

# **Unit - I**

# **Crystal Physics**



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# 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.

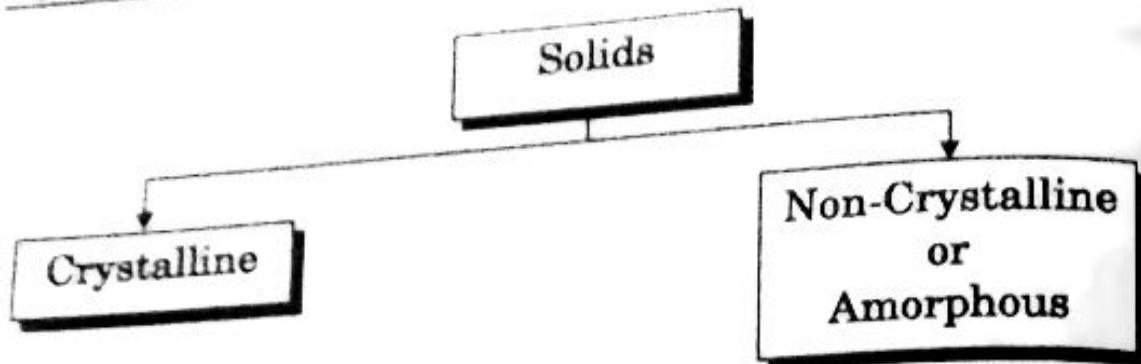
## ***Classification of Solids***

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

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

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### (i) Crystalline Materials or Crystals

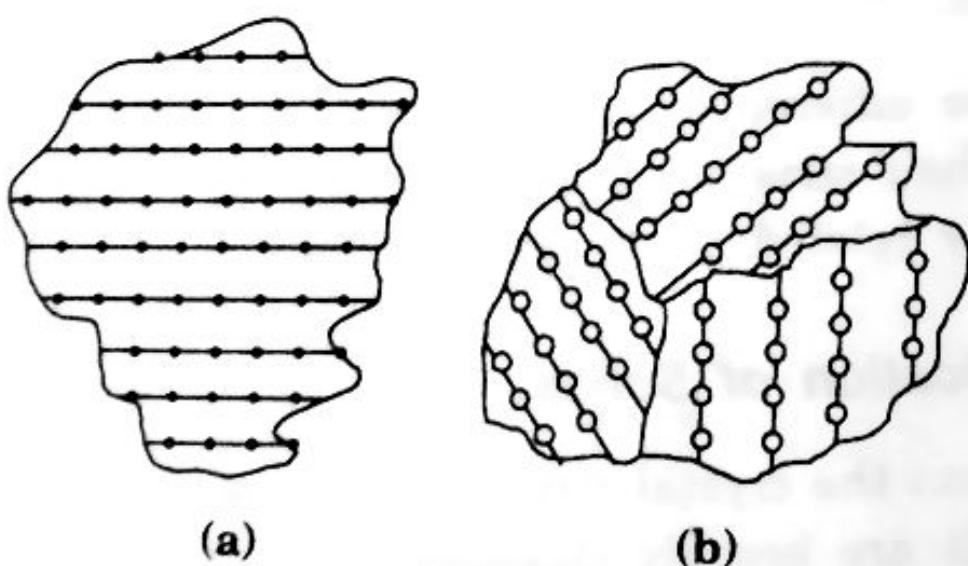
The materials in which the atoms are arranged in a systematic pattern (regular pattern) are known as crystalline materials.

*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

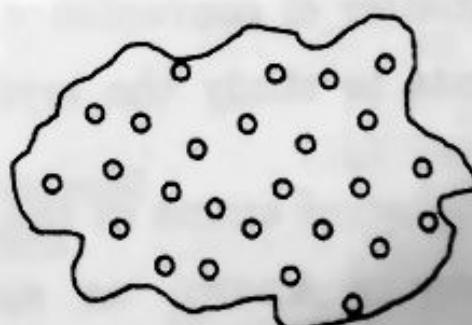
**Amorphous means without form.**

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.



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**Fig. 1.2 Amorphous material**

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 **simply 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.

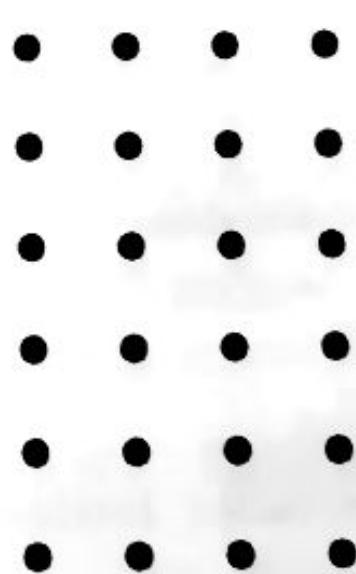
### **Definition**

It is as 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**

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

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

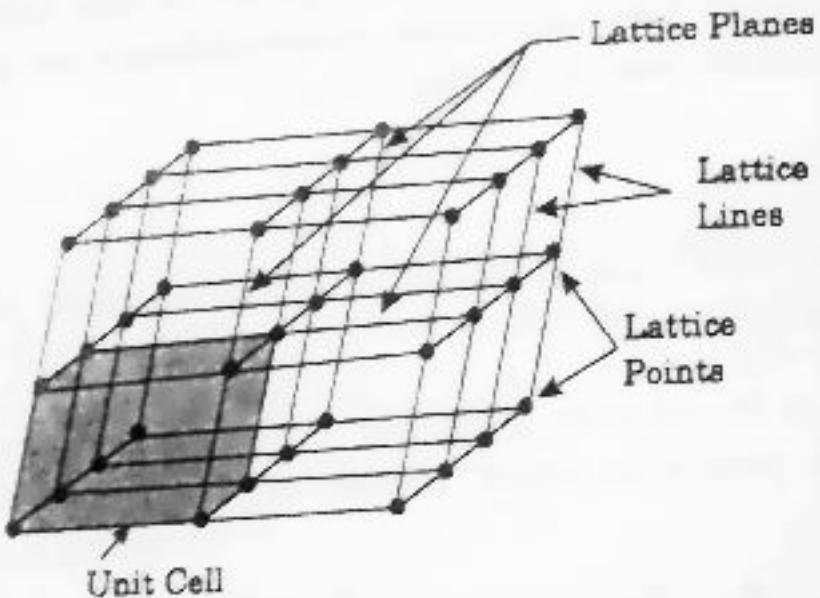


Fig. 1.4 Space lattice in three-dimensions

### 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 known as **lattice lines**.  
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### Lattice plane:

A plane containing lattice points is known as **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., **Space lattice + Basis → 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).

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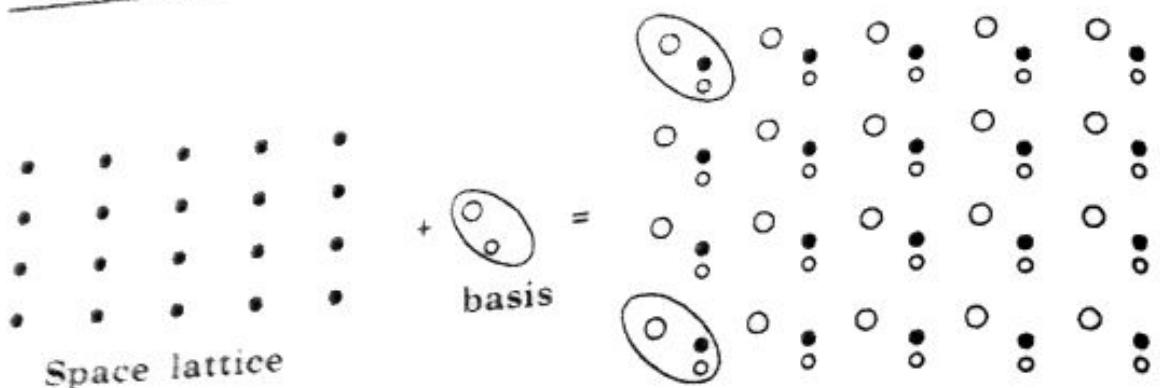


Fig. 1.5 Crystal structure is obtained when a basis is added to each lattice point

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.

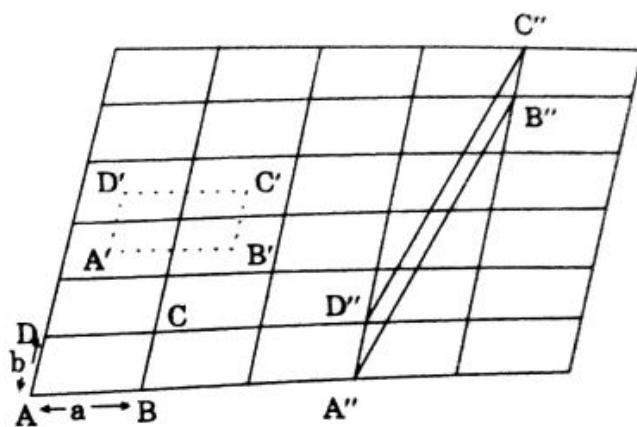
**Note:**

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.

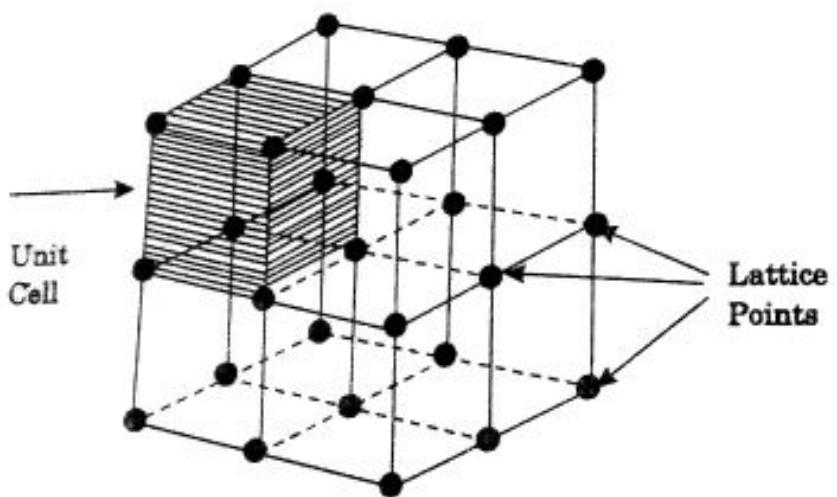
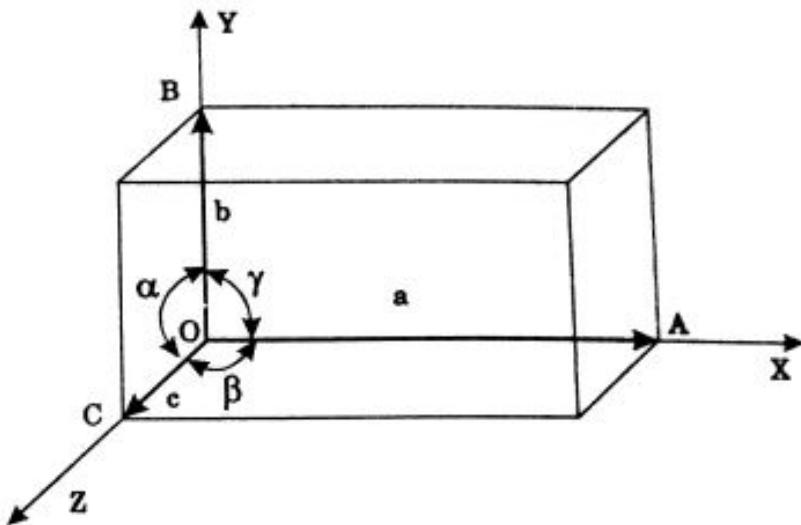


Fig. 1.7 Unit cell in three-dimensions

### *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**

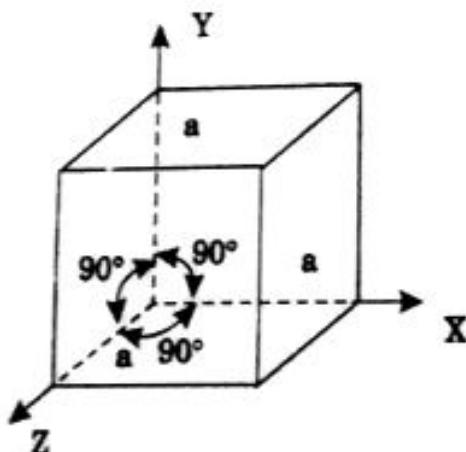
1. Cubic
2. Tetragonal
3. Orthorhombic
4. Monoclinic
5. Triclinic
6. Rhombohedral
7. Hexagonal

### 1. Cubic system

In this crystal system, all the three axial lengths of the unit cell are equal and they are perpendicular to each other (fig. 1.9 [a]).

i.e.,  $a = b = c$  and

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



**Fig. 1.9 (a)**

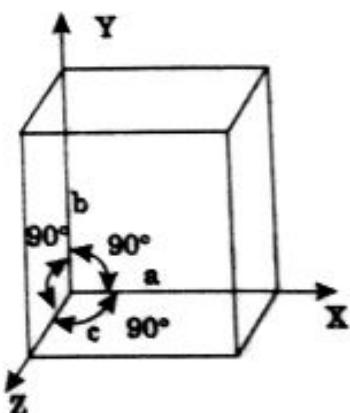
**Example:** Sodium Chloride (NaCl),  
Calcium Fluoride (CaF<sub>2</sub>).

