^3$$

$$v = \frac{24}{3}\pi\left(\frac{a}{2}\right)^3 \quad \left[\because r = \frac{a}{2}\right]$$

$$v = \pi a^3$$

$$\therefore \text{Atomic packing factor} = \frac{\text{Volume of the atoms in unit cell (v)}}{\text{Volume of the unit cell (V)}}$$

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

$$= \frac{2\pi a}{3\sqrt{3}C} \quad \left[\because \frac{C}{a} = \sqrt{\frac{8}{3}}\right]$$

$$= \frac{2\pi}{3\sqrt{3}}\left(\frac{3}{8}\right)^{\frac{1}{2}}$$

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

$$\boxed{\text{APF} = 0.74}$$



Therefore, 74% of the volume is occupied by the atoms and remaining 26% of the volume is vacant in HCP structure.

Thus, the density of packing is 74% and it is a close packed structure.

**Examples :** Zinc, Magnesium, Zirconium and Titanium.

### 5.13 OTHER CUBIC STRUCTURES

Although many elements solidify in one of the structures described above, several other elements and compounds possess combination of the structures discussed below.

#### i) Sodium chloride structure

Sodium chloride crystal is an ionic one. In the sodium chloride lattice, positively charged sodium ion and negatively charged chlorine ion are situated side by side. It consists of two FCC sublattices. One of the chlorine ion has its origin at (0,0,0) point while sodium ion has its origin midway along a cube edge at  $\left(\frac{a}{2}, 0, 0\right)$  point as shown in Fig.(5.29). Due to the electro-static force between sodium and chlorine ions, the two ions are attracted towards each other. When the two ions come closer their outer electron shells come into close proximity giving rise to strong forces of repulsion. When attraction and repulsion balance, equilibrium is obtained. Each ion in the sodium chloride lattice has six nearest neighbour ions at a distance  $a/2$ . (i.e) its coordination number is 6. The ionic radius of chlorine is about 1.81 AU and for sodium, 0.98 AU. Each unit cell of sodium has four sodium ions and four associated chlorine ions. Thus there are 4 molecules in each unit cell. KCl, KBr, MgO, AgBr etc. have NaCl structure.

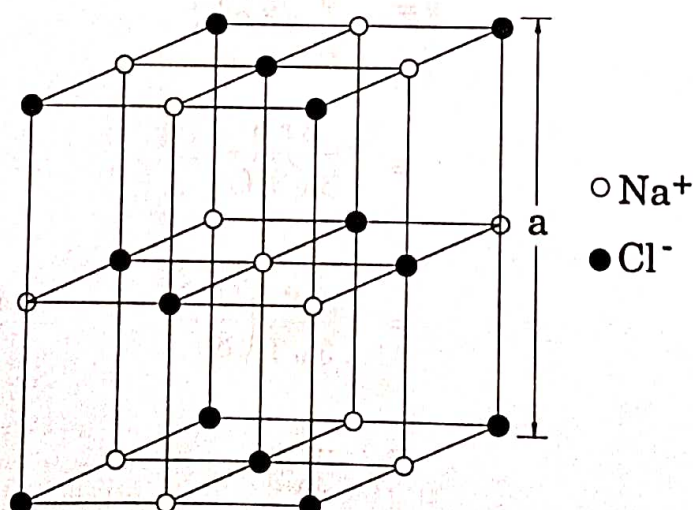


Fig 5.29 Sodium chloride structure

$\therefore$  Total number of  $\text{Cl}^-$  ions per unit cell =  $1 + 3 = 4$  ions.

Thus, there are 4  $\text{Na}^+$  and 4  $\text{Cl}^-$  ions per unit cell in a NaCl crystal.

### Coordination number

Each  $\text{Cl}^-$  ions has 6  $\text{Na}^+$  ions as nearest neighbour. Similarly, each  $\text{Na}^+$  ion has 6  $\text{Cl}^-$  ions as nearest neighbours. Hence, the coordination number of NaCl for opposite kind of ions is 6.

