

# 19. SOLID STATE

## 1. INTRODUCTION

We know that solids are substances which have a definite volume and a definite shape. A solid is a nearly incompressible state of matter with a well-defined shape, rigidity and volume.

## 2. CLASSIFICATION OF SOLIDS

Solids can be broadly classified into two types:

1. Crystalline
2. Amorphous

**Table 19.1:** Difference between crystalline and amorphous solids

S.No.	Property	Crystalline solids	Amorphous solids
1.	Geometry	These have definite regular geometry which extends throughout the crystals i.e., these solids have long range order.	These do not have definite orderly arrangement.
2.	Melting Points	These have sharp m.p.	These do not have sharp m.p.
3.	Symmetry	These possess symmetry.	These do not possess any symmetry.
4.	Heat of Fusion	These have definite heat of fusion.	These do not have definite heat of fusion.
5.	Interfacial angles	Crystals are always guarded by planes so that a definite angle exists between two planes called interfacial angle.	These do not possess interfacial angle.
6.	Volume change	There is a sudden change in volume when it melts.	There is no sudden change in volume on melting.
7.	Isotropy and Anisotropy	These are anisotropes i.e., their physical properties such as refractive index, conductivity etc. have different values in different directions.	These are isotropic i.e., their physical properties such as refractive index, conductivity etc. have same value in all the directions.

### MASTERJEE CONCEPTS

#### Glass Transition Temperature

An important property of amorphous polymer is glass transition temperature at which a glassy polymer transforms into flexible rubber-like mass capable of taking on shapes and forms. This property is used in the processing of polymers.

Vaibhav Krishnan (JEE 2009 AIR 22)

## 3. TYPES OF CRYSTALLINE SOLIDS

On the basis of the nature of the constituent particles and the interparticle forces, crystalline solids may be divided into four classes.

**Table 19.2:** Characteristics of various types of solids

Characteristics	Molecular Solids	Covalent Network	Metallic Solids	Ionic Solids
1. Units that occupy	Atoms or molecules	Atoms	Positive ions in a 'sea of electrons'	Positive and negative ions
2. Binding forces	Vander Waal's forces (weak intermolecular forces) of following two types (i) London (dispersion) forces (ii) Dipole-dipole forces	Covalent bonding (shared pair of electrons)	Metallic bonding (extreme delocalised bond) – positively charged atomic cores surrounded by 'sea' of delocalised electrons	Ionic bonding (electrostatic attraction between positive and negative ions)
3. Physical Properties	(i) Very soft. (ii) Low melting points (iii) Non conductors	(i) Very hard (ii) Very high melting points (iii) Non conductors	(i) Hard or soft (ii) Moderate high melting points (iii) Good conductors	(i) Quite hard and brittle (ii) Fairly high melting points
4. Example	Solid Ne, Solid NH <sub>3</sub> , ice (Solid H <sub>2</sub> O), dry ice (Solid CO <sub>2</sub> )	Diamond, Carborundum (SiC), quartz (SiO <sub>2</sub> )	Cu, Fe, Ag	NaCl, KNO <sub>3</sub> , Na <sub>2</sub> SO <sub>4</sub>

### MASTERJEE CONCEPTS

Stability of a crystal is reflected in the value of its melting point. A more stable structure would require higher energy and hence melt at higher temperature.

Nikhil Khandelwal (JEE 2009 AIR 94)

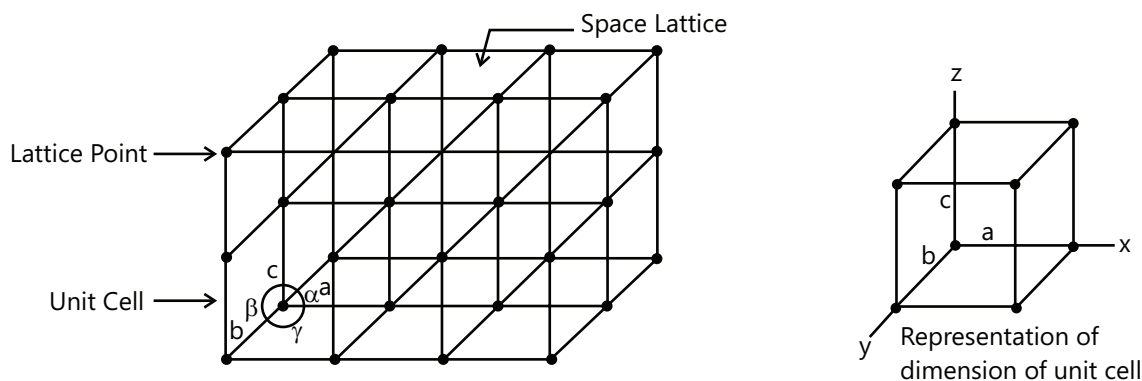
## 4. SALIENT FEATURES OF CYRSTALS

A crystal possesses the following characteristic features:

- 1. Faces:** The surfaces are usually planar and arranged on a definite plane (as a result of internal geometry)., The planes which bind the crystal, are called faces. Faces are of two types:
  - (i) Like:** A crystal having all faces alike, e.g. Fluorspar.
  - (ii) Unlike:** A crystal having all faces not alike, e.g. Galena.
- 2. Form:** All the faces corresponding to a crystal are said to constitute a form.
- 3. Edges:** The intersection of two adjacent faces forms an edge.
- 4. Interfacial Angle:** The angle between the normals to the two intersecting faces is called interfacial angle.
- 5. Zone and Zone Axis:** The faces of a crystal occur in sets called zones, which meet in parallel edges or would do so if the planes of the faces are extended. Each zone forms a complete belt around the crystal.

A line passing through the centre of a crystal in a direction parallel to the edge of zone is known as **zone axis**.

**Space Lattice:** A three dimensional arrangement of points that shows how the atoms or ions are arranged in space is called a Space Lattice. Each point is individually called a lattice point.



**Figure 19.1:** Representation of space lattice and unit cell

**Crystal Lattice:** A space lattice is called a crystal lattice when the lattice points in the space are replaced by actual atoms or ions.

**Crystal System:** The unit cell in a 3-dimension lattice is characterized by the length  $a$ ,  $b$ ,  $c$  and their angles  $\alpha$ ,  $\beta$ ,  $\gamma$ . These are known as unit cell parameters.

**Bravais Lattices:** An arrangement of spheres as given above leads to simple or primitive unit cell, when there are points only at the corner of the unit lattice. However, certain unit cells have lattice points on other sides also in addition to the corners. Such unit cell are called non-primitive unit cells. Bravais (1848) showed from geometrical considerations that there can be only 14 different ways in which similar points (spheres) can be arranged.

These fourteen types of lattice are known as Bravais lattices. They can be divided into seven crystal systems as shown below:

**Table 19.3:** Crystal system table

S.No.	Crystal System	Axial Characteristics	Examples
1.	Cubic (Most symmetrical)	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	NaCl, KCl, CsCl, zinc blende, Cu, Ag, diamond
2.	Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	White tin, $\text{SnO}_2$ , $\text{TiO}_2$

3.	Orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	Rhombic sulphur, $\text{PbCO}_3$ , $\text{PbSO}_4$ , $\text{KNO}_3$
4.	Monoclinic	$a \neq b \neq c$ $\alpha = \gamma = 90^\circ; \beta \neq 90^\circ$	Monoclinic sulphur, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
5.	Rhombohedral or trigonal	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	Calcite, quartz, As, Sb, $\text{NaNO}_3$ , ICl
6.	Triclinic (Most unsymmetrical)	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$	$\text{K}_2\text{Cr}_2\text{O}_7$ , $\text{H}_3\text{BO}_3$ , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
7.	Hexagonal	$a = b \neq c$ $\alpha = \beta = 90^\circ; \gamma = 120^\circ$	Graphite

### MASTERJEE CONCEPTS

The relationship between the plane faces (F), straight edges (e) and interfacial angle (C) for a given crystal can be written as:

$$F + C = e + 2$$

Saurabh Gupta (JEE 2010 AIR 443)

## 4.1 Laws of Crystallography

The geometric crystallography (the outward spatial arrangement of crystal planes and shape of crystals) is based on the following three fundamental laws:

- The Laws of Constancy of Interfacial Angles:** The crystals of a substance can have different shapes depending upon the number and size of the faces but the angle at which the two adjacent faces intersect remains always constant. Depending on the number and size of the faces, the crystals of a substance can have different shapes. However, the angle at which two adjacent faces intersect always remains constant.
- Hauy's Law of Rationality of Indices:** The intercepts of any face of plane of a crystal on suitable crystallographic axes can be expressed by small multiples of three unit distances a, b, c or some simple integral multiple (m, n, p) of these unit distances, i.e., ma: nb: pc or fraction of whole numbers.
- The Law of Constancy of Symmetry:** According to this law, all crystals of the same substance possess the same elements of symmetry.