## 2. Tetragonal system

In this system, two axial lengths of the unit cell are equal and third axial length is either longer or shorter (fig. 1.9 [b]). Three axes are perpendicular to each other.

i.e.,  $a = b \neq c$  and

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



**Fig. 1.9 (b)**

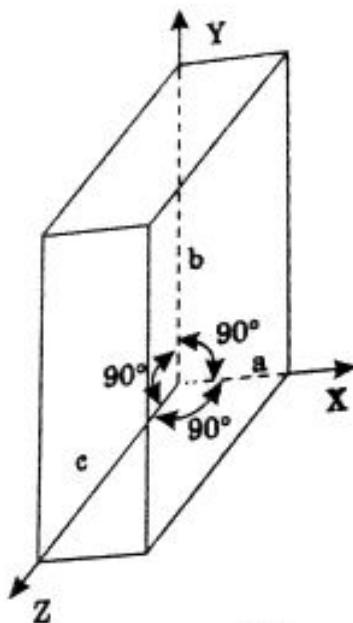
**Example:** Ordinary white tin, Indium.

## 3. Orthorhombic system

In this system, three axial lengths of the unit cell are not equal but they are perpendicular to each other. (fig. 1.9 [c]).

i.e.,  $a \neq b \neq c$  and

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



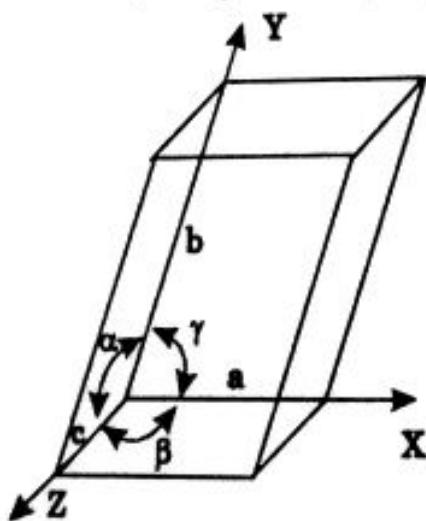
**Fig. 1.9 (c)**

**Example:** Sulphur, Topaz.

#### 4. Monoclinic system

In this system, three axial lengths of unit cell are not equal. Two axes are perpendicular to each other and third is obliquely inclined (fig. 1.9 [d]).

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



**Fig. 1.9 (d)**

**Example:** Sodium sulphite ( $\text{Na}_2\text{SO}_3$ ),

Ferrous sulphate ( $\text{FeSO}_4$ ).

### 5. Triclinic system

In this system, three axial lengths of unit cell are not equal and all the axes are inclined obliquely to each other (fig. 1.9 [e]).

i.e.,  $a \neq b \neq c$  and

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

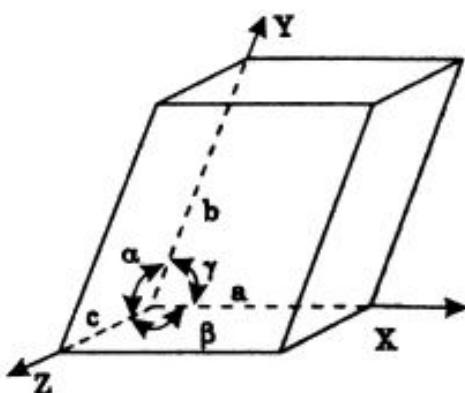


Fig. 1.9 (e)

**Example:** Copper sulphate ( $\text{CuSO}_4$ ),

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

### 6. Rhombohedral system (Trigonal)

In this system, three axial lengths of the unit cell are equal. They are equally inclined to each other at an angle other than  $90^\circ$

(fig. 1.9 [f]).

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

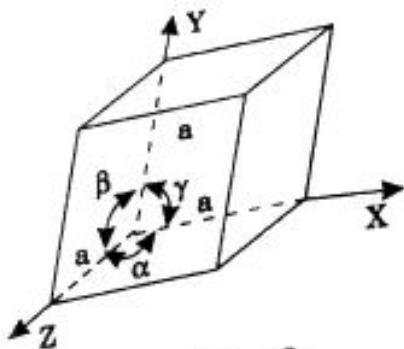


Fig. 1.9 (f)

**Example:** Calcite.

### 7. Hexagonal system

In this system, two axial lengths of unit cell (say horizontal) are equal and lying in one plane at angle  $120^\circ$  with each other. The third axial length (say vertical) is either longer or shorter than other two and it is perpendicular to this plane (fig. 1.9 g).

i.e.,  $a = b \neq c$  and

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

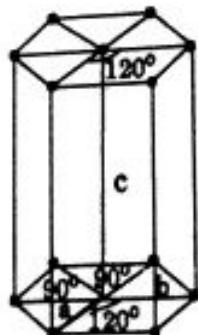


Fig. 1.9 (g)

**Example:** Quartz, Tourmaline.

**Table 1.1  
Seven Crystal Systems**

S. No.	Crystal systems	Axial length ( $a$ , $b$ , $c$ )	Interfacial angles ( $\alpha$ , $\beta$ , $\gamma$ )	Example
1.	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	NaCl, CaF <sub>2</sub>
2.	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Ordinary white tin, indium
3.	Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Sulphur, Topaz
4.	Monoclinic	$a \neq b \neq c$	$\alpha = \beta = 90^\circ$ ; $\gamma \neq 90^\circ$	Na <sub>2</sub> SO <sub>4</sub> , FeSO <sub>4</sub>
5.	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	CuSO <sub>4</sub> , K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>
6.	Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	Calcite
7.	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ$ ; $\gamma = 120^\circ$	Quartz, Tourmaline

### 1.3 BRAVAIS LATTICE

Bravais introduced the concept of space lattice. He showed that there are only 14 ways of arranging points in space such that the environment looks same from each point.

Hence, there are only 14 types of space lattices which can be possibly developed from '7' crystal systems.

These 14 types of space lattices are known as  
Bravais lattices.

Table 1.2  
Bravais lattices

S. No.	Crystal systems	Number of possible types	
1.	Cubic	3	Simple and Body-centred and Face centred
2.	Tetragonal	2	Simple and Body-centred
3.	Orthorhombic	4	Simple, Base-centred, Body-centred and Face-centred
4.	Monoclinic	2	Simple and Base-centred
5.	Triclinic	1	Simple
6.	Rhombohedral (Trigonal)	1	Simple
7.	Hexagonal	1	Simple
	Total	14	

### 1. Cubic lattice

It has 3 possible types of arrangements.

#### (i) Simple (or primitive) cubic lattice

It has lattice points at all 8 corners of the unit cell as shown in fig. 1.10(a).

**(ii) Body-centred cubic (bcc) lattice**

It has lattice points at all 8 corners of the unit cell and one lattice point at the centre of the body as shown in fig. 1.10 (a).

**(iii) Face-centred cubic (fcc) lattice**

It has lattice points at all 8 corners of the unit cell and one lattice point at the centre of each of 6 faces of the cube as shown in fig. 1.10 (a).

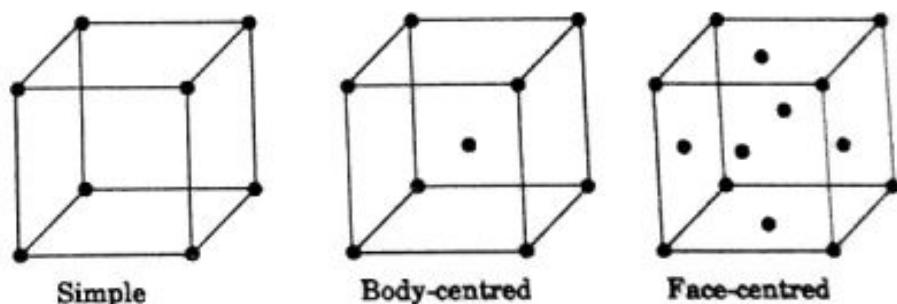


Fig. 1.10 (a) Cubic lattice

## 2. Tetragonal lattice

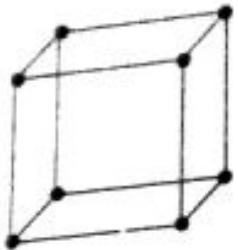
It has two possible types of lattices.

**(i) Simple tetragonal lattice**

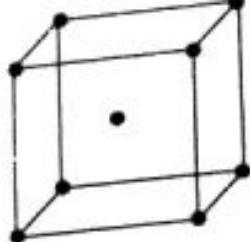
It has lattice points at all 8 corners of the unit cell as shown in figure 1.10 (b).

**(ii) Body-centred tetragonal lattice**

It has lattice points at all 8 corners of the unit cell and one lattice point at the centre of the body as shown in fig. 1.10 (b).



Simple



Body-centred

Fig. 1.10 (b) Tetragonal lattice

### 3. Orthorhombic lattice

It has four possible types of lattices.

#### (i) Simple orthorhombic lattice

It has lattice points at all 8 corners of the unit cell as shown in fig. 1.10(c).

#### (ii) Base-centred orthorhombic lattice

It has lattice points at all 8 corners of the unit cell and 2 lattice points each at the centre of two faces (base of the faces) opposite to each other as shown in fig. 1.10 (c).

#### (iii) Body-centred orthorhombic lattice

It has lattice points at all 8 corners of the unit cell and one lattice point at the centre of the body as shown in fig. 1.10 (c).

**(iv) Face-centred orthorhombic lattice**

It has lattice points at all 8 corners of the unit cell and 6 lattice points at the centre of each of the 6 faces of the unit cell as shown in fig. 1.10 (c).

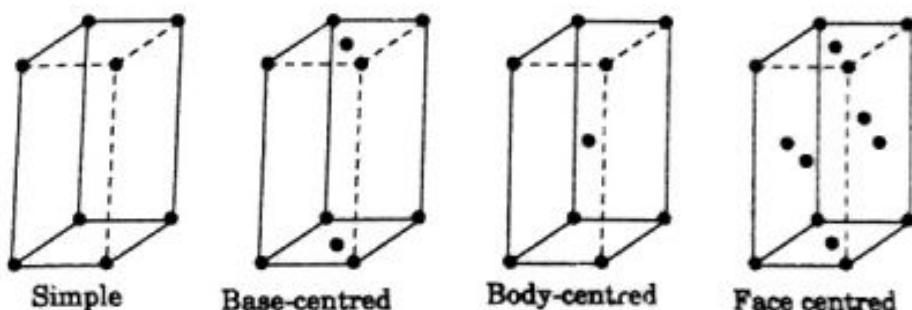


Fig. 1.10 (c) Orthorhombic lattice

**4. Monoclinic lattice**

It has two possible space lattices.

**(i) Simple monoclinic lattice**

It has lattice points at all 8 corners of the unit cell as shown in fig. 1.10 (d)

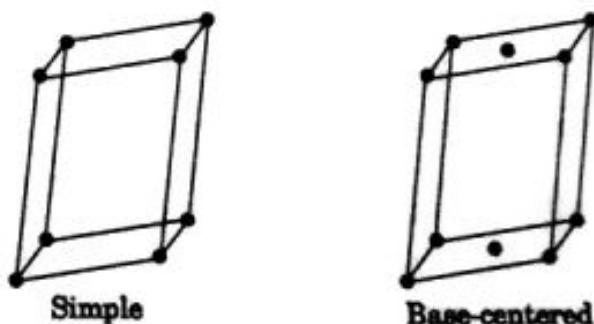


Fig. 1.10 (d) Monoclinic lattice

**(ii) Base-centred monoclinic lattice**

It has lattice points at all 8 corners of the unit cell and 2 lattice points each at the centre of two faces

(base of the faces) opposite to each other as shown in fig. 1.10 (d)

### 5. Triclinic lattice

It has only one possible space lattice.

#### (i) Simple triclinic lattice

It has lattice points at all 8 corners of the unit cell as shown in fig. 1.10 (e).

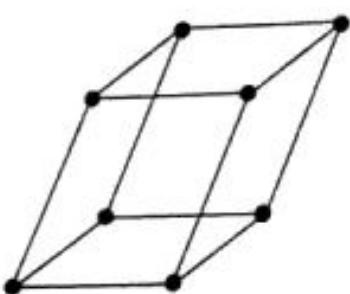


Fig. 1.10 (e) Simple triclinic

### 6. Rhombohedral lattice

It has only one possible space lattice.

