

## 5. Crystal Physics

### Part – A

#### 1. What is Space Lattice?

It is an infinite arrangement of points in three dimensions in which every point has an identical surrounding to every other point.

#### 2. What are basis?

The unit assembly of atoms or molecules which are associated with each lattice points in space lattice to form a crystal structure are called basis

#### 3. What is Crystal Structure?

Space lattice + Basis = Crystal Structure.

#### 4. What is Unit cell?

A unit cell is the smallest volume of a solid from which the entire crystal structure is constructed by translational repetition in three dimensions (space lattice).

#### 5. What is meant by primitive cell?

It is the simplest type of unit cell which contains only one lattice point per unit cell. All the primitive cells are unit cell but primitive and non-primitive cells will be a unit cell

#### 6. Explain the differences between Crystalline & Non crystalline materials?

	Crystalline	Non crystalline
1	Definite shape & Size	No geometrical shape
2	Anisotropic in nature	Isotropic in nature
3	Long range ordering	Short range ordering
4	They are most stable	They are less stable
5	Examples : NaCl, Cu, Au, etc.,	Examples : Plastic, Rubber,

#### 7. Name Seven Crystal Systems?

(i)Cubic (ii) Tetragonal (iii) Orthogonal (iv) Monoclinic (v) Triclinic (vi) Rhombohedral (vii) Hexagonal

#### 8. What is Bravais Lattice?

There are 14 possible ways of arranging points in space such that the environment looks same from each point. The Fourteen possible space lattices of the seven crystal systems are called Bravais Lattice.

#### 9. What are the lattice parameter of a unit cell and define interatomic and interplanar distances?

- (1) The intercepts on the XYZ axis such as  $a$ ,  $b$ ,  $c$  and interfacial angles  $\alpha$ ,  $\beta$ ,  $\gamma$  are the lattice parameters of a unit cell
- (2) The distance between the centers of any two nearest atoms are called inter atomic distance and the perpendicular distance between any two parallel planes are called interplanar distance

### 10. Give the important characteristics of unit cell for SC, BCC, FCC, HCP & Diamond?

Type of Structure	No. of atoms in unit cell	Coordination number	Atomic radius (r)	Atomic packing factor
Simple Cubic	1	6	$\frac{a}{2}$	0.52
Body Centered Cubic	2	8	$\frac{\sqrt{3}a}{4}$	0.68
Face Centered Cubic	4	12	$\frac{\sqrt{2}a}{4}$	0.74
Hexagonal Close Packed	6	12	$\frac{a}{2}$	0.74
Diamond structure	8	4	$\frac{\sqrt{3}a}{8}$	0.34

### 11. Define Coordination number?

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

### 12. Define atomic radius?

The half of the distance between nearest neighbouring atoms which is in contact with each other in a crystal is known as atomic radius. (Symbol: r)

### 13. Define Atomic Packing fraction? What is its unit?

It is the ratio of the total volume occupied by the atoms in the unit cell to the total volume of the unit cell

### 14. State $\frac{c}{a}$ ratio & packing factor of HCP?

$$\frac{c}{a} = \sqrt{\frac{8}{3}} = 1.6333 \quad \& \quad \text{Packing Fraction} = \frac{\pi}{3\sqrt{2}} = 74\%$$

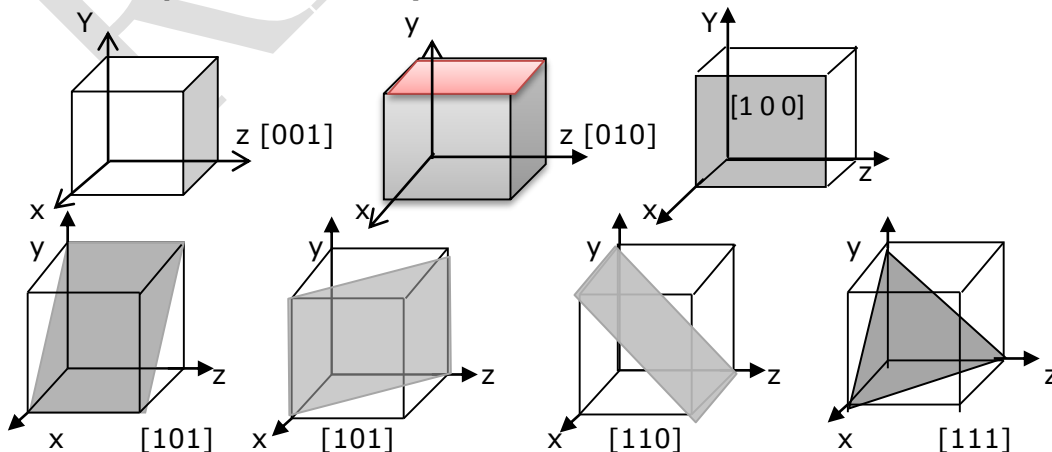
### 15. What are miller indices?

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

### 16. State the expression for interplanar spacing for a cubic system in terms of lattice constant and miller indices.

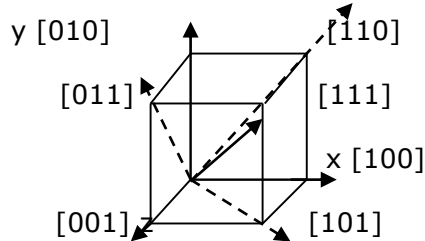
Interplanar Spacing  $d = \frac{a}{\sqrt{h^2+k^2+l^2}}$  where a – lattice constant & h, k, l – miller indices

### 17. Some of the planes in cubic system:



**18. What are the characteristics of unit cell?**

(i) Number of atoms per unit cell (ii) atomic radius (iii) Coordination number (iv) Atomic packing fraction

**19. Some of the Cubic Crystal direction:****20. What are the types of crystal structure? Give the types of Bravais Lattice with example?**

S.No	Types of Crystal Structure	Intercepts	Interfacial angles	Example	Bravais lattice
1.	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	NaCl, CaF <sub>2</sub>	P, I, F
2.	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	White Tin, Indium	P, I
3.	Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Sulphur, Topaz	P, C, F, I
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>	P, C
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>	P
6.	Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	Calcite, Bi	P
7.	Hexagonal	$a = b \neq c$	$\alpha = \beta = 120^\circ; \gamma = 90^\circ$	Quartz, Zn, Mg	P

**21. What are the techniques adapted for growing crystals?**

Solution growth, Melt growth and Vapour growth

**22. List out various type of melt growth?**

Normal freezing, Crystal pulling, Zone melting & Flame fusion

**23. What are the factors to be considered during the growth of crystal from melt?**

(1) Volatility (2) chemical reactivity and (3) melting point

**24. Give the relation between the density of the crystal and the lattice constant**

$$\rho = \frac{nA}{Na^3}$$
 n – No. of atoms per unit cell, N – Avagardo Number, A – atomic weight & a – Lattice constant.

**25. How carbon atoms are arranged in diamond structure?**

The X atom is located with an origin of (0, 0, 0) and the Y atom is located with an origin of (a/4, a/4, a/4) i.e., one quarter of the way along the body diagonal with an interpenetration of two FCC sublattices in a unit cell

**26. What are Frenkel and Schottky imperfections?**

Frenkel defect is an ionic crystal imperfection that occurs when an ion moves into an interstitial site, thereby creating two defects simultaneously i.e., one vacancy and the other self-interstitial.

A pair of ion vacancies in an ionic crystal is termed as Schottky defect.

**27. List the different types of point defects?**

- (i) Schottky defect
- (ii) Frenkel defect
- (iii) Substitutional impurities
- (iv) Interstitial impurities

**28. What are the differences between edge and screw dislocation?**

Sl.No	Edge dislocation	Screw dislocation
1	These dislocation arises due to introduction or elimination of an extra plane of atoms	Screw dislocation results from a displacement of the atoms in one part of a crystal relative to the rest of crystal forming a spiral ramp around the dislocation line
2	Region of lattice disturbance extends along an edge inside a crystal	Region of lattice disturbance extends in two separate planes at right angles to each other
3	AN edge dislocation can glide and climb	A screw dislocation can glide only
4	Burger vector is always perpendicular to the dislocation line	Burger vector is parallel to the dislocation line
5	These are formed during deformation and crystallization	These are also formed during deformation and crystallization

**29. What are vacancies?**

Vacancies are empty atomic sites. Vacancies may occur as a result of imperfect packing during the original crystallization or they may arise from the thermal vibrations of atoms at higher temperatures.

**30. What is burger vector?**

The magnitude and direction of the displacement due to edge dislocation are defined by a vector called Burger's vector

**31. What are twin boundaries?**

IF the atomic arrangement on one side of the boundary is the mirror image of the arrangement on the other side the defect is called twin boundaries.

### 32. What is stacking fault?

It arises due to defect in the stacking of atomic planes. IN some cases part of certain atomic plane will be missing whereas in some other cases a portion of extra atomic plane is present, changing the sequence of arrangement of atoms.