## 5. SYMMETRY IN A CRYSTAL

- Centre of Symmetry:** Centre of symmetry of a crystal may be defined as an imaginary point within a crystal such that any line passing through it, intersects the crystal at equal distances in both directions e.g. staggered form of ethane possesses a centre of symmetry.

### Every Crystal Possesses Only One Centre of Symmetry

- Plane of Symmetry:** It is an imaginary plane passing through the crystal which can divide it into two equal parts in such a way that one part is an exact mirror image of the other. Thus, they are also referred to as mirror planes. There are two types of mirror planes (as shown below).

(A) Rectangular mirror planes

(B) Diagonal mirror plane

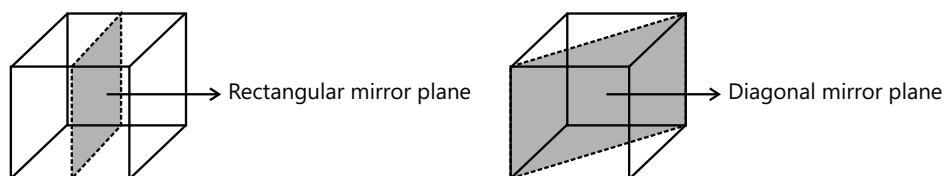


Figure 19.2: Representation of type of plane of symmetry present in a unit cell

## 5.1 Axis of Symmetry or Axis of Rotation

An axis of symmetry or axis of rotation is an imaginary line, passing through the crystal such that when the crystal is rotated about this line, it presents the same appearance more than once in one complete rotation. I.e. through  $360^\circ$ .

When the same appearance of crystal is repeated, on rotating through an angle of  $\frac{360^\circ}{n}$  around an imaginary axis it is called n-fold axis of symmetry where n- is known as order of axis.

**Two-Fold Axis:** If a similar appearance occurs two times in one complete rotation i.e. after a rotation through  $180^\circ$ , the axis is called two fold axis of symmetry or dyad axis.

**Three-Fold Axis:** If the original appearance occurs thrice, then it is called three fold axis of symmetry.

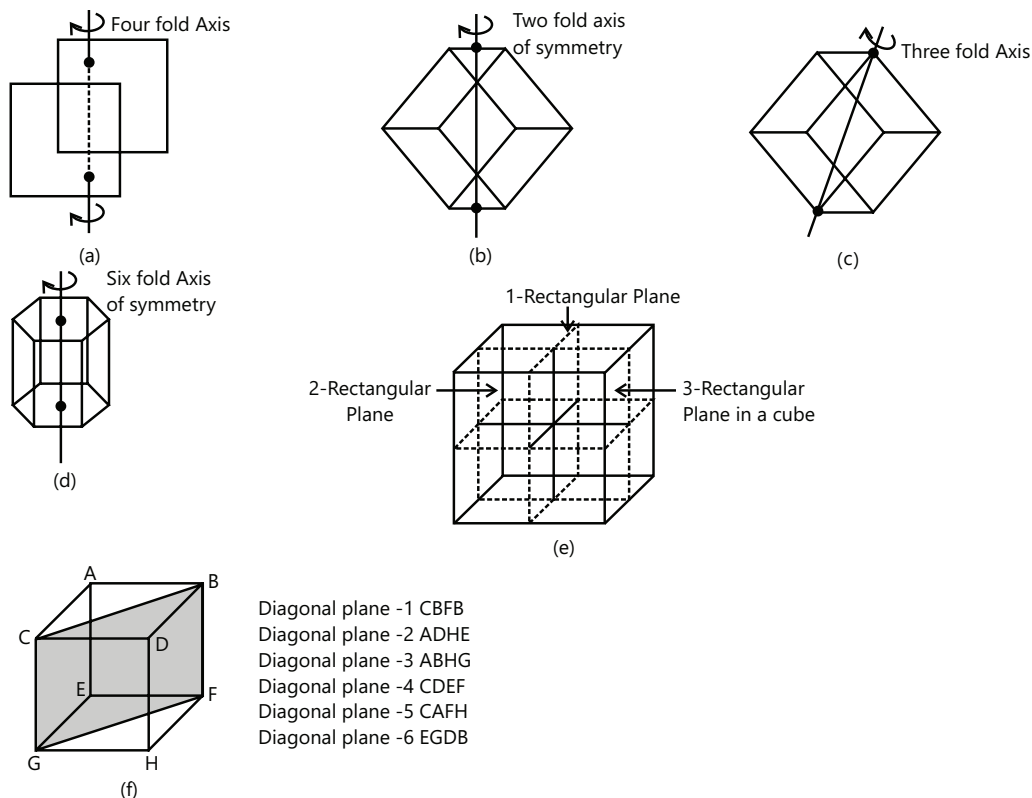


Figure 19.3: Representation of axis of symmetry present in a unit cell

### MASTERJEE CONCEPTS

A crystal may have a number of planes or axis of symmetry but it possesses only one centre of symmetry.