#### (i) Simple rhombohedral lattice

It has lattice points at all 8 corners of the unit cell as shown in fig. 1.10 (f)

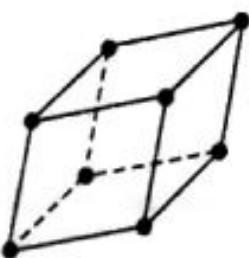


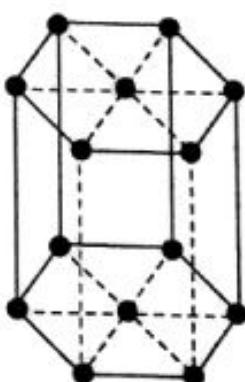
Fig. 1.10 (f) Simple rhombohedral

## 7. Hexagonal lattice

It has only one possible space lattice.

### (i) Simple hexagonal lattice

It has lattice points at all 12 corners of the hexagonal prism and 2 lattice points each at the centre of two hexagonal faces of the unit cell as shown in fig. 1.10 (g).



**Fig. 1.10 (g) Simple hexagonal**

In fact, it is mathematically proved that there are only 14 independent ways of arranging points in three-dimensional space such that each arrangement confirms to the definition of space lattice.

### Characteristics of a unit cell

A unit cell is characterised by the following properties

- (i) **Number of atoms per unit cell**
- (ii) **Coordination number**
- (iii) **Nearest neighbouring distance**
- (iv) **Atomic radius** and

### (v) Packing factor

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

It is the number of atoms possessed by a unit cell. This can be determined if the arrangement of atoms inside the unit cell is known.

#### (ii) Coordination Number (CN)

It is the number of nearest atoms directly surrounding a particular atom in a crystal.

The coordination number gives the information about the packing of atoms in the structure. i.e., whether the crystal structure is closely packed structure or loosely packed structure.

If the coordination number is high, then the structure is more closely packed. If it is low, then the structure is loosely packed.

#### (iii) Nearest neighbouring distance ( $2r$ )

It is the distance between the centres of two nearest neighbouring atoms.

It is expressed in terms of the length of edge of the unit cell 'a' and it is  $2r$ . (Fig. 1.11)

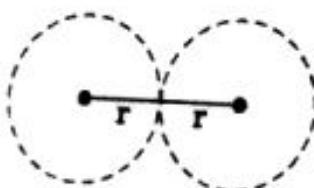


Fig. 1.11

(iv) Atomic radius ( $r$ )

It is half of the nearest neighbouring distance in a crystal. It is denoted by ' $r$ '. It is usually expressed in terms of cube edge ' $a$ ' (lattice parameter). (Fig 1.11).

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

(v) Packing Factor (PF)

It is defined as the ratio of total volume occupied by the atoms in a unit cell to the total volume of a unit cell.

Packing factor

$$= \frac{\text{Total volume occupied by the atoms in a unit cell} (v)}{\text{Total volume of the unit cell} (V)}$$

$$= \frac{\text{Number of atoms present in a unit cell} \times \text{Volume of one atom}}{\text{Total volume of the unit cell}}$$

It is also known as **density of packing**.

The packing factor tells us how closely the atoms are stacked in the unit cell. A high packing factor indicates that atoms are very closely packed and therefore there is very *little* unoccupied space.

On the other hand, a low packing factor indicates loose packing of atoms and hence there is relatively *more* unoccupied space.

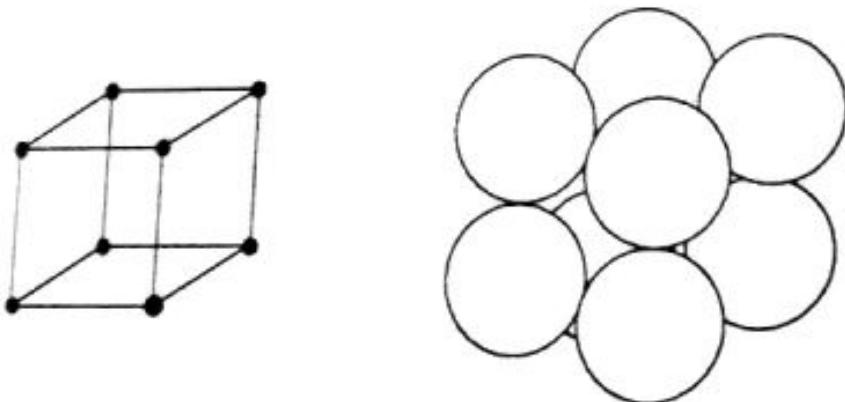
## CRYSTAL STRUCTURES - SC, BCC, FCC, and HCP

It is noted that a large percentage of metallic structures is found to crystallise in hcp, fcc and bcc. Simple Cubic (SC) is very rare in metals.

The alkali metals Li, Na, K, etc., crystallise in bcc structures, some transition elements and rare earths crystallise in fcc structures, elements of second group crystallise in hcp structures.

### **1.4 SIMPLE CUBIC (SC) STRUCTURE**

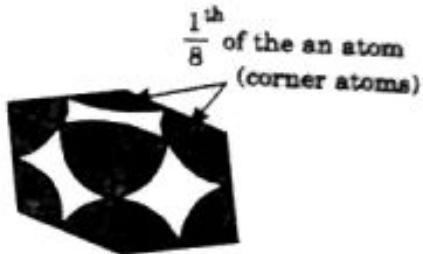
The simple cubic structure is the simplest and easiest crystal structure. In a simple cubic structure, there is one atom at each of the '8' corners of the unit cell. These atoms touch each other along cube edges. (fig 1.12).



**Fig. 1.12 Simple cubic**

#### **1. Number of atoms per unit cell**

The unit cell of a simple cubic structure is shown in fig 1.13.



**Fig. 1.13 Simple cubic unit cell**

There are 8 atoms, one atom at each corner of the unit cell. Each corner atom is shared by 8 surrounding unit cells.

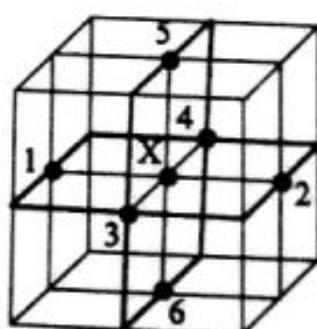
$$\therefore \text{Share of each unit cell} = \frac{1}{8} \text{ of each corner atom}$$

Total number of atoms in one unit cell

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

## 2. Coordination number

Simple cubic unit cell has 8 corner atoms. Let us consider one of the corner atoms (say X). It is shared by 8 adjacent unit cells as shown in fig 1.14.



**Fig 1.14**

1.28

There are 4 nearest neighbouring atoms to this particular atom X which are shown by 1, 2, 3, and 4 in a plane (horizontal plane). Further, there are 2 more nearest atoms, one directly above (atom 5) and the other one directly below (atom 6) to the atom X.

Thus, there are only six ( $4 + 2$ ) nearest neighbours to the atom X.

Hence, the coordination number for simple cubic is 6.

**Note:** Similarly if we consider any corner atom, the total number of nearest neighbours i.e., the co-ordination number is the same.

### 3. Atomic radius

Consider a face of the unit cell of a simple cubic structure (fig 1.15). The atoms touch each other along the edges of the cube.

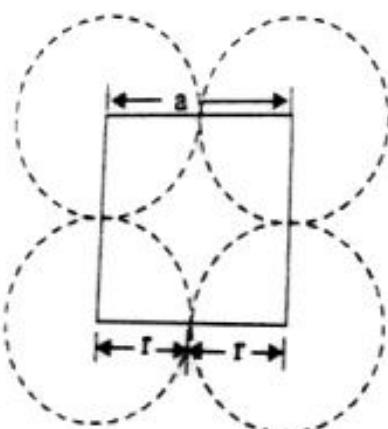


Fig. 1.15 Simple cubic

It is clear that the distance between the centres of two nearest atoms is just equal to the cube edge  $a$ .

If ' $a$ ' is the side of the unit cell and  $r$  its radius, then, from fig. 9.15,

$$2r = a$$

or

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

#### 4. Packing factor

Number of atoms per unit cell = 1

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

where  $r$  is the atomic radius

Side of the unit cell,  $a = 2r$

$$\left( \therefore \text{atomic radius, } r = \frac{a}{2} \right)$$

$$\text{Total volume of the unit cell, } V = a^3$$

$$\text{We know that packing factor} = \frac{v}{V}$$

Substituting for  $v$  and  $V$ , we have

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

Substituting  $a = 2r$ , we get

$$= \frac{\frac{4}{3} \pi r^3}{(2r)^3} = \frac{\frac{4}{3} \pi r^3}{2^3 r^3} = \frac{\frac{4}{3} \pi r^3}{8 r^3} = \frac{4 \pi r^3}{24 r^3}$$

$$= \frac{\pi}{6} = \frac{3.14}{6} = 0.5236$$

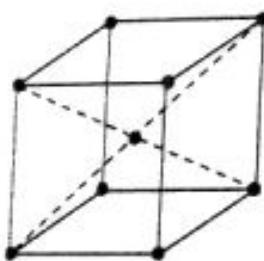
PF = 52%

Thus, 52% of the volume is occupied by the atoms and the remaining 48% volume is vacant.

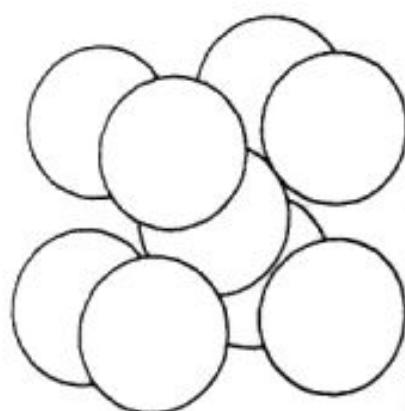
**Example:** Only one element polonium (Po) at a certain temperature range exhibits this crystal structure.

### 1.5 BODY-CENTRED CUBIC (BCC) STRUCTURE

In this crystal structure, the unit cell has one atom at each corner of the cube and one atom at the body centre of the cube. The atoms represented as hard spheres are shown in fig. 1.16.



(a) Unit cell of bcc

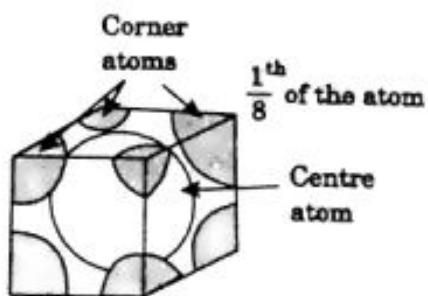


(b) Hard sphere model.

Fig. 1.16 Body-centred cubic cell

### 1. Number of atoms per unit cell

The unit cell of the body-centred cube is shown in fig. 1.17.



**Fig. 1.17 BCC unit cell**

Each corner atom is shared by 8 adjoining or surrounding unit cells.

Hence, the share of one unit cell =  $\frac{1}{8}$  of each corner atom.

There are '8' corner atoms,

∴ Contribution of all corner atoms

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

There is one atom at the body centre of every unit cell.

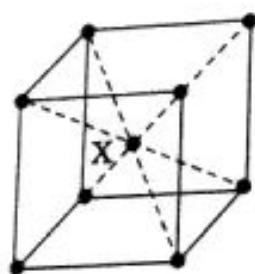
∴ Total number of atoms in one unit cell

$$= 1 + 1 = 2 \text{ atoms}$$

### **Coordination number**

In the unit cell of BCC structure, there is one atom (say atom X) at the body centre of the unit cell. Further there are '8' atoms at the 8 corners of the unit cell as shown in fig. 1.18.

The corner atoms do not touch each other. But all the eight corner atoms of the unit cell touch the body centred atom along the body diagonal. Thus, for body centre atom 'X', there are 8 nearest neighbours (ie., 8 corner atoms).



**Fig. 1.18**

Hence, the co-ordination number of body centred cubic structure is 8.

**Note:** The coordination number can also be determined in another way by taking the corner atom as reference atom as follows.

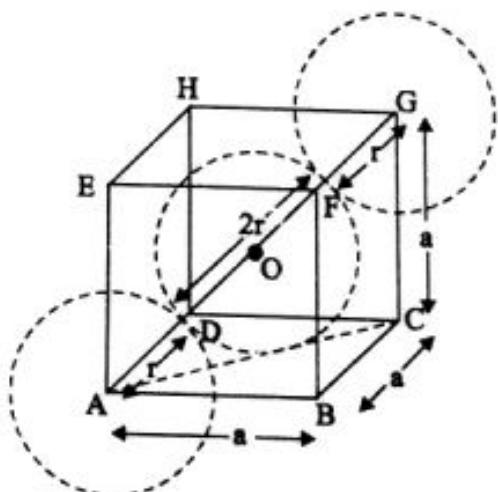
In a BCC structure, each corner atom is surrounded by '8' other body centred unit cells. Therefore, the nearest adjacent neighbours of any corner atom are the '8' body centred atoms of the surrounding '8' unit cells.