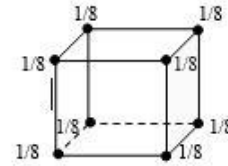
#### Part – B

### 1. Determine the atomic radius, coordination number and packing factor for SC, BCC & FCC structures?

**Simple Cubic Structure:** Example: Polonium (Po)

Number of atoms per unit cell =  $8 \times \frac{1}{8} = 1 \text{ atom}$

Coordination Number = 6



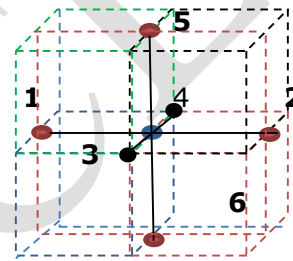
**Atomic radius:**

Consider the simple cubic structure as shown in figure. The atoms touch each other at edges of a cube. Therefore the distance between the centers of two nearest atoms = cube edge 'a'. Where

a – Side of the unit cell

r – Radius of the atom

$$\therefore 2r = a \text{ (or) } r = \frac{a}{2}$$



**Coordination number:**

Simple cube unit cell consists of 8 corner atoms. Let us consider X as any corner atom shared by 8 unit cells. The X atom has 4 nearest atom in its own plane and one above and one below to this plane. Hence the coordination number for simple cube is 6

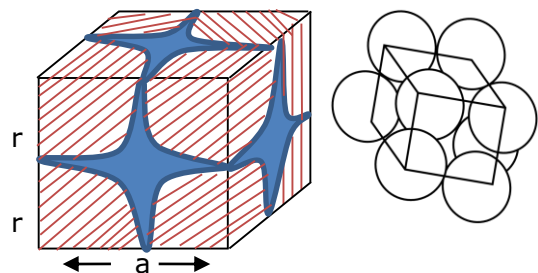
**Atomic Packing Fraction:**

Number of atoms per unit cell = 1

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

Side of unit cell (a) = 2r

Volume of unit cell =  $a^3$



$$\text{Atomic Packing Fraction} = \frac{\text{Total Volume occupied by the atoms in the unit cell}}{\text{Total Volume of the unit cell}}$$

$$\text{APF} = \frac{\frac{4\pi}{3} r^3}{a^3} = \frac{\frac{4}{3} \pi \left[ \frac{a}{2} \right]^3}{a^3} = \frac{4\pi a^3}{3 \times 8 \times a^3} = \frac{\pi}{6} = 0.52$$

52% of volume is occupied by atoms and 48% of volume is vacant.

### **Body Centered Cubic:**

Example: Tungsten, chromium and molybdenum

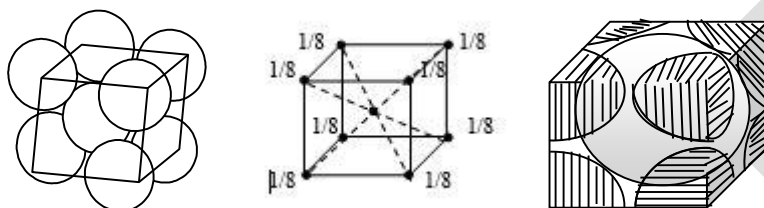
#### **Number of atoms per unit cell**

Each Corner atom is shared by 8 adjoining unit cell atoms with  $\frac{1}{8}$  of each corner atom. It has one central atom too. Total Number of atoms per unit cell =  $\frac{1}{8} \times 8 + 1 = 2$  atoms

#### **Coordination number**

The body centered atom is surrounded by 8 corner atom & hence the centered atom is surrounded by 8 equidistant nearest neighbours.

Coordination Number = 8



#### **Atomic Radius:**

Here each corner atoms touches the central atom. Consider the atoms at A, D. These atoms lie in a straight line & forms a diagonal of the cube.

$$\begin{aligned} \text{From figure, } (AD)^2 &= (AC)^2 + (CD)^2 \\ &= (AB)^2 + (BC)^2 + (CD)^2 \\ (4r)^2 &= a^2 + a^2 + a^2 \\ 16r^2 &= 3a^2 \\ r^2 &= \frac{3a^2}{16} \text{ (or) } r = \frac{\sqrt{3}a}{4} \end{aligned}$$

#### **Atomic Packing Fraction:**

Number of atoms per unit cell = 2

Volume of one atom  $(v) = 2 \times \frac{4}{3} \pi r^3$

Side of unit cell  $(a) = \frac{4r}{\sqrt{3}}$

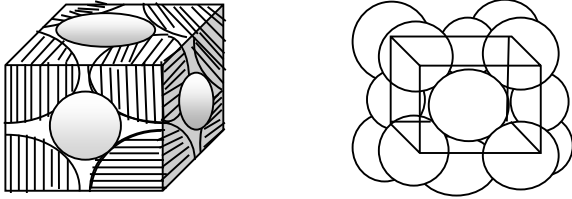
Volume of unit cell =  $a^3$

Atomic Packing Fraction =  $\frac{\text{Total Volume occupied by the atoms in the unit cell}}{\text{Total Volume of the unit cell}}$

$$APF = \frac{2 \times 4\pi r^3}{a^3} = \frac{2 \times 4\pi \times (\frac{\sqrt{3}}{4}a)^3}{3 \times 4 \times 4 \times 4 \times a^3} = \frac{2 \times 4\pi \times (3\sqrt{3})a^3}{3 \times 4 \times 24 \times 4 \times a^3} = \frac{\sqrt{3}\pi}{8} = 0.68$$

$\therefore$  68% of the volume is occupied by atoms and 32% are vacant.

**Face Centered Cubic:** Example: Copper, Aluminum, Nickel, Gold, Lead & Platinum



**Number of atoms per unit cell**

There are 8 corner atoms, one at each of its 8 corners. Each corner atom is shared by 8 adjoining unit cell with  $\frac{1}{8}$  of each in a unit cell. Total atoms at corners =  $\frac{1}{8} \times 8 = 1$

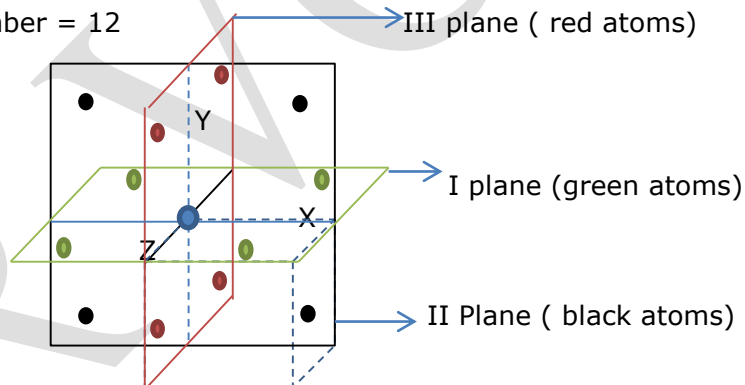
In addition, there are 6 atoms at the face centers and shared by 2 adjoining unit cell with  $\frac{1}{2}$  of each in unit cell. Total atoms at faces =  $\frac{1}{2} \times 6 = \frac{1}{2} \times 6 = 3$

$\therefore$  Total number of atoms in a unit cell =  $1 + 3 = 4$

**Coordination number**

There are 8 atoms at corners & 6 atoms at the center of six faces. Let us consider **X** as the corner atoms and there are three mutually perpendicular planes with a common point of intersection at atom X. There are 4 face centered atoms in its own plane (green atoms), 4 atoms in II plane (black atoms) and 4 in III planes (red atoms)