Neeraj Toshniwal (JEE 2009 AIR 21)

## 5.2 Total Elements of Symmetry in a Cubical Crystal

Total planes of symmetry =  $3 + 6 = 9$   
 Axis of symmetry = 4 (3-fold axis)  
                           3 (Four fold axis)  
                           6 (Six fold axis) = 13 Axes of symmetry  
 Centre of symmetry = 1  
 Hence, a cube has 23 elements of symmetry.

## 6. UNIT CELL

The smallest repeating pattern in a space lattice is called a unit cell.

### 6.1 Types of Unit Cell

Unit cells are classified as simple or primitive, body centred, face centred and end centred. This classification depends on the position of constituent particles in a unit cell.

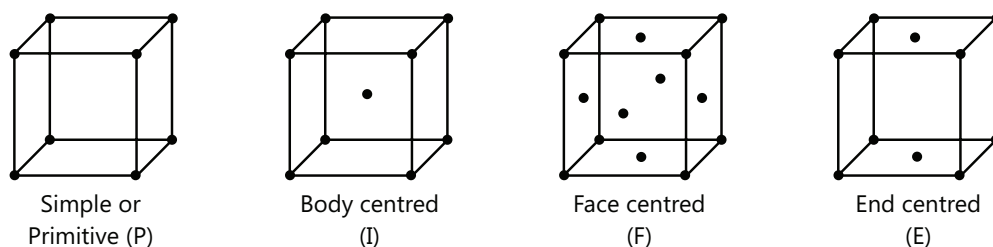


Figure 19.4: Different types of unit cell

### 6.2 Number of Atoms in a Unit Cell

- (i) A point lying at the corner of a unit cell is shared equally by eight unit cells and therefore, only one-eighth ( $1/8$ ) portion of each of such a point belongs to the given unit cell.
- (ii) A point present on an edge is distributed among the four unit cells, therefore only one-fourth ( $1/4$ ) of such a point belongs to the given unit cell.
- (iii) A face-centred point is shared between two unit cells. Therefore one-half ( $1/2$ ) part lies in each unit cell.
- (iv) A body-centred point belongs entirely to one unit cell since it is not shared by any other unit cell. Therefore, its contribution to the unit cell is one.

Table 19.4: Number of atoms in different type of unit cell

Type of cell	Number of atoms at corners	Number of atoms in faces	Number of atoms in the body of cube	Total
Simple or primitive cubic	$8 \times \frac{1}{8} = 1$	0	0	1
Body-centred cubic (bcc)	$8 \times \frac{1}{8} = 1$	0	$1 \times 1 = 1$	2
Face-centred cubic (fcc)	$8 \times \frac{1}{8} = 1$	$6 \times \frac{1}{2} = 3$	0	4

**Illustration 1:** A solid has a cubic structure in which X atoms are located at the corners of the cube, Y atoms are at the cube centres and O atoms are at the edge centres. What is the formula of the compound? **(JEE MAIN)**

**Sol:** X atom is occupying simple cubic structure, y atom occupies body center and O occupies edge centre. So calculate the no of atoms of X, Y and O present in a unit cell.

Atoms of X are present at all the eight corners of the cube. Therefore, each atom of X at the corner makes  $\frac{1}{8}$  contribution towards the unit cell.

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

Y atom is present at the body centre, thus contribution of Y towards unit cell =  $1 \times 1 = 1$

O atom is present at each of the edge centre (number of edges of cube = 12)

And each O atom present at edge centre will make  $\frac{1}{4}$  contribution towards the unit cell.

$$\text{The number of O atoms per unit cell} = 12 \times \frac{1}{4} = 3$$

The formula of the compound is, therefore  $\text{XYO}_3$ .

**Illustration 2:** A cubic crystalline solid contains P atoms at the corners and Q atoms at the body centres. If one atom from the corner is missing, what will be the simplest formula of the resulting solid? **(JEE MAIN)**

$$\text{Sol: } Z_P = 7 \times \frac{1}{8} = \frac{7}{8}$$

$$Z_Q = 1$$

$\therefore$  The simplest formula is  $\text{P}_{\frac{7}{8}}\text{Q} = \text{P}_7\text{Q}_8$ .