**Thus, the co-ordination number is 8.**

### 3. Atomic radius

The corner atoms do not touch each other. However, each corner atom touches the central atom. The unit cell for bcc is shown in fig. 1.19. The side of the unit cell is 'a'.

It is clear from fig. 1.19 that the nearest neighbouring atoms are corner atoms A and G and the body centre atom O.



**Fig. 1.19 Unit cell of Body-centred cubic**

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

From the right angled  $\triangle$  ABC,

$$AC^2 = AB^2 + BC^2$$

substituting for AB and BC from the fig 1.19, we have

$$AC^2 = a^2 + a^2$$

$$AC^2 = 2a^2$$

From the geometry of figure 1.19,

$$AG = r + 2r + r = 4r$$

on squaring on both sides, we get

$$AG^2 = (4r)^2$$

From the right angled  $\Delta ACG$ ,

$$AG^2 = AC^2 + CG^2$$

Substituting for  $AG^2$ ,  $AC^2$  and  $CG^2$ , we have

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

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

$$\text{or } r^2 = \frac{3a^2}{4^2}$$

Taking square root on both sides, we have

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

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

#### 4. Packing factor

Number of atoms per unit cell = 2

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

$$\text{Side of the unit cell, } a = \frac{4r}{\sqrt{3}}$$

$$\left( \therefore \text{atomic radius } r = \frac{\sqrt{3} a}{4} \right)$$

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

$$\text{Packing factor} = \frac{v}{V}$$

Substituting for  $v$  and  $V$ , we have

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

Substituting for  $a$

$$PF = \frac{2 \times \frac{4}{3} \pi r^3}{\left( \frac{4r}{\sqrt{3}} \right)^3} = \frac{\frac{8}{3} \pi r^3}{\frac{4^3 r^3}{(\sqrt{3})^3}}$$

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

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

$$PF = \frac{\sqrt{3} \times 3.14}{8} = 0.68$$

$$PF = 68\%$$

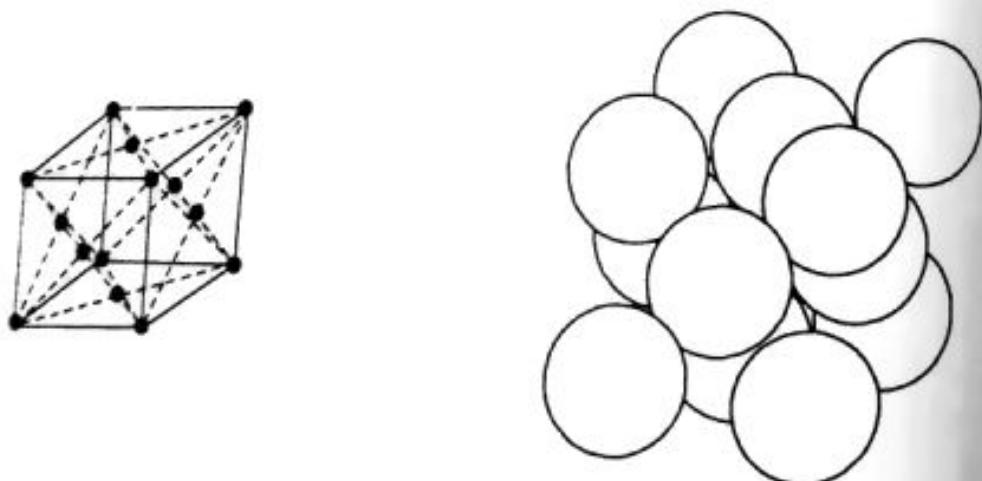
Thus, packing factor is 68% i.e., 68% of the volume of unit cell is occupied by atoms and the remaining 32% volume is vacant.

**Common examples of this type of structure**

Tungsten, Chromium and Molybdenum.

### 1.6 FACE-CENTRED CUBIC (FCC) STRUCTURE

In this type of crystal structure, the unit cell has one atom at each corner of the cube and in addition one atom at the centre of each face. (fig. 1.20).



**Fig. 1.20 Face-centred cube**

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.

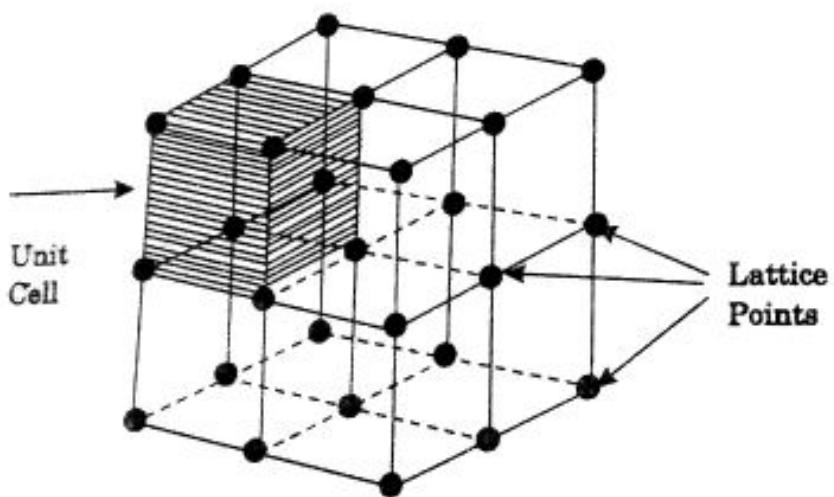


Fig. 1.7 Unit cell in three-dimensions

### *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).

Hence, the share of each unit cell =  $\frac{1}{2}$  of each face-centred atom.

∴ Number of atoms in the unit cell from the contribution of face-centered atom

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

∴ Total number of atoms in the unit cell

$$= 1 + 3 = 4$$

## 2. Coordination number

In FCC structure, there are 8 corner atoms and 6 face centred atoms one at the centre of each face of the unit cell.

To determine the coordination number, let us consider a corner atom (X) of a unit cell as shown in fig. 1.22. There are three mutually perpendicular planes

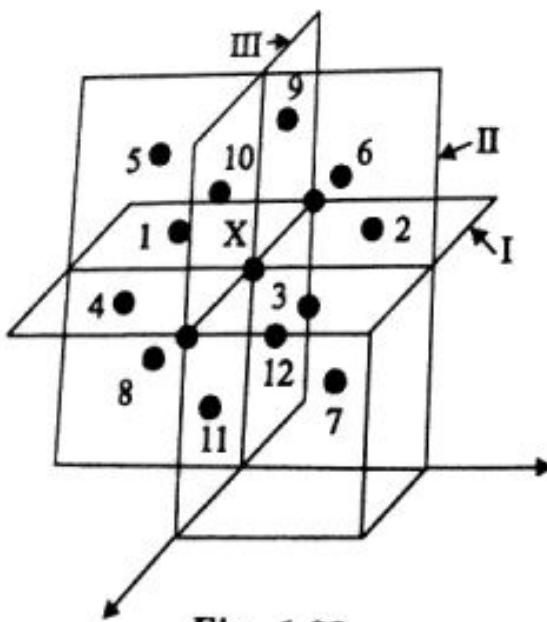


Fig. 1.22

with a common point of intersection on the atom X. In plane I it has 4 face centred atoms (1, 2, 3, 4) as nearest neighbours.

In plane II, it has 4 more face centred atoms (5, 6, 7, 8) as nearest neighbours for the corner atom X.

Similarly plane III has 4 more face centred atoms, (9, 10, 11, 12) as nearest neighbours to the corner atom X.

∴ The total number of nearest atoms to any corner atom is  $4 + 4 + 4 = 12$

**Hence, coordination number is 12.**

**Note:** The co-ordination number can also be found by taking face centred atom as the reference atom and it is found to be the same, i.e., 12.

### 3. Atomic radius

The atoms touch each other along the diagonal of any face of the cube. The length of diagonal of the face is  $4r$ .

In this case, the neighbouring atoms are a corner atom (such as A) and an atom at the centre of adjacent face (such as O) as shown in fig. 1.23.

In right angled  $\Delta ABC$

$$AC^2 = AB^2 + BC^2$$

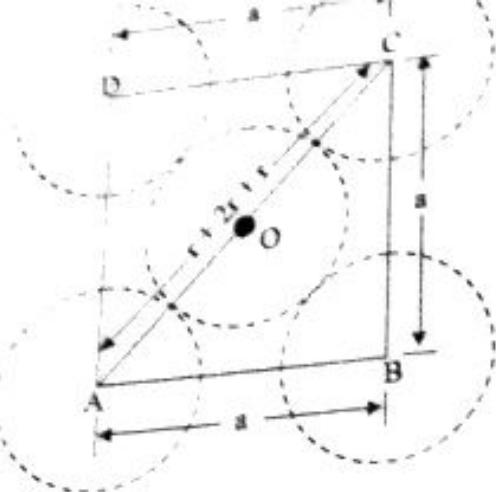


Fig. 1.23

Substituting for  $AC^2$ ,  $AB^2$  and  $OC^2$ , (from fig 9.23)  
we have

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

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

$$4^2 r^2 = 2a^2$$

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

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

Taking square root on both sides, we have

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

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

#### 4. Packing factor

Number of atoms per unit cell = 4

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

$$\text{Side of the unit cell, } a = \frac{4r}{\sqrt{2}}$$

$$\left( \therefore \text{atomic radius } r = \frac{\sqrt{2} a}{4} \right)$$

$$\text{Volume of the unit cell } V = a^3 = \left( \frac{4r}{\sqrt{2}} \right)^3$$

$$\text{Packing factor} = \frac{v}{V}$$

Substituting for  $v$  and  $V$ , we have

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

$$= \frac{\frac{16}{3} \pi r^3}{\frac{64r^3}{\sqrt{2}\sqrt{2}\sqrt{2}}}$$

$$PF = \frac{\frac{16}{3} \pi r^3}{\frac{64r^3}{2\sqrt{2}}}$$

$$PF = \frac{16}{3} \pi r^3 \times \frac{2\sqrt{2}}{64r^3}$$

$$= \frac{\pi \sqrt{2}}{6}$$

$$= \frac{3.14 \times \sqrt{2}}{6} = 0.74$$

$$PF = 0.74\%$$

Thus, the packing factor is 74% ie., 74% of the volume of unit cell is occupied by atoms and the remaining 26% volume is vacant.

### **Common examples of this type of structure**

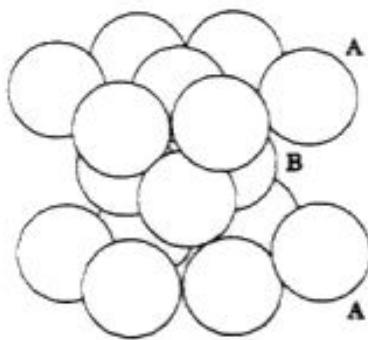
Copper, aluminum, nickel, gold, lead and platinum

### **1.7) HEXAGONAL CLOSE-PACKED STRUCTURE**

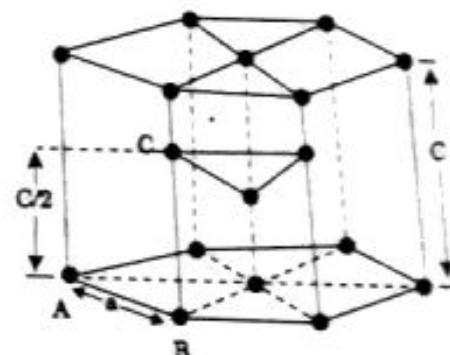
A unit cell of a close-packed hexagonal structure is shown in fig 1.24 (a).

In this type of crystal structure, the unit cell has one atom at each of the 12 corners of the hexagonal prism, one atom at the centre of the two hexagonal faces and 3 atoms symmetrically arranged in the body of the unit cell.

There are 3 layers of atoms in it. At the bottom layer (A), the central atom has '6' nearest neighbouring atoms in the same plane. The second layer (B) which is at a distance  $\frac{c}{2}$  from the bottom layer has 3 atoms as shown in fig. 1.24(b).



(a)



(b)

Fig. 1.24 Hexagonal close-packed structure.