$\therefore$  Total Coordination Number = 12



**Atomic Radius:**

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

From figure,  $(AC)^2 = (AB)^2 + (BC)^2$

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

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

$$r^2 = \frac{2a^2}{16} \text{ (or) } r = \frac{\sqrt{2}a}{4}$$

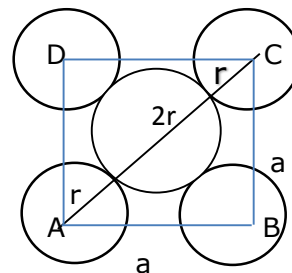
**Atomic Packing Factor:**

Number of atoms per unit cell = 4

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

Side of unit cell  $(a) = \frac{4r}{\sqrt{2}}$

Volume of unit cell =  $a^3$

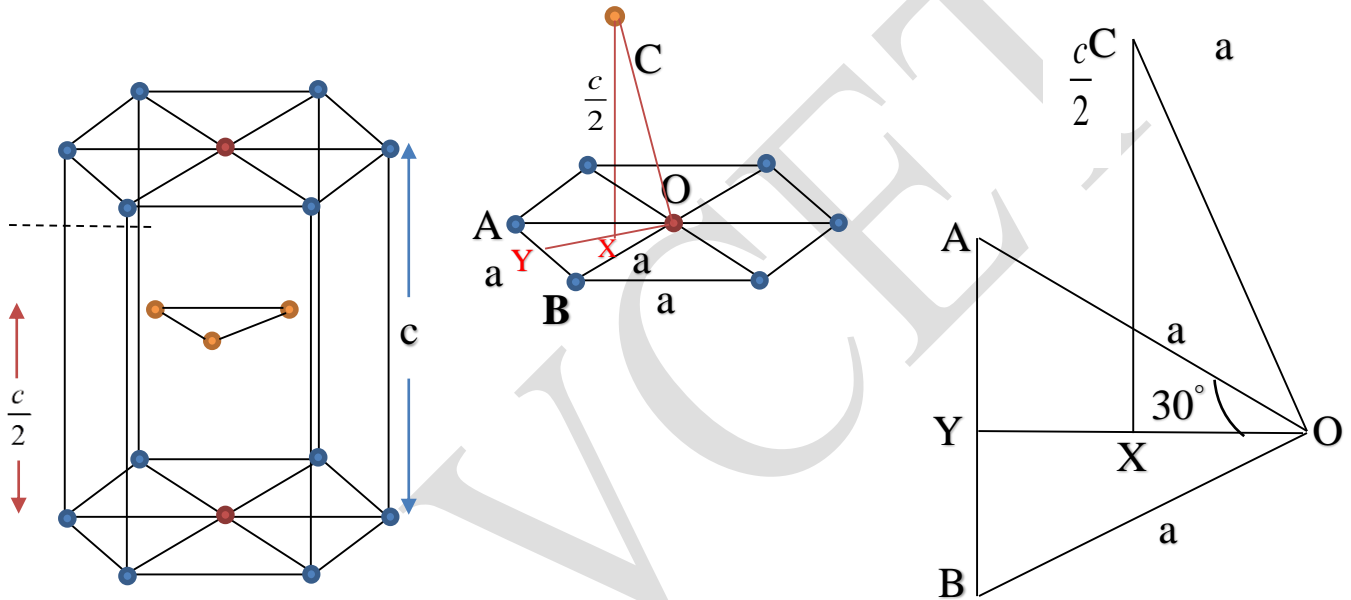


$$\text{Packing Fraction} = \frac{\text{Total Volume occupied by the atoms in the unit cell}}{\text{Total Volume of the unit cell}}$$

$$\frac{4 \times 4\pi r^3}{3a^3} = \frac{4 \times 4\pi \times (\sqrt{2})^3 a^3}{4 \times 4 \times 4 \times 3a^3} = \frac{4 \times 4\pi \times (2\sqrt{2})a^3}{4 \times 4 \times 24 \times 3a^3} = \frac{\sqrt{2}\pi}{6} = 0.74$$

∴ 74% of the volume is occupied by atoms and 26% are vacant.

**2. Describe the HCP structure of a crystal? Give details about its atomic radius, atomic packing factor and axial ratio?(C/A ratio)**



Example: Magnesium, Zinc, Titanium, Zirconium, beryllium and cadmium.

In this type of crystal, the unit cell has one atom at each of the 12 corners of the hexagon one atom at the center of the two hexagonal faces and three atoms symmetrically arranged in the body of the unit cell.

HCP has 12 nearest neighbours, 6 on its plane, 3 in the plane above and 3 in the plane below. There are three layers in this structure.

(i) At bottom layer (A), the central atom has '6' nearest neighbouring atoms in the same plane.

(ii) The second layer (B) is at distance  $\frac{c}{2}$  from 'A', has three atoms.

(iii) The top layer is at a distance 'C' from (A) is as same as bottom layer & it has the stacking sequence of AB,AB,.....

**Number of atoms per unit cell:**

Each corner atom is shared by '6' with other unit cell and gives its  $\frac{1}{6}$  Th of its share

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

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



Each central atom is shared by two unit cells .i.e., the upper & lower plane contains  $\frac{1}{2}$  atom each.

$\therefore$  Total number of central atom in both upper and lower planes =  $\frac{1}{2} \times 2 = 1$  atom.

Also, there are three atoms in the center of unit cell which will not share by adjacent unit cell.

$\therefore$  Total number of atoms in the unit cell =  $1 + 1 + 1 + 3 = 6$  atoms.

### Coordination number:

Let us consider X (blue atom) be the center atom. The X atom is surrounded by 6 nearest neighbouring atoms on the same plane. At the distance  $c/2$  from bottom layer, the first unit cell has 3 atoms and another 3 atoms from the second unit cell above the plane as shown in figure

$\therefore$  Coordination number = 12

### Atomic radius:

Atoms touch each other along the edges of the side of a cube  $\therefore 2r = a$  (or)  $r = \frac{a}{2}$

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

In HCP structure 'C' is the height of the unit cell, 'a' is the distance between two nearest atoms.

In  $\Delta ABO$ , A, B, O are lattice points and exactly above these at a  $\perp r$  distance  $\frac{c}{2}$ . The next layer atom lies at 'C'

In  $\Delta OYA$ ,  $\cos 30^\circ = \frac{OY}{OA}$  (or)  $OY = OA \cos 30^\circ = \frac{a\sqrt{3}}{2}$  [ $\because OA = a$ ]

But,  $OX = \frac{2}{3} OY$ . (law of orthocenter of equilateral triangle)

i.e.,  $OX = \frac{2}{3} \times \frac{a\sqrt{3}}{2} = \frac{a}{\sqrt{3}}$

In  $\Delta OXC$ ,  $(OC)^2 = (OX)^2 + (XC)^2$

i.e.,  $a^2 = \left(\frac{a}{\sqrt{3}}\right)^2 + \left(\frac{c}{2}\right)^2$  (or)  $a^2 = \frac{a^2}{3} + \frac{c^2}{4}$  (or)  $\frac{c^2}{4} = a^2 - \frac{a^2}{3}$

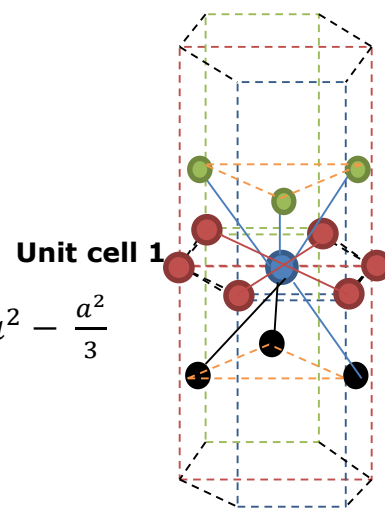
$\therefore \frac{c^2}{4} = \frac{2a^2}{3}$  (or)  $\frac{c^2}{a^2} = \frac{8}{3}$  (or)  $\frac{c}{a} = \sqrt{\frac{8}{3}} = 1.6333$

$\therefore \frac{c}{a} = 1.6333$

**Atomic Packing Factor:** Area of base = 6 x Area of  $\Delta AOB$

$\therefore$  Area of  $\Delta AOB = \frac{1}{2} (BO) (AY) = \frac{1}{2} \times a \times \frac{a\sqrt{3}}{2} = \frac{a^2\sqrt{3}}{4}$

Area of Base =  $6 \times \frac{a^2\sqrt{3}}{4} = \frac{a^2 3\sqrt{3}}{2}$



**Unit cell 2**

$$\text{Volume of atoms in unit cell} = \text{Area} \times \text{height} = \frac{a^2 3\sqrt{3}}{2} c$$

$$\text{Atomic Radius (r)} = \frac{a}{2}$$

Number of atoms per unit cell = 6 atoms

$$\therefore \text{Volume of the unit cell} = \frac{4}{3} \pi r^3$$

$$\text{Volume of atoms in unit cell} = 6 \times \frac{4}{3} \pi \left(\frac{a}{2}\right)^3 = \frac{8\pi a^3}{8} = \pi a^3$$

$$\text{Atomic Packing Fraction} = \frac{\text{Total Volume occupied by the atoms in the unit cell}}{\text{Total Volume of the unit cell}}$$

$$\text{APF} = \frac{\pi a^3}{\frac{a^2 3\sqrt{3}}{2} c} = \frac{2\pi a}{3\sqrt{3} c} = \frac{2\pi \sqrt{3}}{3\sqrt{3} \sqrt{8}} = \frac{2\pi}{3 \times 2\sqrt{2}} = \frac{\pi}{3\sqrt{2}} = 0.74$$

$\therefore$  74% of the volume is occupied by atoms and 26% are vacant.

### 3) Explain Bravais lattice in detail with necessary Diagrams?

There are 14 possible ways of arranging points in space such that the environment looks same from each point. The Fourteen possible space lattices of the seven crystal systems are called Bravais Lattice.