### Atomic radius

The distance between any two nearest neighbours is  $\frac{a}{2}$

**Examples :** KCl, KBr, CaO, etc.

### ii) Zinc sulphide or zinc blende cubic structure

This structure is identical to the diamond structure except that the two interpenetrating sub lattices are occupied by two different elements. Zinc sulphide structure results when Zn atoms are placed on one FCC lattice and S atoms on the other FCC lattice as shown in Fig.(5.30). Some of the important compounds which process this structure are semiconductors like  $\text{InSb}_2$ , GaAs, ZnS and CuCl.

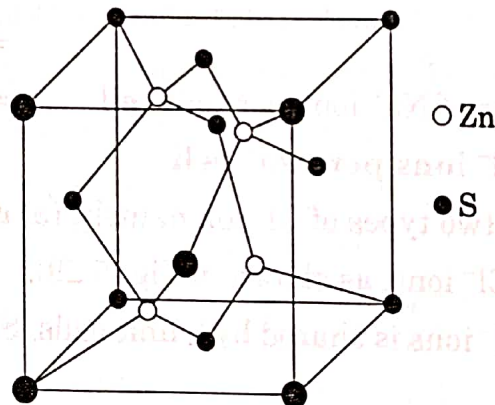


Fig 5.30 Zinc sulphide structure

### (iii) Diamond cubic structure

The diamond lattice can be considered to be formed by interpenetrating two FCC lattice along the body diagonal by  $\frac{1}{4}$  cube edge. One sub lattice has its origin at the point (0, 0, 0) and other at a point quarter of the way along the body diagonal



at  $\left(\frac{a}{4}, \frac{a}{4}, \frac{a}{4}\right)$ . The basic diamond lattice and the atomic positions in the cubic cell of diamond projected on a cube face are shown in Fig.(5.31).

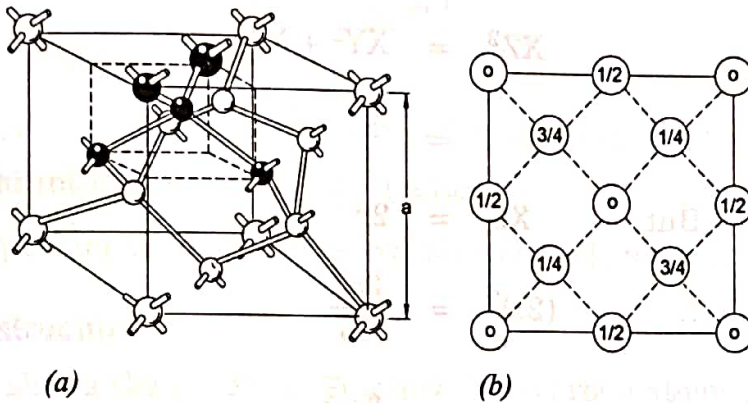


Fig. 5.31 Diamond cubic structure

In diamond cubic unit cell, in addition to 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 atoms is shared by two unit cells.

**a. Number of atoms per unit cell**

Number of atoms contributed by 8 corner atoms =  $8 \times \frac{1}{8} = 1$  atom

Number of atoms contributed by face centred atoms =  $6 \times \frac{1}{2} = 3$  atoms.

Number of atoms contributed by body diagonal = 4 atoms.

∴ Total number of atoms in unit diamond cell = 8 atoms.

**b. Co-ordination number**

To calculate the co-ordination number, consider an atom lying along the body diagonal. It is tetragonally bonded with four atoms. These tetragonally bonded atoms are the nearest neighbours of the atoms and hence, the coordination number is 4.

**c. Atomic radius**

Consider a corner atom, the corner atom touches a body diagonal lies at a distance of  $\frac{1}{4}$  as shown in Fig.(5.32).

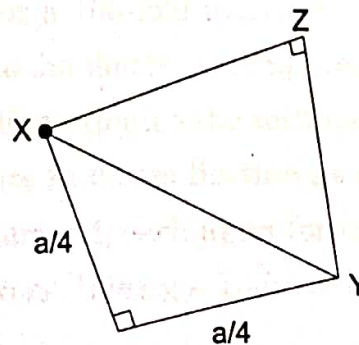


Fig. 5.32

From the Fig.(5.33)