The third layer i.e., the layer similar to the bottom layer and at a distance 'c' from the bottom layer. Thus, HCP structure has the stacking sequence of **AB, AB ...**

### 1. Number of atoms per unit cell

Each corner atom is shared by 6 surrounding unit cells, i.e., each corner atom gives  $\frac{1}{6}$  th of its share to unit cell.

$$\left. \begin{array}{l} \text{Number of atoms in} \\ \text{the upper hexagonal plane of} \\ \text{the unit cell due to corner atoms} \end{array} \right\} = \frac{1}{6} \times 6 = 1$$

$$\left. \begin{array}{l} \text{Number of atoms in} \\ \text{the lower hexagonal plane of} \\ \text{the unit cell due to corner atoms} \end{array} \right\} = \frac{1}{6} \times 6 = 1$$

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

$$\therefore \left. \begin{array}{l} \text{Total number of central atoms in} \\ \text{both upper and lower planes} \end{array} \right\} = \frac{1}{2} \times 2 = 1$$

There are '3' atoms inside the unit cell which are **not** shared by any other adjacent unit cells. (Fig. 1.24(c))

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

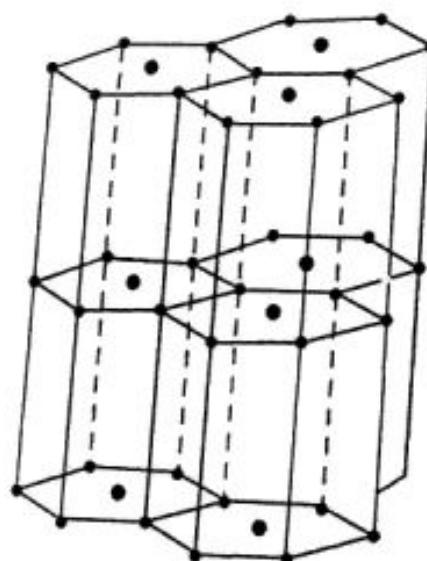


Fig. 1.24 (c)

## 2. Coordination number

Let us 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 above and the other below the bottom layer containing 3 atoms in each layer. In total, there are 12 ( $3 + 6 + 3$ ) nearest neighbouring atoms. (Fig. 1.24(d))

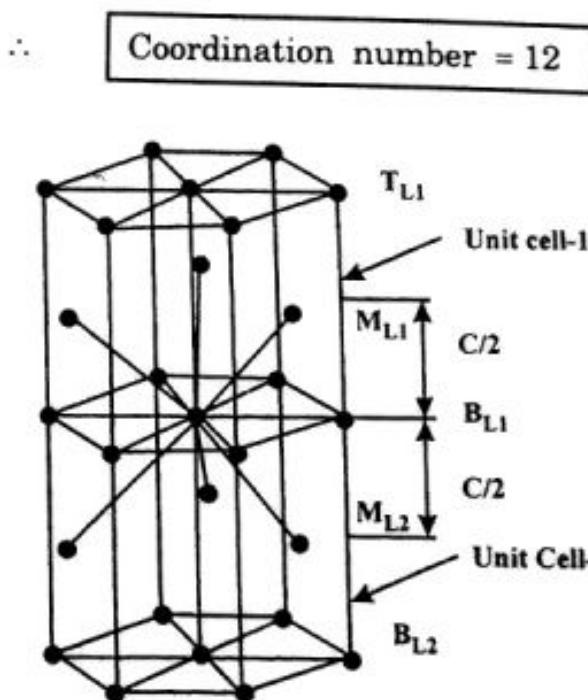


Fig. 1.24(d)

## 3. Atomic radius ( $r$ )

Atoms touch each other along the edges of the hexagon. Thus, from the figure 1.24(e), the nearest neighbouring distance  $a = 2r$ .

Atomic radius

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

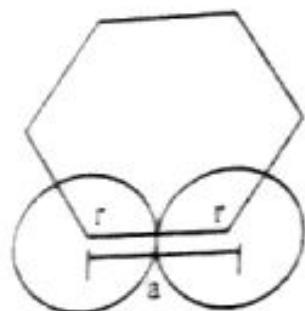
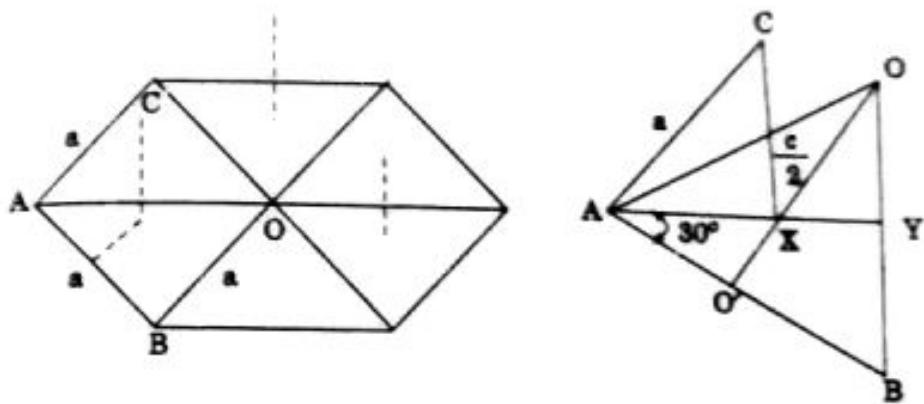


Fig. 1.24 (e)

#### 4. Calculation of $\frac{c}{a}$ ratio

Let ' $c$ ' be the height of the unit cell of HCP structure and ' $a$ ' be the distance between two neighbouring atoms.

Now consider a triangle ABO in the bottom layer (fig 1.25). Here A, B and O are the lattice points and exactly above these atoms at a perpendicular distance  $\frac{c}{2}$  the next layer atom lies at C.



(a) Bottom layer of HCP structure

(b) Triangle ABO

Fig. 1.25

$\Delta ABO$  is an equilateral triangle.  $AY$  is drawn  $\perp r$  to  $BO$ . Then,

$$\cos 30^\circ = \frac{AY}{AB}$$

$$AY = AB \cos 30^\circ = \frac{a \times \sqrt{3}}{2}$$

$$AY = \frac{a \sqrt{3}}{2} \quad \dots (1)$$

$$\left( \because AB = a, \cos 30^\circ = \frac{\sqrt{3}}{2} \right)$$

X is the orthocentre for  $\Delta ABO$

$$\therefore AX = \frac{2}{3} AY \quad \dots (2)$$

Substituting for  $AY$ , we get

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

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

$$AX = \frac{a}{\sqrt{3}} \quad \dots (3)$$

In the  $\Delta$   $AXC$ ,

$$AC^2 = AX^2 + CX^2 \quad \dots (4)$$

Substituting the values for  $AC = a$ ,  $AX = \frac{a}{\sqrt{3}}$

and  $CX = \frac{c}{2}$  in eqn (4), we get

$$a^2 = \left( \frac{a}{\sqrt{3}} \right)^2 + \left( \frac{c}{2} \right)^2 \quad \dots (5)$$

$$a^2 = \frac{a^2}{(\sqrt{3})^2} + \frac{c^2}{2^2}$$

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

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

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

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

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

$$\frac{c^2}{a^2} = \frac{8}{3} \quad \dots (6)$$

Taking square root on both sides, we have

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

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

$$\frac{c}{a} = 1.633$$

... (7)

## 5. Packing factor

**Volume of all the atoms in a unit cell ( $v$ )**

Nearest neighbouring distance,  $2r = a$

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

Number of atoms per unit cell  $n = 6$

Volume of all 6 atoms in the unit cell

$$v = 6 \times \frac{4}{3} \pi r^3$$

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

$$V = \frac{24}{3} \pi \left[ \frac{a}{2} \right]^3$$

$$V = \frac{24\pi}{3} \frac{a^3}{2^3} = \frac{24}{3} \frac{\pi a^3}{8}$$

$$V = \pi a^3$$

Volume of the unit cell (V)

Area of the base = 6 × Area of triangle AOB

$$\text{Area of triangle AOB} = \frac{1}{2} (\text{BO}) (\text{AY})$$

$$\text{Substituting for BO} = a \text{ and AY} = \frac{a\sqrt{3}}{2}$$

$$\text{Area of } \triangle \text{AOB} = \frac{1}{2} \times a \times \frac{a\sqrt{3}}{2}$$

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

$$\therefore \text{Area of the base} = 6 \times \frac{a^2 \sqrt{3}}{4}$$

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

Volume of the unit cell of the HCP } = Base area  $\times$  height

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

$$\text{Packing factor} = \frac{v}{V}$$

Substituting  $v$  and  $V$ , we have

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

$$\text{PF} = \frac{2\pi}{3\sqrt{3}} \left( \frac{a}{c} \right)$$

$$\text{PF} = \frac{2\pi}{3\sqrt{3}} \left[ \frac{3}{8} \right]^{1/2} \quad \left[ \because \frac{c}{a} = \left( \frac{8}{3} \right)^{1/2} \right]$$

$$= \frac{2\pi}{3\sqrt{3}} \frac{3^{1/2}}{8^{1/2}}$$

$$= \frac{2\pi}{3\sqrt{3}} \frac{\sqrt{3}}{\sqrt{8}} = \frac{2\pi}{3\sqrt{4 \times 2}} = \frac{2\pi}{3 \times 2 \sqrt{2}}$$

$$\text{Packing factor} = \frac{\pi}{3\sqrt{2}} = \frac{3.14}{3\sqrt{2}} = 0.74 = 74\%$$

Packing factor 74%

Therefore, packing factor is 74% i.e., 74% of the volume of unit cell is occupied by the atoms and the remaining 26% volume is vacant.

### Common examples of this type of structure

Magnesium, zinc, titanium, zirconium, beryllium and cadmium.

**Table 1.3**

### Comparision of SC, BCC, FCC and HCP crystal structures

Properties	Simple cube (SC)	Body-centred cube (BCC)	Face-centred cube (FCC)	Hexagonal close-packed (HCP)
Number of atoms per unit cell	1	2	4	6
Coordination number	6	8	12	12
Atomic radius ( $r$ )	$\frac{a}{2}$	$\frac{a\sqrt{3}}{4}$	$\frac{a\sqrt{2}}{4}$	$\frac{a}{2}$
Packing factor	0.52	0.68	0.74	0.74
Example	Polonium	Iron, barium, chromium	Aluminium, copper, lead, gold	Zinc, magnesium

### **Relation between lattice constant ( $a$ ) and density ( $\rho$ )**

Consider a cubic crystal of lattice constant  $a$ .

Density of the crystal =  $\rho$

Volume of the unit cell =  $a^3$

$\therefore$  Mass of the unit cell =  $\rho a^3$  ... (1)

$$\left( \therefore \text{Density} = \frac{\text{Mass}}{\text{Volume}} \right)$$

Number of atoms per unit cell =  $n$

Atomic weight of the material =  $M$

Avogadro's number =  $N$

Avogadro's number is the number of atoms per kg mole of the substance

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

Mass of each unit cell = Mass of each atom in unit cell  
 $\times$  Number of atoms per unit cell

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

(for  $n$  atoms per unit cell)

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

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

$$\boxed{\rho = \frac{nM}{Na^3}}$$

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

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

### ANNA UNIVERSITY SOLVED PROBLEMS

#### Problem 1.1

Calculate the lattice constant of Fe. Given: density of Iron  $7860 \text{ kg/m}^3$ , atomic weight 55.85 and Avagadro's number  $6.023 \times 10^{26} \text{ atoms/mol}$

(A.U. May 2004)

#### *Given data*

$$\text{Density of iron} = 7.86 \times 10^3 \text{ kg/m}^3$$

$$\text{Atomic weight (M)} = 55.85$$

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

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

#### Solution

We know that

$$\rho = \frac{nM}{Na^3}$$

$$a^3 = \frac{nM}{\rho N}$$

Substituting the given values, we have

$$= \frac{2 \times 55.85}{6.023 \times 10^{26} \times 7860}$$

$$a^3 = 2.359 \times 10^{-29} \text{ m}^3$$

$$a = 2.868 \times 10^{-9} \text{ metre}$$

$\therefore$  Lattice constant of Fe = 2.868 nm

### Some special cubic crystal structures

In addition to SC, BCC, FCC and HCP, there are some special cubic structures. Some of these structures are derivatives from or combination of the basic structures described above.

#### 1.8 DIAMOND CUBIC (DC) STRUCTURE

The diamond cubic structure is a very important crystal structure. Besides diamond, the elemental semiconductors silicon and germanium have this structure. The unit cell of diamond cubic structure is shown in fig. 1.26.

This structure is a combination of two interpenetrating face-centred-cubic (FCC) sub lattices.

One sub-lattice has its origin at (0, 0, 0) (atom X). The other sub-lattice has its origin (atom Y) quarter of the way along the body diagonal i.e., at the point  $\left(\frac{a}{4}, \frac{a}{4}, \frac{a}{4}\right)$

This is closely packed structure since each atom has four nearest neighbours i.e. coordination number 4.