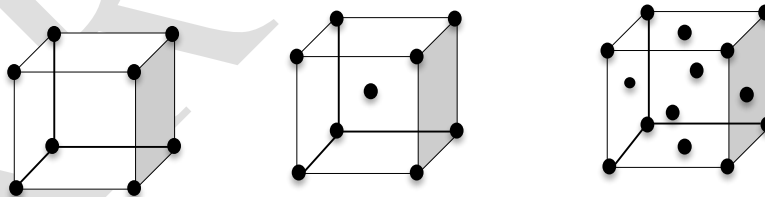
Let us now discuss how the seven crystal systems vary according to their lattice parameters.

#### 1. Cubic System

In this crystal system, fig.1.2 (a) all three axial lengths of the unit cell are equal and they are perpendicular to each other. Three possible forms are possible (SC, BCC, FCC)

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

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



**Fig 1.2 (a)**

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

#### 2. Tetragonal System

In this system, fig.1.2 (b) two axial lengths of the unit cell are equal and third axial length is either longer or shorter. There axes are perpendicular to each other. Two possible forms are possible such as SC, BCC.

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

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

fig 1.2 (b)



Example: Ordinary white tin, Indium.

### 3. Orthorhombic System

In this system, fig.1.2 (c) three axial lengths of the unit cell are not equal but they are perpendicular to each other.

Four possible forms are possible such as SC, BCC, FCC, BC

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

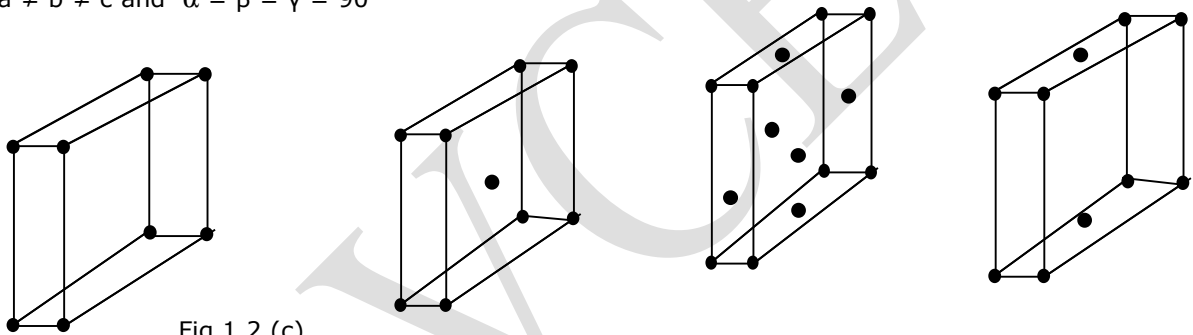


Fig 1.2 (c)

Example: Sulphur, Topaz.

### 4. Monoclinic System

In this system, fig.1.2 (d) three axial lengths of unit cell are not equal. Two axes are perpendicular to each other and third is obliquely inclined. Two possible forms are possible (SC, BC)

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

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

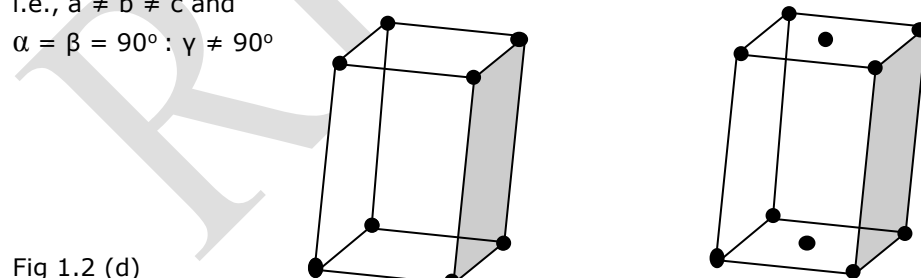


Fig 1.2 (d)

Example: Sodium Sulphite ( $\text{Na}_2\text{SO}_3$ )  
Ferrous Sulphate ( $\text{FeSO}_4$ )

### 5. Triclinic System

In this system, fig.1.2 (e) three axial lengths of unit cell are not equal and all the axes are inclined obliquely to each other.

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

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

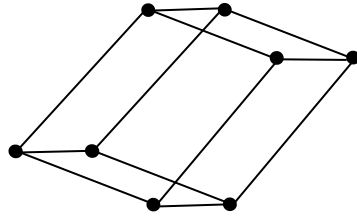


fig 1.2 (e)

Example: Copper Sulphate ( $\text{CuSO}_4$ ), Potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ )

### 6. Rhombohedral System (Trigonal)

In this system, fig.1.2 (f) all three axial lengths of the unit cell are equal. They are equally inclined to each other at an angle other than  $90^\circ$

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

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

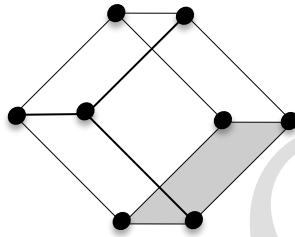


fig 1.2 (f)

Example: Calcite.

### 7. Hexagonal System

In this system, Fig.1.2 (g) two axial lengths of unit cell (Say horizontal) are equal and lying in one plane at  $120^\circ$  with each other. The third axial length (Say vertical) is either or shorter than the other two and it is perpendicular to this plane.

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

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

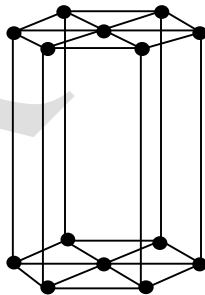


Fig 1.2 (g)

Example: Quartz, Tourmaline

**4) What are miller indices? What are the procedures and features for finding Miller indices? Show that for a cubic structure the distance between two successive planes ( $h k l$ ) is given by  $d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$**

**(i) Definition:** Miller indices are three possible integers that have the same ratio as the reciprocals of the intercepts of the plane concerned on the three axes.

**(ii) Procedure:** consider a crystal plane. Let us find its Miller indices as follows:

(1) Find the intercepts of the plane along the coordinate axes  $X, Y, Z$ . The intercepts are measured as the multiples of axial lengths.

(2) Take the reciprocal of these intercepts.

(3) Reduce the reciprocals in to whole numbers. This can be done by multiplying each reciprocal by the number obtain from LCM of the denominators.

(4) Write these integers within parentheses to get Miller indices.

**(iii) Features:**

(1) If a plane is parallel to any one of the coordinate axes, then its intercept will be infinity. Hence the miller indices for that particular axis is zero.

(2) The plane passing through the origin has non zero intercepts

(3) All equally spaced parallel planes have the same Miller indices ( $h k l$ )

(4) This ( $h k l$ ) indices define a set of parallel plane than a particular plane

(5) Miller indices is not only the ratio of indices but the notation to find all such planes

(6) If a plane cuts the axis on the negative side, then a bar is put just above the particular miller index.

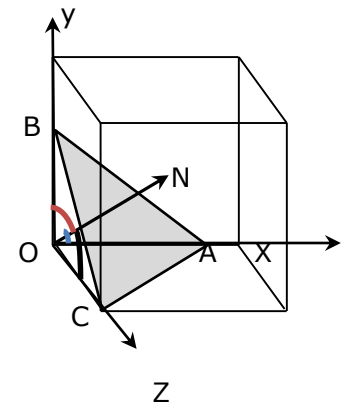
Consider a cubic crystal of 'a' as side of a cube and a plane ABC as shown in figure. Let this plane belong to a family of planes whose miller indices are  $[h k l]$ . A normal ON is drawn  $\perp$  from the origin of the cube to the plane ABC. Let ON represents the interplanar spacing ( $d$ ) of this family of plane.

The plane ABC makes OA, OB & OC as intercepts on crystallographic axes OX, OY & OZ respectively.  $\alpha'$ ,  $\beta'$  and  $\gamma'$  are the angles between the crystallographic axes. We know that the miller indices of a plane are the smallest integers of the reciprocals of the intercepts.