**Illustration 3:** A compound alloy of gold and copper crystallizes in a cube lattice in which the gold atoms occupy the lattice points at the corners of a cube and the copper atoms occupy the centres of each of the cube faces. Determine the formula of this compound. **(JEE MAIN)**

**Sol:** Determine the number of atoms of Au (Occupying simple primitive structure) present in one unit cell and no. of atoms of Cu (occupying face center arrangement) present in one unit cell .

One-eighth of each corner atom (Au) and one-half of each face-centred atom (Cu) are contained within the unit cell of the compound.

Thus, number of Au atoms per unit cell =  $8 \times \frac{1}{8} = 1$  , and

$$\text{Number of Cu atoms per unit cell} = 6 \times \frac{1}{2} = 3 .$$

The formula of the compound is  $\text{AuCu}_3$ .

**Illustration 4:** A compound formed by elements A and B crystallizes in cubic structure where A atoms are at the corners of a cube and B atoms are at the body centre of the cube. What is the formula of the compound? **(JEE MAIN)**

**Sol:** Determine the number of atoms of A (Occupying Corner of a cube) present in one unit cell and no. of atoms of Ag (occupying Body center arrangement) present in one unit cell

An atom at the corner of the cube is shared by 8 cubes and hence, contributes only  $\frac{1}{8}$  to a particular cube. There are eight corners of a cube.

$$\therefore \text{The number of A atoms in the unit cell} = 8 \times \frac{1}{8} = 1$$

An atom at the body centre of cube belongs only to one unit cell.

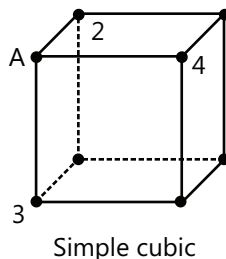
$$\therefore \text{Number of atoms of B in the unit cell} = 1 \times 1 = 1.$$

Thus, formula is AB.

### 6.3 Coordination Number

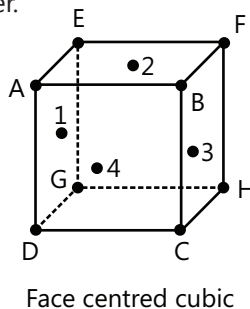
The number of nearest neighbours that an atom has in a unit cell is called the coordination number. In ionic crystal, the number of oppositely charged ions surrounding each ion is called its co-ordination number. The co-ordination number of a crystal depends upon its structure.

- (a) **Simple Cubic Structure:** It is clear from the Figure that each atom say (A) has 4 nearest neighbours 2, 3, 4 and one to the left of A of another unit cell in one plane. In addition, it also possesses one atom vertically above of another unit cell. Thus, in all, A possesses six neighbour atoms and therefore, a simple cubic structure reveals a co-ordination number of six, e.g., NaCl.



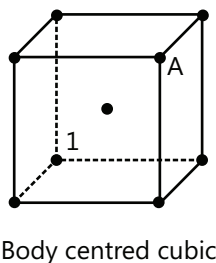
**Figure 19.5-a:** Diagrammatic representation of simple unit cell

- (b) **Face Centred Cubic Structure (fcc):** It is clear, from the figure, that the nearest neighbour of a corner atom is the face centred atom and thus, each atom say (A) has 4 nearest neighbours 1, 2, 4 and the other is on its left side from another cell. In addition, it also possesses four face centred atoms in planes below and above it. Thus, in all, A possesses 12 neighbour atoms and therefore, face centred cubic structure reveals a co-ordination number of twelve, e.g., Copper.



**Figure 19.5-b:** Diagrammatic representation face centred unit cell

- (c) **Body Centred Cubic Structure (bcc):** It is clear from the figure, that the nearest neighbour of a corner atom is body centred atom. Thus, each atom say (A) has eight body centred atoms of 8 surrounding unit cells as neighbours in one plane, since A is surrounded by 8 surrounding unit cells. Thus, a body centred cubic structure reveals a co-ordination number of eight, e.g., CsCl.



**Figure 19.5-c:** Diagrammatic representation of body centred unit cell



**MASTERJEE CONCEPTS**

Pressure and temperature changes the coordination number of a crystal.

- High pressure increases the co-ordination number.
- High temperature decreases the co-ordination number.