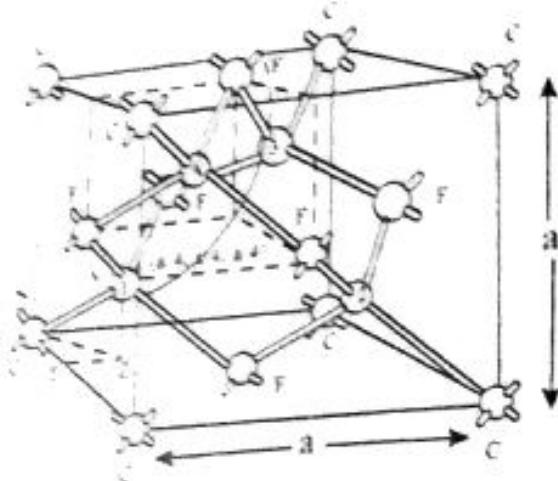


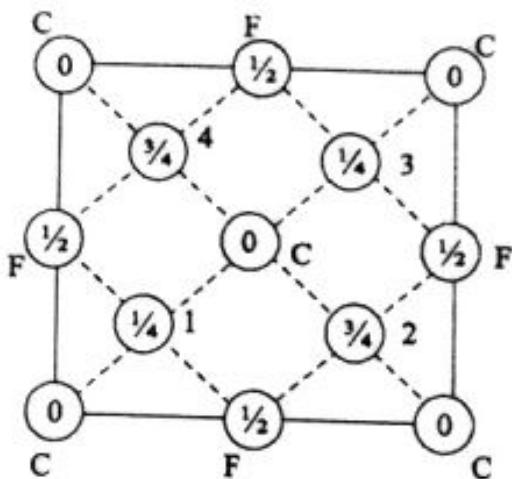
Fig. 1.26 Basic diamond structure and **Tetrahedral** bonding

i. Number of atoms per unit cell

In the given unit cell of diamond, there are **carbon** atoms at three different positions of the unit cell.

- i. Corner atoms represented by 'C' in fig. 1.26.
- ii. Face centred atoms represented by 'F' in fig. 1.26
- iii. Four atoms present fully inside the unit cell represented as 1, 2, 3 and 4, in fig. 1.26

The positions of atoms projected on a **cube face** is shown in fig. 1.27



**Fig. 1.27 Diamond structure - atomic position projected on a cube face**

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

Each corner atom is shared by 8 unit cells. There are 8 corner atoms in an unit cell.

Therefore, the number of atoms due to corner atoms per unit cell

$$= \frac{1}{8} \times 8$$

$$= 1 \text{ atom}$$

**(ii) Number of face centred atoms per unit cell**

Each face centred atom is shared by 2 unit cells. We have 6 face centred atoms.

∴ Number of face centred atom per unit cell

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

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(iii) Number of atoms inside unit cell

Inside the unit cell, we have 4 atoms represented by 1, 2, 3, 4 in fig. 1.26 which are not shared by any other unit cells

∴ Total number of atoms per unit cell  
 $= 1 + 3 + 4 = 8$

2. Atomic radius

The corner atoms do not contact with each other. Similarly the face centred atoms also do not contact with each other.

But both face centred atoms and corner atoms have contact with the atoms (1, 2, 3, 4) situated inside the unit cell as shown in fig. 1.26.

For example, the nearest two neighbours which have direct contact (shown by double line) are atoms 'X' and 'Y' as shown in fig 1.26.

Let us draw a perpendicular to Y atom which meets the unit cell at a point 'Z' as shown in fig. 1.28 which is at a distance of  $a/4$ .

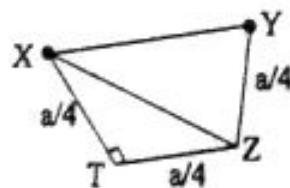


Fig. 1.28

From fig. 1.28,

$$XY^2 = XZ^2 + ZY^2$$

$$XY^2 = [XT^2 + TZ^2] + ZY^2$$

$$[\because XZ^2 = XT^2 + TZ^2]$$

Substituting for  $XT^2$ ,  $TZ^2$  and  $ZY^2$ , we have

$$\begin{aligned} XY^2 &= \left(\frac{a}{4}\right)^2 + \left(\frac{a}{4}\right)^2 + \left(\frac{a}{4}\right)^2 \\ &= \frac{a^2}{4^2} + \frac{a^2}{4^2} + \frac{a^2}{4^2} \\ &= \frac{a^2}{16} + \frac{a^2}{16} + \frac{a^2}{16} \\ XY^2 &= \frac{3a^2}{16} \end{aligned}$$

Since  $XY = 2r$ , we can write

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

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

$$4r^2 = \frac{3a^2}{16}$$

$$r^2 = \frac{3a^2}{16 \times 4} = \frac{3a^2}{64}$$

Taking square root on both sides, we have

$$\sqrt{r^2} = \sqrt{\frac{3a^2}{64}}$$

Atomic radius

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

Lattice constant

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

### 3. Coordination number

From fig 1.26 the number of nearest atoms (shown by double line) for Y atom is 4. Therefore, the coordination number of diamond is 4.

**Note:** The coordination number is found to be same even if it is calculated with respect to atoms say (1), (3), (4), corner (or) face centred atoms.

### 4. Packing factor

We know that Packing factor (PF)

$$= \frac{\text{Volume occupied by the atoms per unit cell } (v)}{\text{Volume of the unit cell } (V)} \dots (1)$$

Volume occupied by 1 atom (spherical)

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

In diamond, we have 8 atoms per unit cell

Volume occupied by all the '8' atoms per unit

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

### Lattice plane:

A plane containing lattice points is known as 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., **Space lattice + Basis → 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).

1.62  
Substituting eqns (2) and (3) in (1) we get

$$PF = \frac{v}{V} = \frac{\frac{\pi a^3 \sqrt{3}}{16}}{\frac{a^3}{a}} = \frac{\pi a^3 \sqrt{3}}{16a^3}$$

$$\therefore PF = \frac{\pi \sqrt{3}}{16}$$

Packing factor = 0.34

Packing factor = 34%

Thus we can say that 34% volume of the unit cell in diamond cubic structure is occupied by atoms and the remaining 66% volume is vacant.

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

### 1.9 GRAPHITE STRUCTURE

The graphite structure is shown in fig. 1.29. The carbon atoms are arranged in regular hexagons in flat parallel layers such that each atom is linked by the neighbouring atoms.

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 Vander walls force with a spacing about 3.4 Å.

#### 4. Packing factor

Number of atoms per unit cell = 2

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

$$\text{Side of the unit cell, } a = \frac{4r}{\sqrt{3}}$$

$$\left( \therefore \text{atomic radius } r = \frac{\sqrt{3} a}{4} \right)$$

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

$$\text{Packing factor} = \frac{v}{V}$$

Substituting for  $v$  and  $V$ , we have

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

Substituting for  $a$

$$PF = \frac{2 \times \frac{4}{3} \pi r^3}{\left( \frac{4r}{\sqrt{3}} \right)^3} = \frac{\frac{8}{3} \pi r^3}{\frac{4^3 r^3}{(\sqrt{3})^3}}$$

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

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

$$PF = \frac{\sqrt{3} \times 3.14}{8} = 0.68$$

$$PF = 68\%$$

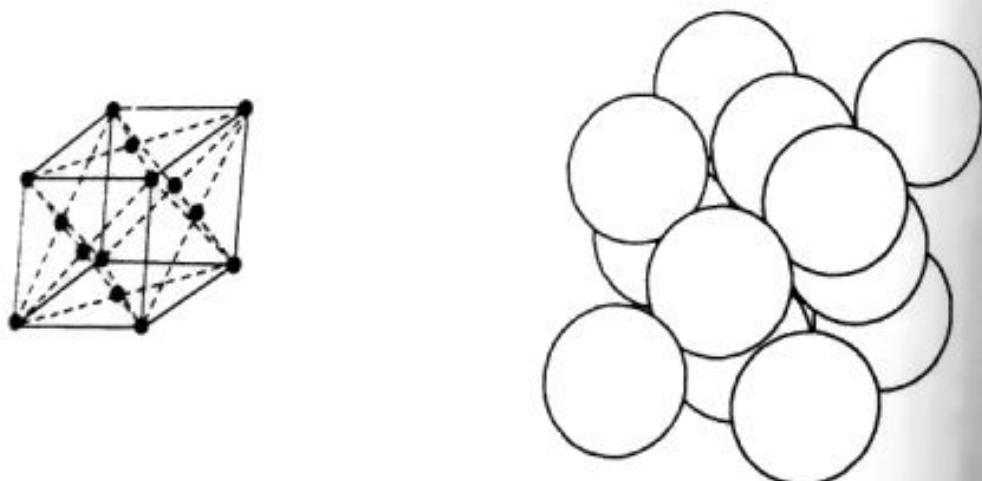
Thus, packing factor is 68% i.e., 68% of the volume of unit cell is occupied by atoms and the remaining 32% volume is vacant.

**Common examples of this type of structure**

Tungsten, Chromium and Molybdenum.

### 1.6 FACE-CENTRED CUBIC (FCC) STRUCTURE

In this type of crystal structure, the unit cell has one atom at each corner of the cube and in addition one atom at the centre of each face. (fig. 1.20).

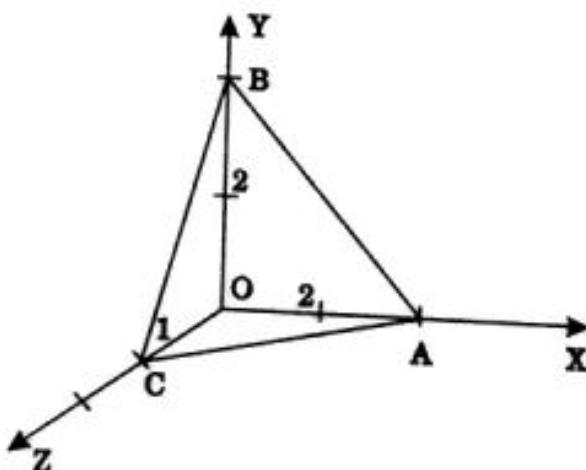


**Fig. 1.20 Face-centred cube**

### Explanation

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

For example, a plane ABC in fig. 1.31 has intercepts of 2 axial units on X-axis, 2 axial units on Y-axis and 1 axial unit on Z-axis. In other words, the numerical parameters of this plane are 2, 2 and 1. Hence, its orientation is (2, 2, 1).



**Fig. 1.31 Miller indices**

Miller suggested that it is better to describe the orientation of a plane by the *reciprocal* of its intercepts.

These reciprocals are converted into whole numbers and they are known as **Miller indices** of the concerned plane.

Hence Miller indices of a plane ABC (fig. 1.31) are

1/2 : 1/3 : or simply 112

We understand that for getting the whole numbers, all three reciprocals are multiplied by 2. It is noted that multiplying all intercepts or reciprocals of intercepts by the same number does not change the orientation of a plane.

The numbers for these planes are written within parentheses and not in brackets.

The general expression for Miller indices of a plane is  $(h k l)$ . The symbol for a family of parallel planes is  $\langle h k l \rangle$ .

#### Definition

*Miller indices are three possible integers that have the same ratios as the reciprocals of the intercepts of the plane concerned on the three axes.*

#### Procedure for finding Miller indices

Consider a crystal plane. Let us find its Miller indices as follows.

- Step . 1** Find the intercepts of the plane along the coordinate axes X, Y, Z. (The intercepts are measured as multiples of axial length units)
- Step . 2** Take the reciprocal of these intercepts.

**Step - 3** Reduce the reciprocals into whole numbers. This can be done by multiplying each reciprocal by a number obtained after taking LCM (Least Common Multiplier) of the denominators.

**Step - 4** Write these integers within parentheses to get Miller indices.

### ANNA UNIVERSITY SOLVED PROBLEM

#### Problem 1.2

Obtain Miller indices of a plane whose intercepts are 4, 4 and 2 units along the three axes.

(A.U. Jan 2008)

#### Solution

- Intercepts are 4, 4, 2.
- Reciprocal of these intercepts are  $\frac{1}{4}, \frac{1}{4}, \frac{1}{2}$
- L.C.M of denominators 4, 4 and 2 is 4. Hence, multiplying by 4, we have 1, 1, 2. Thus, the Miller indices of this plane are (1 1 2).

#### *Miller indices of cubic crystal planes*

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

- (i) When a plane is parallel to one of the coordinate axes, it is said to meet that axis at infinity. Since  $\frac{1}{\infty} = 0$ , Miller index for that axis is zero.

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(ii) When the intercept of a plane is on the negative part of any axis, Miller index is distinguished by a bar put directly over it.

Consider a shaded plane in fig. 1.32. This plane ADEF cuts X-axis at the point A and it is parallel to Y and Z axes. If the side of the cube is taken as one unit in length, then intercepts made by this plane on three axes are

$$1 : \infty : \infty$$

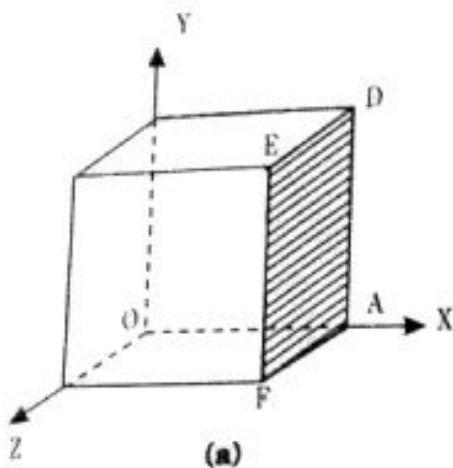


Fig. 1.32 (a)

The reciprocals of the cuts are

$$\frac{1}{1} : \frac{1}{\infty} : \frac{1}{\infty}$$

$$\text{i.e., } 1 : 0 : 0$$

Hence, Miller indices of this plane are (100).