But here, Intercepts are expressed as reciprocals of miller indices

Of the plane. *i.e.*,  $OA : OB : OC = \frac{1}{h} : \frac{1}{k} : \frac{1}{l} = \frac{a}{h} : \frac{a}{k} : \frac{a}{l}$

$\therefore OA = \frac{a}{h} ; OB = \frac{a}{k} ; OC = \frac{a}{l}$  [Multiply by lattice constant 'a']



From the Geometry of right angles OAN, OBN & OCN, we have

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

$$\text{Similarly } \cos \beta' = \frac{ON}{OB} = \frac{d}{\frac{a}{k}} = \frac{dk}{a} \quad \& \quad \cos \gamma' = \frac{ON}{OC} = \frac{d}{\frac{a}{l}} = \frac{dl}{a} \quad (\text{blue - } \alpha', \text{ Red - } \beta' \text{ and Black - } \gamma')$$

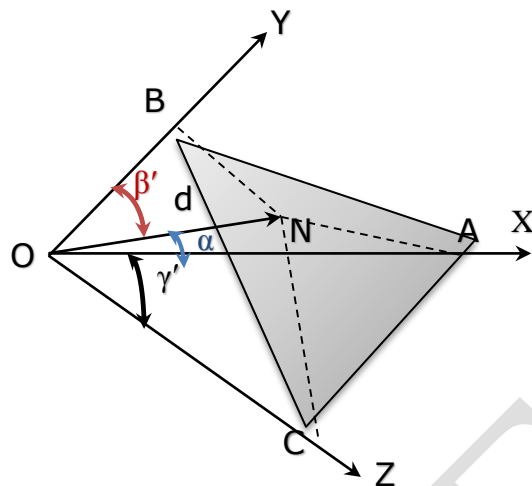
The law of direction cosines is  $\cos^2 \alpha' + \cos^2 \beta' + \cos^2 \gamma' = 1$

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

$$\text{i.e., } \frac{d^2}{a^2} (h^2 + k^2 + l^2) = 1 \quad (\text{or}) \quad d^2 = \frac{a^2}{h^2 + k^2 + l^2}$$

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

This is the relationship between interplanar spacing 'd' cube edges 'a' & miller indices [h k l].

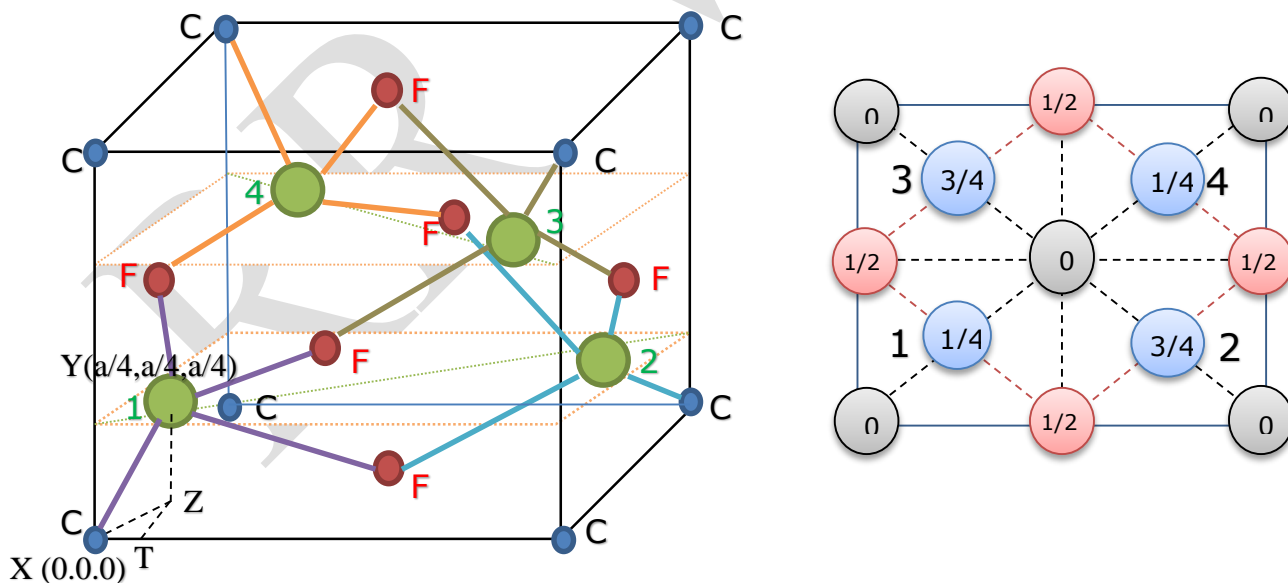


### 5) Explain the essential parameters of unit cell in diamond structure?

Diamond has face centered cubic structure with the basis of two carbon atoms viz; X and Y. The 'X' atom is located with an origin (0,0,0) and the "Y" atom is located with the origin of (a/4,a/4,a/4) (i.e.) one quarter way along the body diagonal as shown in figure.

Thus from figure we can see that the diamond structure is formed due to the combination of two interpenetrating FCC sublattices, having the origin (0,0,0) and (1/4,1/4,1/4) along the body diagonal.

Let us discuss some parameters of the diamond



In diamond there are three types of atoms namely

- (i) Corner atoms represented by 'C'
- (ii) Face centered atom represented by "F"
- (iii) Four atoms present inside the unit cell represented as 1,2,3,4 in figure

The three types of atoms position projected on a cube face as shown in figure

### Number of atoms per unit cell

Each corner is shared by 8 unit cells. Similarly we have 8 corner atoms in an unit cell.

The number of atoms/unit cell =  $\frac{1}{8} \times 8 = 1$  atom

*Number of face centered atoms/unit cell:*

Each face centered atom is shared by 2 unit cells. Similarly, we have 6 face centered atoms

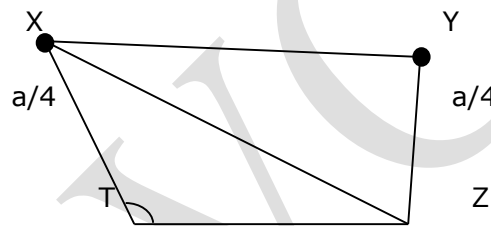
The number of atoms/unit cell =  $\frac{1}{2} \times 6 = 3$  atoms

**Number of atoms inside the unit cell:**

Inside the unit cell we have 4 atoms, represented 1,2,3,4 in figure which is shared by that particular unit cell alone. The number of atoms/unit cell =  $1 + 3 + 4 = 8$

### Atomic Radius

Here the corner atoms do not have contact with each other and the face centered atoms also do not have contact with corner atoms. But both the face centered atom and corner atom have contact with 4 atoms(1,2,3,4) situated inside the cell as shown in fig.5.20.



**Fig. 5.22**

From fig.5.22 we can see that the nearest two neighbours which have direct contact are atoms "X" and "Y".

Let us draw perpendicular to the "Y" atom, which meets the unit cell at a point "Z" as shown in fig.5.22 which is at a distance of  $a/4$ .

$$\begin{aligned}
 \text{From fig.5.22 } (XY)^2 &= (XZ)^2 + (ZY)^2 \\
 &= \left[ (XT)^2 + (TZ)^2 + (ZY)^2 \right] \\
 &= \left( \frac{a}{4} \right)^2 + \left( \frac{a}{4} \right)^2 + \left( \frac{a}{4} \right)^2 \\
 &= \frac{a^2}{16} + \frac{a^2}{16} + \frac{a^2}{16} \\
 &= (XY)^2 = \frac{3a^2}{16}
 \end{aligned}$$

Since  $XY = 2r$  we can write  $(2r)^2 = \frac{3a^2}{16}$

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

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

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

$$\text{The lattice constant } a = \frac{8r}{\sqrt{3}}$$

### **Coordination Number**

We know the coordination number is the number of nearest neighbouring atoms to a particular atom.

From fig. the number of nearest atoms for "Y" atom is 4.

Therefore the coordination number of diamond is 4.

### **Atomic Packing Factor**

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

$$\text{Atomic Packing Fraction} = \frac{\text{Total Volume occupied by the atoms in the unit cell}}{\text{Total Volume of the unit cell}}$$

$$\text{Volume occupied by 1 atom} = \frac{4}{3}\pi r^3$$

In a diamond we have 8 atoms/unit cells

$$\text{Volume occupied by all the 8 atoms per unit cell } (v) = 8 \times \frac{4}{3}\pi r^3$$

$$\text{We know the atomic radius for diamond structure } r = \frac{a\sqrt{3}}{8}$$

$$\text{Volume occupied by the atoms per unit cell } (v) = 8 \times \frac{4}{3}\pi \left(\frac{a\sqrt{3}}{8}\right)^3$$

$$\text{Volume occupied by the atoms per unit cell } (v) = \frac{\pi a^3 3\sqrt{3}}{16}$$

Since diamond has cubic structure the volume of the unit cell ( $v$ ) =  $a^3$

$$(\text{APF}) = \frac{\pi a^3 3\sqrt{3}}{16a^3}$$

$$(\text{APF}) = \frac{\pi\sqrt{3}}{16}$$



Atomic packing factor = 0.34

∴ 34% of the volume is occupied by atoms and 66% are vacant.

## 6) Write a brief notes on defects in crystals?

*The disturbance occurred in the regular orientation of atoms is called crystal defect or imperfection.*

The imperfection or defects are always present in the actual crystal and their effects are often very important in understanding the properties of crystals. Some properties of crystal defects are *structure sensitive*. i.e., properties such as mechanical strength, ductility, crystal growth, magnetic hysteresis, dielectric strength are greatly affected by the relatively minor changes in crystal structure caused by the imperfections.

Some other properties of crystals are structure – insensitive. i.e., properties such as stiffness and density are not affected by the presence of imperfections.