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

Also,

$$\begin{aligned} XZ^2 &= XY^2 + YZ^2 \\ &= \frac{a^2}{8} + \frac{a^2}{16} = \frac{3a^2}{16} \end{aligned}$$

$$\text{But } XZ = 2r$$

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

$$2r = \frac{a\sqrt{3}}{4}$$

$$\therefore \text{Atomic radius } r = \frac{a\sqrt{3}}{8}$$

#### d. Atomic packing factor

Number of atoms per unit cell = 8

$$\text{Volume of 8 atoms (v)} = 8 \times \frac{4}{3} \pi r^3$$

Radius of atom is diamond cubic structure

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

$$\text{Volume of the unit cell (V)} = a^3$$

$$\text{Atomic packing factor} = \frac{\text{Volume occupied by the total number of atoms per unit cell (v)}}{\text{Total volume of the unit cell (V)}}$$

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

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



$$= \frac{32 \pi r^3 3\sqrt{3}}{3(8r)^3} = \frac{32 \pi \sqrt{3}}{512}$$

$$\text{APF} = 0.34$$

$\therefore$  Packing density = 34%

Therefore, 34% of the volume is occupied by the atoms and remaining 66% of the volume is vacant in diamond cubic structure.

Since the packing density is very low, it is a loosely packed structure.

#### iv) Graphite structure

Fig.(5.33) shows the graphite structure. The carbon atoms are arranged in layer or sheet structure.

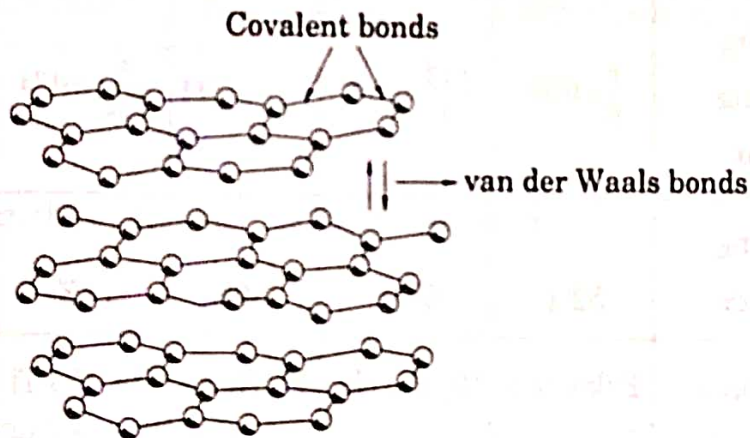


Fig 5.33 Graphite structure

When each carbon atom forms three covalent bonds with three other carbon atoms in the same plane, with bond length 1.42 Å, sheets of graphite are produced. The sheets are held together in a crystal by van der Waals bonds with a spacing of about 3.4 Å. The fourth bonding electron of carbon is delocalized and resonates between the three covalent bonds. This only accounts for a 100-fold increase in electrical and thermal conductivity in a direction parallel to the sheets, as compared to the perpendicular direction. The weak intersheet bonding explains the softness of graphite in sharp contrast to diamond. Graphite, hence finds application as a lubricant. In the other crystal form of carbon namely diamond, each atom forms four covalent bonds and produce a three dimensional network. It is a good electrical insulator.

### SOLVED PROBLEMS

1. Copper has FCC structure and its lattice parameter is  $3.6 \text{ \AA}$ . Find the atomic radius.

Given data

$$\text{Lattice parameter of copper (a)} = 3.6 \text{ \AA}$$

Solution

$$\begin{aligned} \text{Atomic radius of copper 'r'} &= \frac{a\sqrt{2}}{4} \\ &= \frac{3.6 \times 10^{-10} \times \sqrt{2}}{4} \\ &= 1.273 \times 10^{-10} \text{ m} \\ r &= 1.273 \text{ \AA} \end{aligned}$$

2. Silver has FCC structure and its atomic radius is  $1.414 \text{ \AA}$ . Find the spacing of (110) plane

Given data

$$\text{atomic radius } r = 1.414 \text{ \AA}$$

$$r = 1.414 \times 10^{-10} \text{ m}$$

Solution

$$\text{For FCC, lattice constant } a = \frac{4r}{\sqrt{2}}$$

$$\text{Therefore } a = \frac{4 \times 1.414 \times 10^{-10}}{\sqrt{2}}$$

$$a = 4 \times 10^{-10} \text{ m}$$

We know in the case of cubic system

$$\left. \begin{array}{l} \text{The inplanar spacing between} \\ \text{planes of Miller indices (hkl)} \end{array} \right\} d = \frac{a}{\sqrt{h^2 + k^2 + \ell^2}}$$