The plane ABC in fig. 1.32 (b) has equal intercepts on the three axes and hence its Miller indices are (111). Miller indices of the plane GBAF are (110) as shown in fig. 1.32 (c).

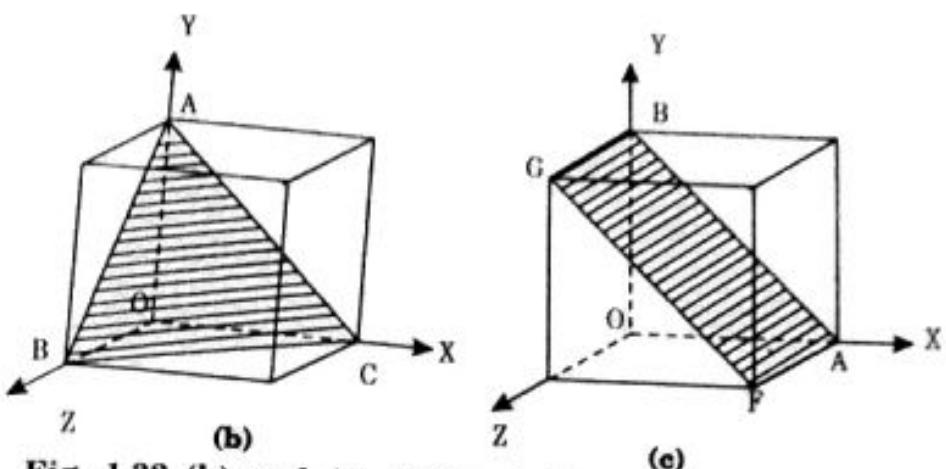


Fig. 1.32 (b) and (c) Miller indices for cubic planes

### 1.12 'd' SPACING IN CUBE LATTICE [Derivation]

Consider a cubic crystal with  $a$  as length of the cube edge and a plane ABC as shown in figure 1.36. Let this plane belong to a family of planes whose Miller indices are  $(h k l)$ .

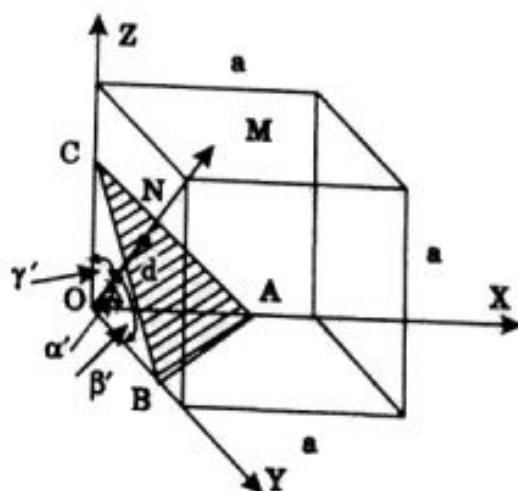


Fig. 1.33 d - spacing in cubic lattice

The perpendicular ON from the origin of the cube to the plane ABC represents interplanar spacing ( $d$ ) of this family of plane..

t.v

Assume that the origin is lying on the plane immediately next to plane under consideration.]

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 ON.

We know that Miller indices of a plane are the smallest integers of the reciprocals of their intercepts. Therefore, the intercepts are expressed as reciprocals of Miller indices.

$$\text{i.e., } OA : OB : OC = \frac{1}{h} : \frac{1}{k} : \frac{1}{l}$$

$$= \frac{a}{h} : \frac{a}{k} : \frac{a}{l}$$

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

From the geometry of right angles OAN, OBN and OCN (fig. 9.37), we have,

$$\cos \alpha' = \frac{ON}{OA} = \frac{d}{\frac{a}{h}} = \frac{dh}{a}$$

$$\cos \beta' = \frac{ON}{OB} = \frac{d}{\frac{a}{k}} = \frac{dk}{a}$$

$$\cos \gamma' = \frac{ON}{OC} = \frac{d}{\frac{a}{l}} = \frac{dl}{a}$$

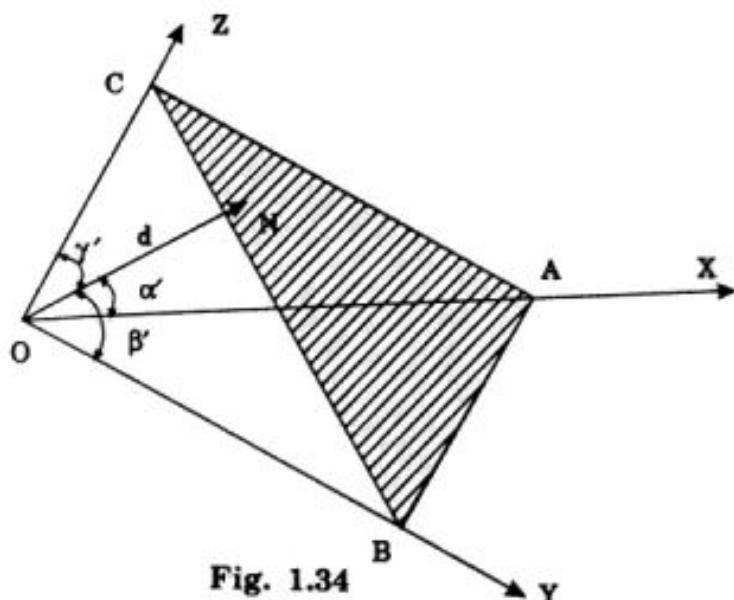


Fig. 1.34

The law of direction cosines is

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

Substituting the values for  $\cos \alpha'$ ,  $\cos \beta'$ ,  $\cos \gamma'$  we have

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

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

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

$$d^2 (h^2 + k^2 + l^2) = a^2$$

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

Taking square root on both sides

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

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

This is the relation between interplanar spacing  $d$ , cube edge  $a$  and Miller indices  $(h k l)$ .

### ANNA UNIVERSITY SOLVED PROBLEMS

Problem 1.3

The lattice constant for a unit cell of aluminium is 4.049 Å. Calculate the spacing of (220) plane.

(A.U. Dec 2004)

Given data

$$a = 4.049 \text{ \AA}$$

$$h = 2, k = 2, l = 0$$

**Solution:** We know that  $d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$

Substituting the given values, we have

$$d_{220} = \frac{4.049 \text{ \AA}}{\sqrt{2^2 + 2^2 + 0^2}} = \frac{4.049 \text{ \AA}}{\sqrt{4+4}} = \frac{4.049 \text{ \AA}}{\sqrt{8}} = 1.432 \text{ \AA}$$

$$d_{220} = 1.432 \text{ \AA}$$

## Crystal growth

### Solidification and Crystallization

In order to understand the crystalline state and its difference from the amorphous state, it is important to consider the process of solidification.

**Solidification is the transformation of material from liquid to the solid state on cooling.**

When the liquid solidifies, the energy of each atom is reduced. This energy is given out as latent heat during

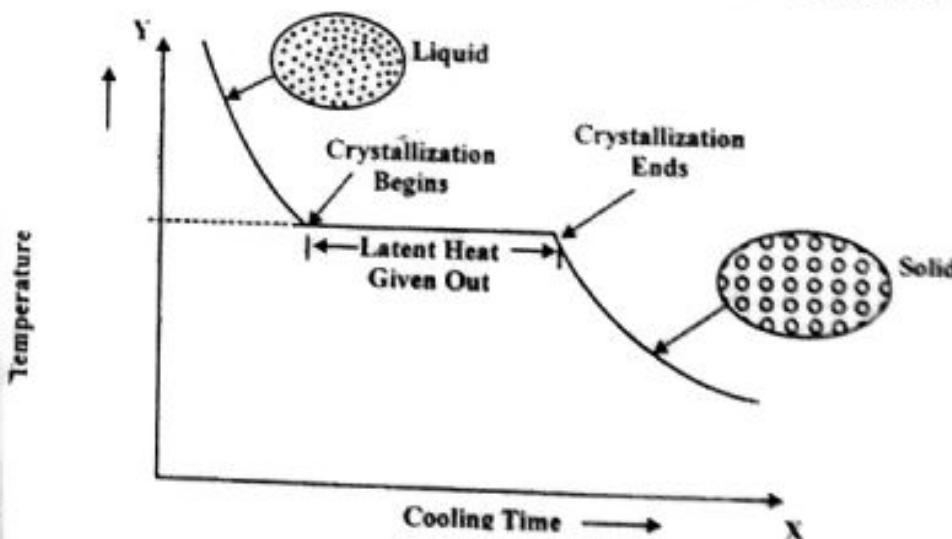


Fig. 1.35 A pure metal solidifies at a fixed temperature ( $T_s$ ) and atoms arrange themselves in some regular manner

1.74

the solidification process, which for a pure metal occurs at a fixed temperature,  $T_s$  (Fig. 1.35).

During solidification, the disordered structure of the liquid constituents of material in liquid state have more velocity, more collisions and hence have random position) transforms to the orderly arrangement depending upon the time of solidification.

### **1.13 CRYSTAL GROWTH TECHNIQUES**

The crystal growth technique is classified into 6 categories namely,

- (i) Melt growth
- (ii) Low temperature solution growth
- (iii) High temperature solution growth (Flux growth)
- (iv) Hydrothermal growth
- (v) Gel growth
- (vi) Epitaxial growth

#### **Melt growth**

Melt Growth is the process of crystallization by fusion and resolidification of the starting materials.

The growth from melt is further sub-grouped into various techniques. The main techniques are:

- (i) Czochralski Technique
- (ii) Bridgman Technique

**(iii) Verneuil method****(iv) Zone melting Technique**

The major practical factors to be considered during growth of crystals from melt are, (a) volatility, (b) chemical reactivity and (c) melting point

**1.14****CZOCHRALSKI METHOD****Basic principle**

**The Czochralski method is a crystal pulling technique from the melt.** The process is based on a liquid-solid phase transition driven by a seed crystal in contact with the melt.

Basically, the seed is to be considered as a heat sink, by which the latent heat of solidification escapes and as a nucleation center: the solidified fraction at the surface of the seed will reproduce its single-crystal structure.

By raising the seed slowly, a crystal is “pulled” from the melt. Decreasing the melt temperature makes the crystal diameter increasing and vice versa.

**Description and Working**

Large, single crystals of Si (for IC fabrication) are grown by the Czochralski method. It involves growing a single-crystal ingot from the melt, using solidification on a seed crystal as illustrated in fig. 1.36.

1.76  
Molten Si is held in a quartz (crystalline  $\text{SiO}_2$ ) crucible in a graphite susceptor. It is heated by radio frequency induction coil (RF heating).

A small dislocation - free crystal, called a seed, is moved down to touch the melt and then slowly pulled out of the melt.

A crystal grows by solidifying on the seed crystal. The seed is rotated during the pulling stage, to obtain a cylindrical ingot.

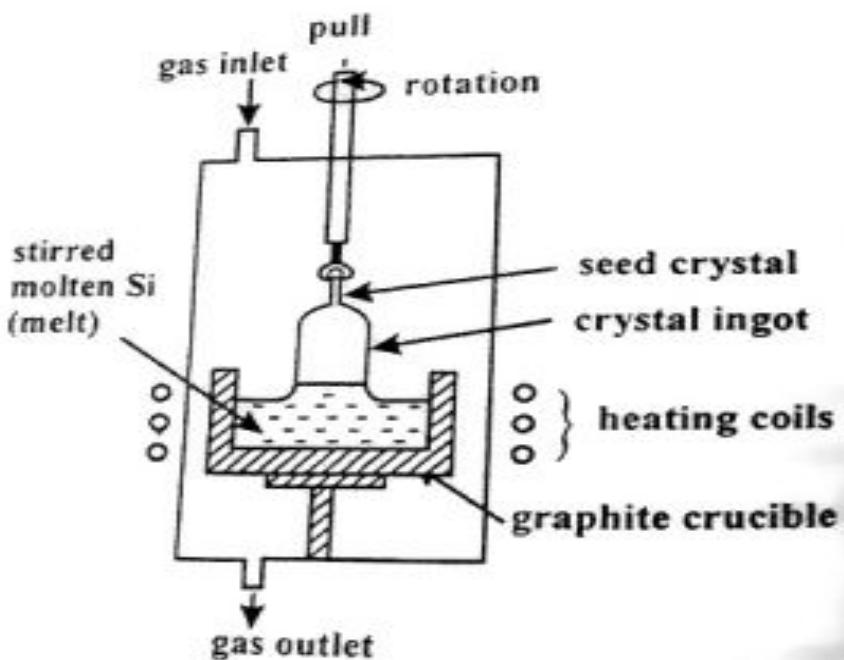


Fig. 1.36 Czochralski method for growing an ingot of silicon crystal. The cylindrical ingot forms as it is rotated and pulled slowly from the melt

### Advantages

- Growth from free surface
- Growth of large oriented single crystals
- Convenient chemical composition
- Control of atmosphere

### Limitations

- High vapor pressure materials
- Liquid phase encapsulation
- Possible contamination of the melt by the crucible
- No reproducibility of the crystal shape

### 1.15 BRIDGMAN TECHNIQUE

A common technique for growing single crystals. It involves selective cooling of the molten material, so that solidification occurs along a particular crystal direction.