### **Classification of crystal imperfections (or) defects**

Crystalline imperfections are classified on the basis of their geometry as follows:

#### **(i) Point defects**

- (a) Vacancies
- (b) Interstitials
- (c) Impurities

#### **(ii) Line defects**

- (a) Edge Dislocation
- (b) Screw Dislocation

#### **(iii) Surface Defects**

- (a) Grain boundaries
- (b) Tilt boundaries
- (c) Stacking faults

#### **(iv) Volume defects**

- (a) Cracks.

#### **Point defect**

Point defects are crystalline irregularities of atomic dimensions. They are imperfect points like regions in the crystal. One or two atomic diameter is the typical size of a point imperfection.

- (i) Point defects take place due to imperfect packing of atoms during crystallization
- (ii) They produce distortion inside the crystal structures.
- (iii) They produce strain only in its surrounding but does not affect the regularity in other parts of the crystal.

## Types of point defects

The different types of point defects are

- (a) Vacancies
- (b) Interstitial
- (c) Impurities

### Vacancies

A vacancy is the simplest point defect in a crystal. *It refers to a missing atom or vacant atomic site. Whenever one or more atoms are missing from a normally occupied position as shown in fig 5.90, the defect caused is known as vacancy.*



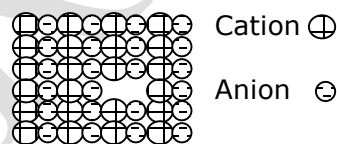
**Fig 5.25.**

Vacancy may be single as shown in figure 5.25 or two or more of them. These defects may arise due to imperfect packing during original crystallization and thermal vibrations of the atoms at high temperature.

The atoms surrounding the vacancies are displaced inwards thereby distorting the regularity of arrangement. There are different kinds of vacancies like Frenkel defect, Schottky defect, color center, etc.

### Schottky defect

*It refers to the missing of a pair of positive and negative ions in an ionic crystal. Here two oppositely charged ions are missing from an ionic crystal, therefore a cation – anion divacancy is created. (Fig 5.26) This is known as Schottky defect or Schottky imperfection since a pair is missing, the electrical neutrality is maintained.*

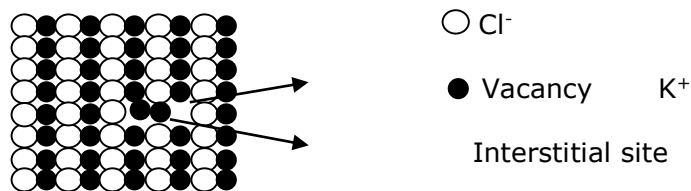


**Fig 5.26. Schottky defect**

### Frenkel Defect

*A vacancy associated with interstitial impurity is called Frenkel defect. Here a missing atom occupies interstitial position as shown in figure 5.27.*

This defect always occurs in ionic crystal. If a positive ion moves into an interstitial site in an ionic crystal, a cation vacancy is created in the normal ion site, a cation vacancy is created in the normal ion site, this vacancy – interstitial pair is known as Frenkel defect.



**Fig.5.27. Frenkel defect. An ion get transferred from the lattice site to interstitial site**

- (i) Frenkel defect does not change the overall electrical neutrality of the crystal.
- (ii) The presence of these defects in ionic crystals causes an increase in electrical conductivity

### Interstitial defect

When an extra atom occupies interstitial space (i.e., Voids) within the crystal structure without removing the parent atom the defect is called interstitial defect.

An atom can enter into interstitial space only if it is smaller than the parent atom otherwise it will produce atomic distortion or strain because an interstitial atom tends to push the surrounding atoms further apart.

### Types of interstitial defect

- (i) Self-interstitial
- (ii) Foreign interstitial

#### Self-interstitial

If an atom from the same crystal occupies interstitial site, then it is called self-interstitial (Fig 5.28 (a))

#### Foreign interstitial

If an impurity atom occupies interstitial site, then it is called foreign interstitial (Fig 5.28. (b))

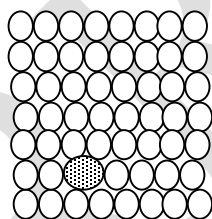


Fig 5.28 (a)

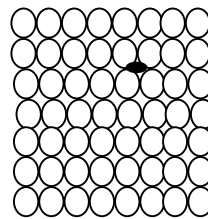


Fig 5.28 (b)

### Impurities

When the foreign atoms are added to crystal lattices, they are known as impurities. The defect is called impurity defect. The impurity atom may fit in the structure in two ways giving rise to two kinds of impurity defects. They are

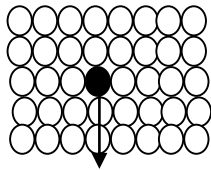
- (i) Substitutional impurity defect
- (ii) Interstitial impurity defect

#### Substitutional impurity defect

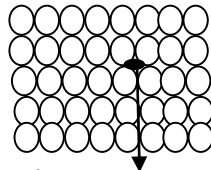
A Substitutional impurity refers to a foreign atom that replaces a parent atom in the lattice as shown in figure 5.29.(a) Substitutional impurities change the electrical properties enormously.

### Interstitial impurity defect

An interstitial impurity is a small size atom occupying the empty space (interstitial) in the parent crystal, without dislodging any of the parent atoms from their sites. (Fig 5.29(b)). An atom can enter into the interstitial or empty space only when it is substantially smaller than the parent atom.



5.29. (a) Substitutional impurity



5.294 (b). Interstitial impurity

### Line defects or Dislocations

The defects due to dislocation or distortion of atoms along in a line are known as line defects. Line defects are also called dislocations. In the geometrical sense, they are one dimensional defect. In line defect, a portion of a line of atoms is missing or displaced from its regular site.

#### Types of line defect

##### Edge Dislocation

An edge dislocation arises when one of the atomic planes forms only partially and does not extend through the entire crystal as shown in figure 5.30. The atomic plane AB abruptly terminates at B. It is viewed as an extra plane inserted in between a set of parallel planes. The edge of such a plane forms a line defect and it is called edge dislocation. The atomic row 1 passing through point B has one atom more than the row 2 adjacent to it.

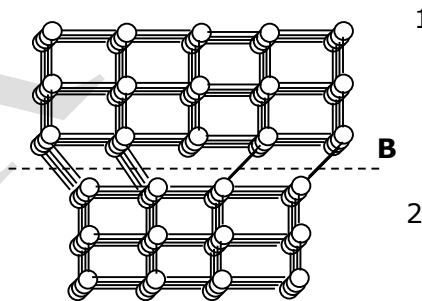


Fig 5.30. Edge dislocation

##### Classification of edge dislocation

Edge dislocation are symbolically represented by  $\perp$  or  $\top$  depending on whether the incomplete plane starts from top or bottom of the crystal. These two configuration are referred as Positive edge dislocation and negative edge dislocation

##### Positive edge dislocation

The edge dislocation is called positive if the extra plane of atoms is above the slip plane of the crystal as shown in figure 5.31. It is denoted by the symbol  $\perp$

### Negative edge dislocation

The edge dislocation is called negative, if the extra plane of atoms is below the slip plane as shown in figure 5.31. it is denoted by the symbol  $\bar{\tau}$

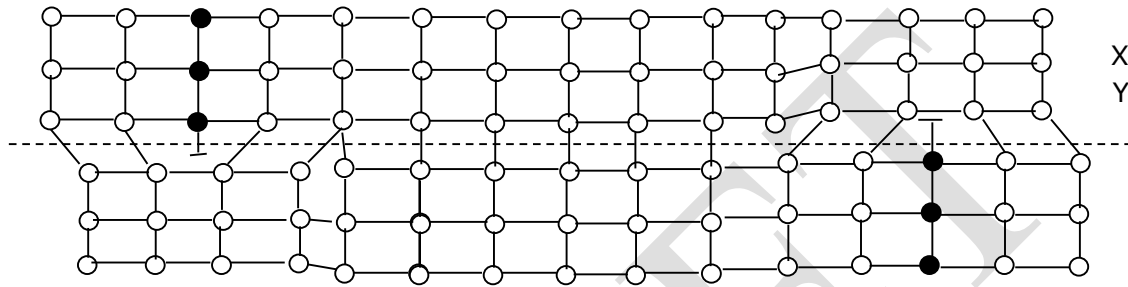


Fig. 5.31.

### Screw dislocation

Screw dislocation is due to a displacement of atoms in one part of a crystal relative to rest of the crystal. The displacement terminates within the crystal. This dislocation forms a spiral ramp around the dislocation line (Fig.5.32.)

In a screw dislocation, there is a line of atoms about which the crystal planes are warped to give an effect similar to the threads of a screw. The row of atoms making the termination of the displacement is the screw dislocation. EF indicates the dislocation line.