$$\left. \begin{array}{l} \text{Therefore the spacing of the} \\ \text{plane with Miller indices (110)} \end{array} \right\} d = \frac{4 \times 10^{-10}}{\sqrt{1^2 + 1^2 + 0}}$$

$$d = 2.828 \times 10^{-10} \text{ m}$$

3. Iron is BCC with atomic radius  $0.123 \text{ \AA}$ . Find the lattice constant and also the volume of the unit cell.



**Given data**  $r = 0.123 \text{ \AA} = 0.123 \times 10^{-10} \text{ m}$

**Solution**

$$\text{For BCC Lattice, } a = \frac{4r}{\sqrt{3}}$$

$$= \frac{4 \times 0.123 \times 10^{-10}}{\sqrt{3}}$$

$$a = 0.284 \times 10^{-10} \text{ m}$$

$$\begin{aligned} \therefore \text{Volume of the unit cell (V)} &= a^3 = (0.284 \times 10^{-10})^3 \\ &= 2.2906 \times 10^{-32} \text{ m}^3 \end{aligned}$$

4. The interplanar distance between the planes of a crystal is  $2.9 \text{ \AA}$ . It is found that first order Bragg's reflection occurs at an angle of  $9.5^\circ$ . What is the wavelength of x - rays ?

**Given data**

$$d = 2.9 \text{ \AA}$$

$$= 2.9 \times 10^{-10} \text{ m}$$

$$\theta = 9.5^\circ$$

$$n = 1$$

**Solution**

$$\text{From Bragg's law } n \lambda = 2d \sin \theta$$

$$\text{Therefore } \lambda = \frac{2d \sin \theta}{n} = \frac{2 \times 2.9 \times 10^{-10} \times \sin 9.5^\circ}{1}$$

$$\lambda = 0.957 \times 10^{-10} \text{ m}$$

$$\lambda = 0.957 \text{ \AA}$$

5. The Bragg angle corresponding to the first order reflection from (110) plane in a crystal is  $32^\circ$ . When X - rays of wavelength of  $1.7 \text{ \AA}$  is used. Find the interatomic spacing in a cubic lattice.

**Given data**

$$(hkl) = (110)$$

$$\text{Therefore } d_{110} = \frac{a}{\sqrt{2}}$$

$$\lambda = 1.7 \text{ \AA} = 1.7 \times 10^{-10} \text{ m}$$

$$\theta = 32^\circ$$

$$\text{Also } n = 1$$

**Solution**

For a Cubic lattice, the lattice constant 'a', and interplanar spacing 'd' for a plane of Miller indice (hkl) is given by

$$d_{hkl} = \frac{a}{(h^2 + k^2 + \ell^2)^{1/2}}$$

Substituting the above values in

Bragg's Law,  $2d \sin\theta = n\lambda$

$$2 \times \frac{a}{\sqrt{2}} \sin 32^\circ = 1.7 \times 10^{-10}$$

Therefore  $a = \frac{\sqrt{2} \times 1.7 \times 10^{-10}}{2 \sin 32}$

$$a = 2.268 \times 10^{-10} \text{ m}$$

6. Copper has FCC structure and atomic radius 1.278 Å. The atomic weight of copper is 63.54. Avagadro's number is  $6.023 \times 10^{26} \text{ kg.mole}^{-1}$ .

Given data

atomic radius  $r = 1.278 \text{ \AA} = 1.278 \times 10^{-10} \text{ m}$

Atomic weight of copper  $M = 63.54$

Avagadro's number  $N = 6.023 \times 10^{26} \text{ kg.mole}^{-1}$

**Solution**

In FCC No of atoms per unit cell  $n = 4$

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

$$a = \frac{4 \times 1.278 \times 10^{-10}}{\sqrt{2}}$$

$$a = 3.615 \times 10^{-10} \text{ m}$$

We know the density of copper  $\rho = \frac{nM}{Na^3}$

$$= \frac{4 \times 63.54}{(3.615 \times 10^{-10})^3 \times 6.023 \times 10^{26}}$$

$$= \frac{254.16}{0.0285}$$

$$\rho = 8.932 \times 10^3 \text{ Kgm}^{-3}$$