In this technique, the melt in a sealed crucible is progressively frozen from one end. This can be achieved by

- Moving the crucible down the temperature gradient (or)
- Moving the furnace over the crucible (or)
- By keeping both the furnace and the crucible stationary and cooling the furnace so that the

freezing isotherm moves steadily through the originally molten charge.

### Growth process

The fig 1.37 shows a platinum crucible filled with high quality nature grown material, to which the desired impurities may be added. The crucible is fixed in the upper furnace until the contents are completely melted. It is then lowered from upper furnace into the lower furnace with help of electrical motor and reduction gearing. Since the pointed tip enters the lower furnace first, the grown material start to crystallise over there.

As the crucible continues to be lowered, crystallisation proceeds until all the melts become solid crystal. A bulk single pure crystal can be grown in the

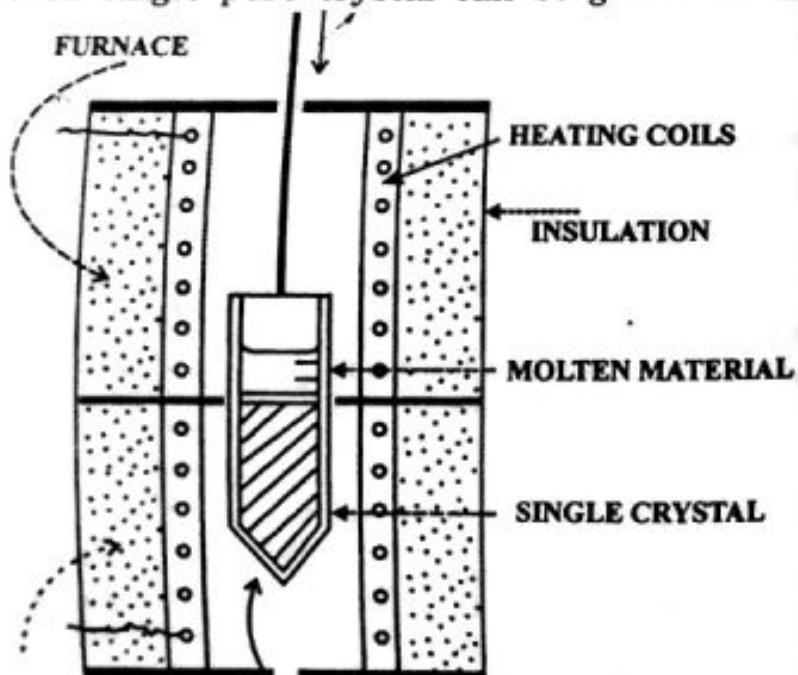


Fig. 1.37

crucible by lowering the crucible at steady rate and keeping the temperature constant.

Examples of the crystals grown by this method are

Sodium chloride      NaCl

Potassium chloride    KCl

Calcium fluoride     CaF<sub>2</sub>

Silver bromide      AgBr

### **Advantages**

- Simple technique
- Control over vapor pressure
- Containers can be evacuated and sealed
- Control of shape and size of growing crystals
- Stabilization of thermal gradients

### **Limitations**

- Confinement of crystals
- Crystal perfection is not better than that of the seed
- No visibility

## 1.16] SOLUTION GROWTH

### Low temperature solution growth

The low temperature solution growth is suitable for the materials which decompose at high temperatures and undergo phase transformation below the melting point.

There are two methods of low temperature solution growth. They are

(i) Slow cooling method

(ii) Slow evaporation method

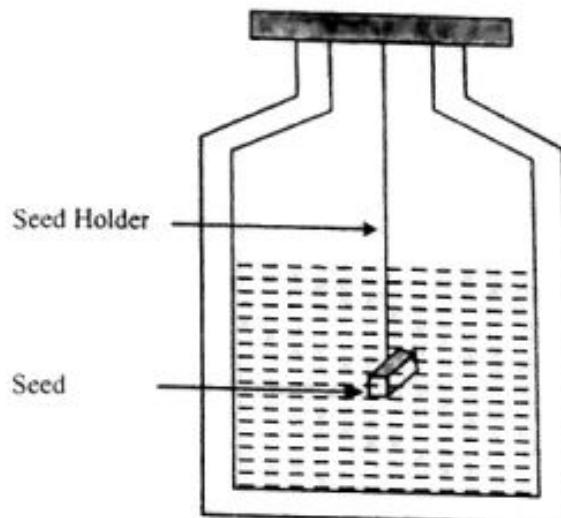
#### (i) Slow cooling method

Slow cooling is the easiest method to grow bulk single crystals from solution. This technique needs only a vessel for the solution, in which the crystals grow.

The temperature at which crystallization begins is in the range of  $45^{\circ}\text{C}$  -  $75^{\circ}\text{C}$  and the lower limit of cooling is the room temperature.

#### (ii) Slow evaporation method

In this method, the saturated solution is kept at a particular temperature and provision is made for evaporation.



**Fig. 1.38 Manson Jar Crystallizer**

The basic apparatus (Manson Jar Crystallizer) used for the solution growth technique is shown in figure 1.38.

Typical growth conditions involve a temperature stabilization of about  $0.05^{\circ}\text{C}$  and rate of evaporation of a few  $\text{mm}^3/\text{h}$ .

### Advantages

- (i) This is a simple and convenient method of growing single crystals of large size.
- (ii) Growth of strain and dislocation free crystals.
- (iii) Permits the growth of prismatic crystals by varying the growth conditions.

- (iv) Only method which can be used for substances that undergo decomposition before melting.

### Disadvantages

- (i) The growth substance should not react with the solvent.
- (ii) This method is applicable for substances fairly soluble in a solvent.
- (iii) Small crystals are also formed on the walls of the vessel near the surface of the liquid. These tiny crystals fall in the solution and hinder the growth of the crystal.
- (iv) A variable rate of evaporation may affect the quality of the crystal.

### Epitaxial growth

The process of growing an oriented single crystal layer on a substrate wafer is called **Epitaxial growth**.

The term "epitaxy" is derived from greek word "epi" literally means "arranged upon".

In this method, a thin layer of single crystal (typically a few nanometers to a few micron) is grown on an existing crystalline substance such that film has the same lattice structure as the substrate.

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Epitaxy is further classified into

- (i) **Vapour Phase Epitaxy (VPE)**
- (ii) **Liquid Phase Epitaxy (LPE)**
- (iii) **Molecular Beam Epitaxy (MBE)**

### **1.17 VAPOUR PHASE EPITAXY (VPE)**

Epitaxial growth of silicon is exclusively carried out by VPE

#### **Construction**

The process is carried out in reaction chamber consisting of a long cylindrical quartz tube encircled by radio frequency induction coil as shown in fig. 1.39.

The silicon wafers are placed on a rectangular graphite rod called **boat**. This boat is placed in the reaction chamber and heated inductively to a temperature 1200°C.

The various gases required for the growth of desired epitaxial layers are introduced into the system through a control devices.

The reaction is surface-catalysed and silicon is deposited on the wafer surface. However, the deposition temperature is very high. Also, as the reaction is reversible and can proceed in both directions.

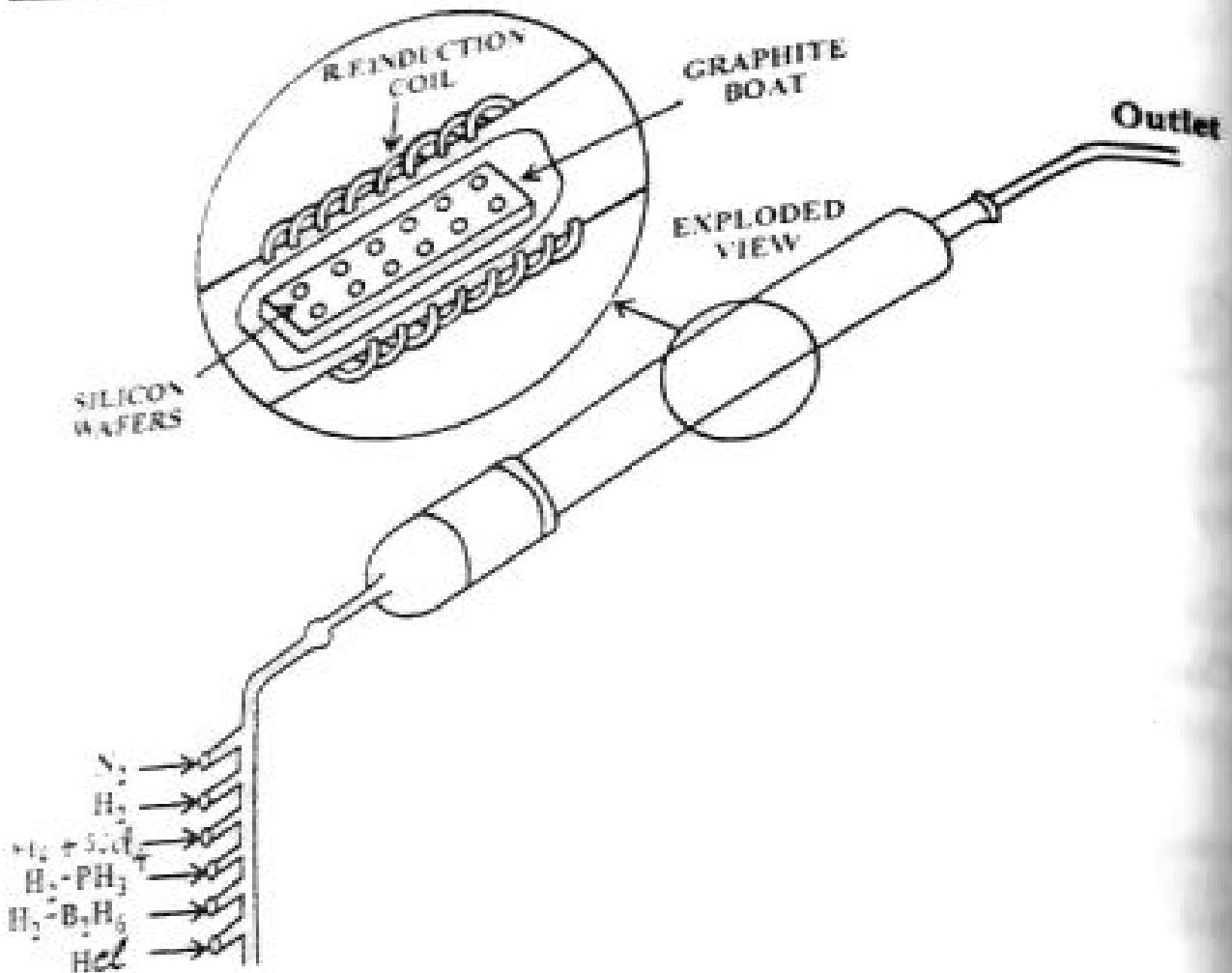


Fig. 1.39 Apparatus for growth of silicon epitaxial films

#### Growth process

Mostly epitaxial films with specific impurity concentration (*P* - type (or) *N* - type) are required. This is accomplished by introducing phosphine ( $\text{PH}_3$ ) for *n*-type doping and Biborane ( $\text{B}_2\text{H}_6$ ) for *p* - type doping.

There is a control console which permits only the required gases at suitable pressure so that it is possible to form an almost step *p* - *n* junction layer by this process.

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Vapour Phase Epitaxy (VPE) of compound semiconductor, for example, GaAs is performed using gallium (Ga) and Arsenic Chloride ( $\text{AsCl}_3$ ) as source materials.

### Advantages

- Halogen based VPE produces high pure single crystal layers with limited defects.
- Hydride based VPE allows proper control over the ratio of group III to group V vapour phase species.

### Disadvantages

- Higher growth temperature results in higher impurity diffusion. So uniform distribution of impurities cannot be obtained.

### Application

- This method is mainly used in the manufacture of LED's and detectors.

## ANNA UNIVERSITY SOLVED PROBLEMS

### Problem 1.4

Lattice constant of a BCC crystal is 0.36 nm. Find its atomic radius. [A.U. Dec 2002]

### Given data

$$a = 0.36 \text{ nm}$$

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