The term screw is to represent that one part of the crystal is moving in spiral manner about the dislocation line. If spiral motion of one part of the crystal is in clockwise direction then the dislocation is right handed on the other hand spiral motion is in anti-clockwise direction then the dislocation is left handed

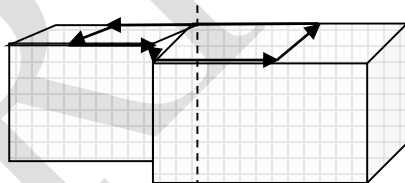


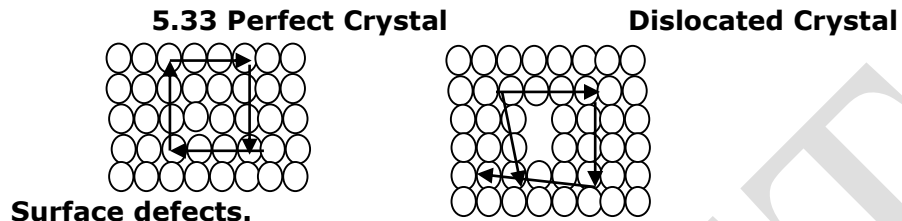
Fig 5.32 **Screw dislocation**

### Burger vector

The dislocation lines are expressed by burger vector  $\bar{b}$ . It indicates the amount and direction of shift in the lattice on the slip plane. The figure 5.33 shows a perfect crystal and a crystal with positive edge dislocation.

Consider a point starting from P (Fig 5.33) which moves in a particular direction as shown and it completes the atomic distances in the form of a circuit called 'Burger circuit' or 'burger loop'.

If the same circuit is drawn starting from P in figure 5.98 then the circuit would not complete, this is because of the presence of a dislocation. If we wish to arrive at the starting point P from Q, then we must move an extra distance 'b' as shown in figure 5.98 the vector  $\vec{b} = \overline{PQ}$  connects the endpoint with the starting point. This is the burger's vector of the dislocation



### Surface defects.

*The defects on the surface of a material are called surface defects or plane defects. They are also known as two dimensional imperfections.*

Surface defects are due to a change in the stacking of atomic planes on or across a boundary. Some important internal defects are discussed below:

### Grain boundaries

Whenever the grains of different orientations separate the general pattern of atoms and exhibits a boundary, the defect caused is called grain boundary. A grain boundary is formed when two growing grain surfaces meet. The shape of the grain is usually influenced by the presence of surrounding grains. This type of defect generally takes place during the solidification of the liquid metal.

### Tilt and twist boundaries

Tilt boundary is another surface imperfection. It is an array of parallel edge dislocation of same sign (i.e., either  $\uparrow$  or  $\downarrow$ ) arranged one above the other in an array or series as shown in figure 6. Tilt boundary is a type of low angle boundaries (i.e., less than  $10^\circ$ ). By rotation of an axis in the boundary, it is possible to bring the axis of two bordering grains into coincidence, then Angle of tilt  $\tan \theta = \frac{b}{D}$  where

D – dislocation spacing; b – Length of Burger's vector. When  $\theta$  is very small, then  $\tan \theta = \theta \therefore \theta = \frac{b}{D}$

### Twin boundaries

If the boundaries in which the atomic arrangement on one side of the boundary is somewhat a mirror image of the arrangement of atoms of the other side as shown in figure 6.1, the defect caused is called Twin boundary. The region in which a twin boundary defect occurs is between the twinning plane as shown in figure 5.34.

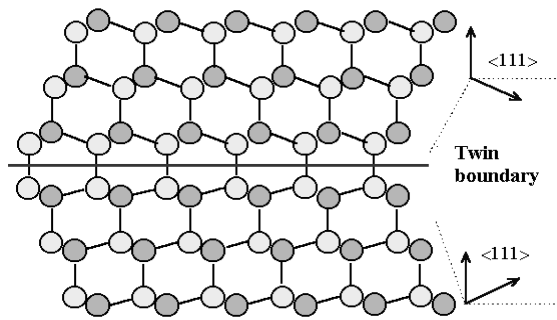


Figure 5.34.

### Stacking Fault

It is a surface imperfection. Whenever the stacking of atoms is not in proper sequence throughout the crystal, the defect caused is called stacking fault.

#### Explanation

Fig 5.35 shows the proper sequence of atomic planes if we read from bottom to top as A-B-C-A-B-C-A-B-C. But Figure 6.3b shows the sequence of atomic planes as A-B-C-A-B-A-B-A-B-C. The region in which the stacking fault occurs (A-B-A-B) forms a thin region of a hexagonal close packing in a FCC crystal.



Fig 5.35. Stacking Fault

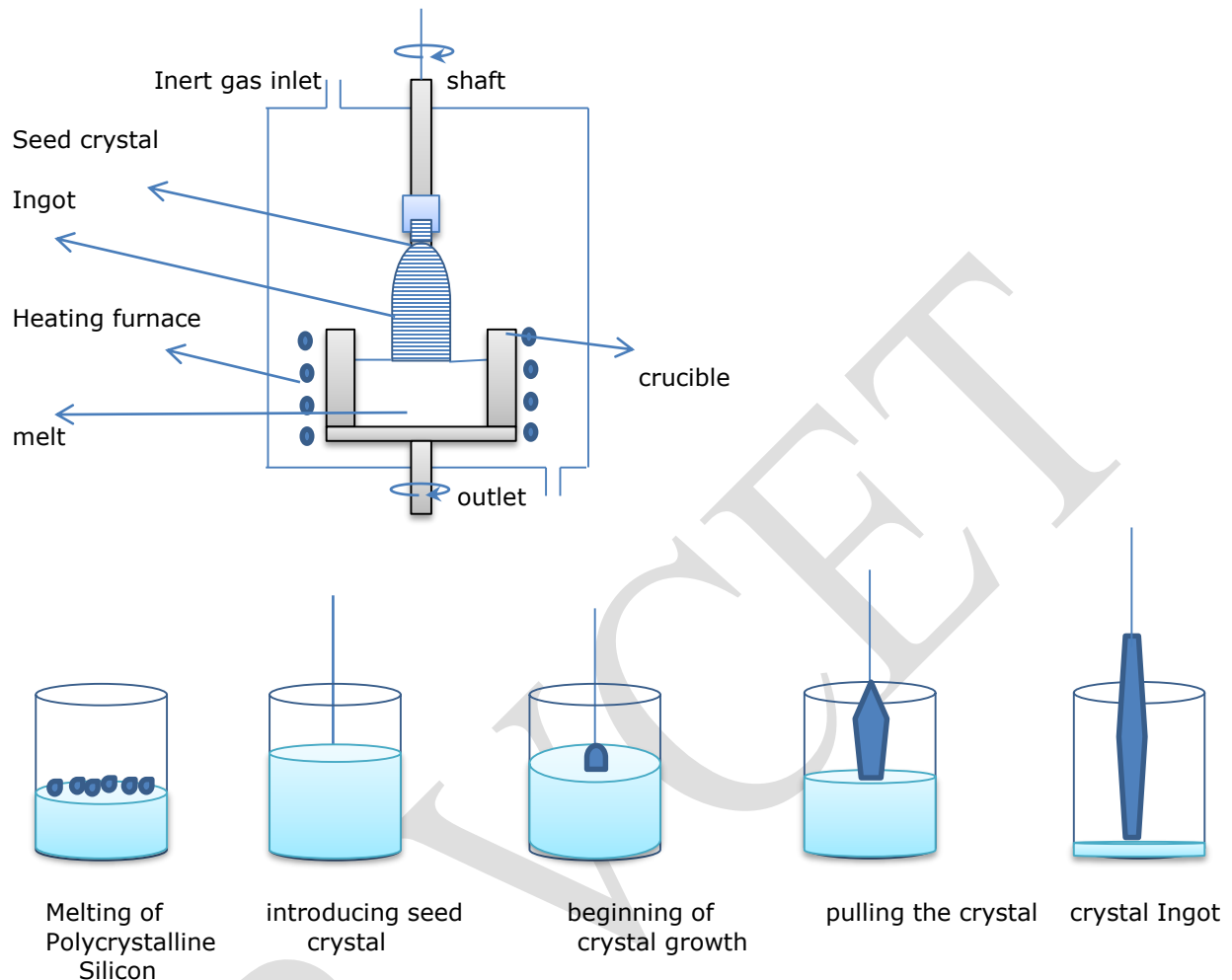
### Volume Defects

The defects such as cracks or pores occurs at the surface of the crystal results in variation of properties and that type of defect is called volume defects

## 6). Explain in detail about Czochralski and Bridgman methods for growing a crystal through melt with necessary diagrams?

### (i)Czochralski method (crystal pulling)

It is basically a crystal pulling technique from melt. Czochralski method or pulling from the melt is the principal method for the production of bulk single crystals of silicon. A schematic of the technique is shown in figure below



At first the polycrystalline material (say silicon) to be grown into a crystal is first melted by heating furnace under a controlled atmosphere in a non - reacting quartz crucible. The melt is kept for a certain time at a temperature above the melting point and the temperature is then reduced to a value slightly above the freezing point.

Then a seed crystal mounted on a rod is dipped into the melt. Dopant impurity atoms such as boron or phosphorus can be added to the molten intrinsic silicon in precise amounts in order to dope silicon, thus changing it into  $n$ - type or  $p$ - type extrinsic silicon. This influence the electrical conductivity of the silicon

### Working

The seed crystal rod is pulled upwards and rotated at the same time. The seed crystal is a single crystal and ensures a single crystal growth along a certain crystallographic orientation. By controlling the temperature gradients, rate of pulling and speed of rotation precisely, it is possible to exact cylindrical ingots of desired dimensions from the melt.

The entire process is performed in an inert atmosphere such as argon and in an inert crucible such as quartz. Silicon ingots of 200mm to 300mm in diameter and 1 to 2 meters in length are commonly formed. Silicon wafers of desired thickness are sliced from these ingots and are processed to create IC's.



## Advantages

This technique is essential for the growth of dislocation free large size single crystals of semiconductors (Eg: Silicon), metals (Platinum, silver, gold, etc.,) and many oxide crystals (YAG,  $\text{LaAlO}_2$ , etc.,) and are called "necking procedure"

## (ii) Bridgman Techniques

(i) This method also employs the crystal growth from melt. There are basically two different types of Bridgman technique (i) Horizontal Bridgman technique and (ii) Vertical Bridgman technique.

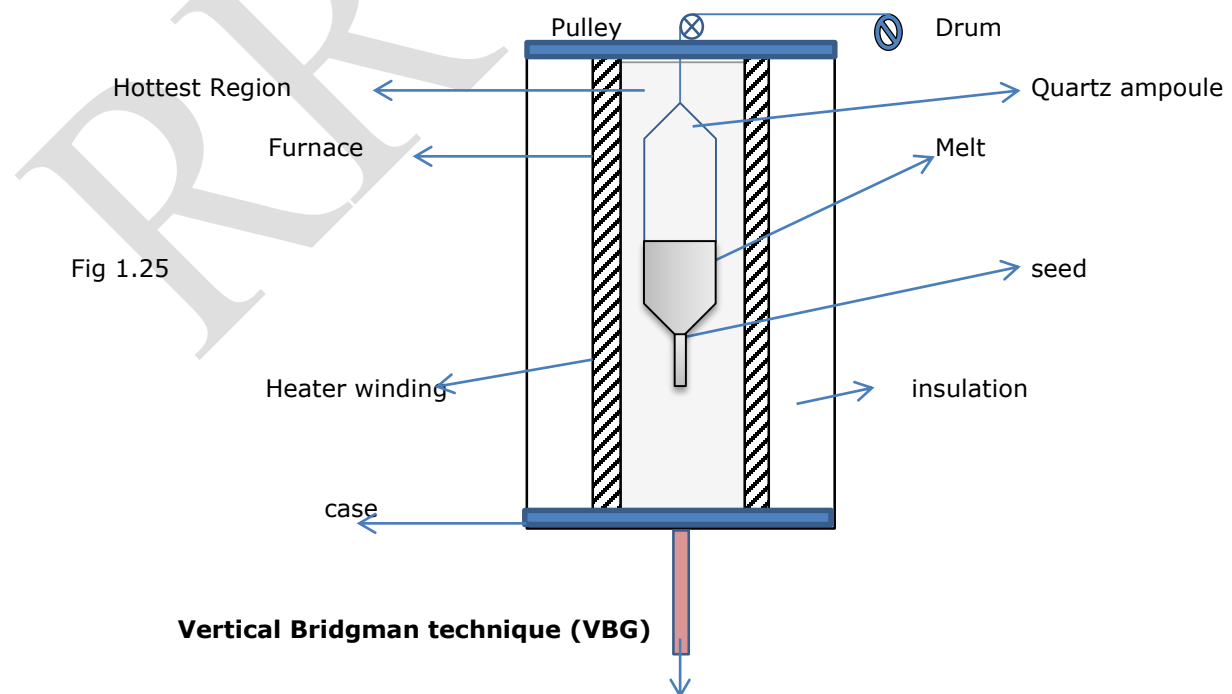
Principle

*In both the techniques a boat with the molten charge is moved (translated) across a temperature gradient so as to allow the molten charge contained in the boat to solidify starting from an oriented seed.*

## Bridgman Growth Technique (VBG)

### Arrangement & Crystallization

The starting material, a powder is filled into a quartz ampoule, sealed under high vacuum and put into Bridgman furnace. Using a pulley, the container can be moved up and down during crystallization process so as to heat / cool the melt. The furnace is switched ON and the material is heated to a very high temperature. Now when the material attains molten state, it is slowly comes into contact with a seed at the bottom of the ampoule. This seed is a single crystal and ensures a single crystal growth on a certain crystallographic orientation. Then the ampoule (crucible) is lowered from the hot zone to the cold zone, the temperature at the bottom of the crucible falls below the solidification temperature and the crystal growth is initiated by the seed at the melt – seed interface. After the whole ampoule is moved through the cold zone the entire melt converts to a solid single crystalline ingot (single crystal). Generally it took 10 – 14 days.



### Advantages

- Relatively cheaper when compared to other pulling techniques.
- Simpler technology
- Melt composition can be controlled during the growth
- The thermal gradients can be easily minimized with a consequent reduction of the dislocation density and in addition it gives cylindrical crystals with no need of sophisticated diameter control device

### Disadvantages

- Growth rate is very low
- Since the material is in contact with the walls of the container for long period, it lead to dislocations of the nucleus.
- Sometimes instead of single crystal, polycrystals may grow.
- This technique can't be used for materials which decompose before melting

## 7) Explain in detail about solution growth of single crystals with necessary diagrams?

### Solution growth

Low temperature solution growth

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

The solvent such as ethyl alcohol, acetone, and carbon tetra chloride are used to prepare solution. In some cases, mixtures of different solvents are also used.

Figure shows apparatus for low temperature solution growth. It consists of a large tank and a constant temperature bath. The solution is prepared by dissolving the substance in a solvent.

The seed crystal is a small piece of same crystalline substance. This seed crystal is introduced inside the solution and gently rotated by an electric motor

The crystallization from solution takes place in three steps

- (1) Super saturation of solvent
- (2) Growth of crystal nuclei
- (3) Successive growth of crystal to get distinct faces

When the solution is super saturated, the growth of seed crystal is accompanied by one of the following procedure:

- (1) Slow cooling of the solution
- (2) Slow evaporation of solvent
- (3) Temperature gradient

#### (i) Slow cooling method

In this method, the saturated solution is kept at a particular temperature is taken in bath. A seed crystal is suspended in the solution and the temperature is reduced at slow rate

The crystallization begins at  $45^{\circ}\text{C}$  –  $75^{\circ}\text{C}$  and the lower limit of cooling is room temperature. As a result the seed crystal produces a large size single crystal

### (ii) Slow evaporation method

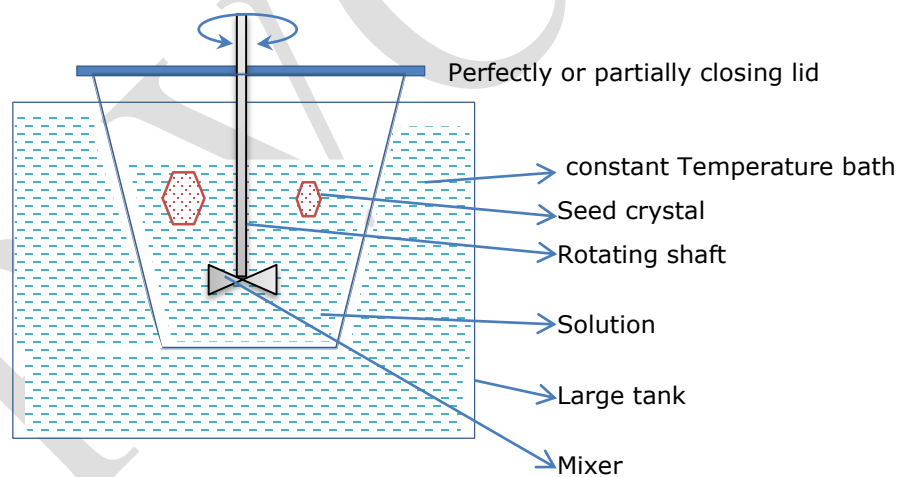
In this method, the super saturation of solution is achieved by evaporating the solvent at a fixed temperature. The solute temperature increases and grows in to single crystal on seed crystal. Typical growth conditions involve a temperature stabilization of about  $0.05^{\circ}\text{C}$  and rate of evaporation of 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.



**Note:** In university exam, if they ask " Show that FCC and HCP are same / 0.74, then you have to explain FCC part alone in question 1 and entire part of question 2