**Aman Gour (JEE 2012 AIR 230)**

**6.4 Density of Lattice Matter**

It is defined as the ratio of mass per unit cell to the Volume of unit cells.

$$\text{Density of lattice matter} = \frac{\text{mass per unit cell}}{\text{volume of unit cell}}$$

$$\text{Mass per unit cell} = \text{No. of Atoms} \times \text{Mass of one of atom} = n \times \frac{\text{Atomic mass}}{\text{Avog. No.}}$$

$$\text{Density of lattice matter} = \frac{n \times \text{at. wt.}}{\text{Av. no.} \times \text{volume of unit cell}}$$

$$\rho = \frac{n \times \text{atomic mass (or molar mass)}}{N_A \times V}$$

$$\rho = \frac{n \times \text{atomic mass}}{N_A \times a^3}$$

Where 'a' is edge length of cube. (in cm)

Where 'n' is number of atoms per unit cell; volume of unit cell is to be derived for given crystal system. It is equal to  $a^3$  for cubic crystal systems.

**Illustration 5:** The edge length of a cubic crystal of an element is found (by X-ray diffraction) to be 'a' picometres. Show how you can calculate its density. **(JEE MAIN)**

**Sol:** The density of the unit cell is the same as the density of the substance.

$$\text{Edge length of unit cell} = a \text{ pm} = a \times 10^{-10} \text{ cm}$$

$$\text{Volume of the unit cell} = a^3 \times 10^{-30} \text{ cm}^3$$

$$\text{Density of the unit cell} = \frac{n \times M}{a^3 \times N_A \times 10^{-30}} \text{ gcm}^{-3}$$

**Illustration 6:** Chromium metal crystallizes with a body centred cubic lattice. The edge length of the unit cell is found to be 287 pm. Calculate the atomic radius. What would be the density of chromium in  $\text{g/cm}^3$ ? (At. wt. of Cr = 51.99) **(JEE MAIN)**

**Sol:** From the given value of edge length first determine the atomic radius for a bcc crystal lattice and density can be determined using the following formula,

$$\text{Density} = \frac{n \times \text{at. wt.}}{V \times \text{Av. no.}} = \frac{n \times \text{at. wt.}}{a^3 \times \text{Av. no.}}$$

$$\text{For bcc lattice, } r = \frac{\sqrt{3}a}{4} = \frac{\sqrt{3}}{4} \times 287 = 124.27 \text{ pm}$$

$$\text{Now, Density} = \frac{n \times \text{at. wt.}}{V \times \text{Av. no.}} = \frac{n \times \text{at. wt.}}{a^3 \times \text{Av. no.}}$$

$$n = 2 \text{ for bcc; } a = 287 \text{ pm} = 287 \times 10^{-10} \text{ cm}$$

$$\therefore \rho = \frac{2 \times 51.99}{(287 \times 10^{-10})^3 \times (6.023 \times 10^{23})} = 7.31 \text{ g/cm}^3$$

**Illustration 7:** An element (density  $6.8 \text{ g cm}^{-3}$ ) occurs in bcc structure with unit cell edge of  $290 \text{ pm}$ . Calculate the number of atoms present in  $200 \text{ g}$  of the element. **(JEE ADVANCED)**

**Sol:** First determine the molecular mass of the element by using following equation,

$$\text{Density} = \frac{n \times M}{\text{Av.no.} \times a^3}$$

And from molecular mass determine the number of atoms present in  $200 \text{ g}$  of the element.

Let  $M$  be the molecular mass of the element.

$$\text{Volume of the unit cell} = a^3 = (290 \times 10^{-10} \text{ cm})^3 = 24.4 \times 10^{-24}$$

In a body centred cubic (bcc) structure  $n = 2$ .

$$\text{Density} = \frac{n \times M}{\text{Av.no.} \times a^3}$$

$$6.8 = \frac{2 \times M}{6.023 \times 10^{23} \times 24.4 \times 10^{-24}}$$

$$M = \frac{6.8 \times 6.023 \times 10^{23} \times 24.4 \times 10^{-24}}{2} = 50 \text{ g}$$

$\therefore$   $50 \text{ g}$  of the element contain  $6.023 \times 10^{23}$  atoms

$$200 \text{ g of the element would contains} = \frac{6.023 \times 10^{23} \times 200}{50} = 24.09 \times 10^{23} \text{ atoms}$$

## 6.5 Nearest Neighbouring Distance in Case of Identical Spheres

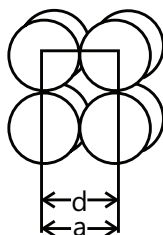
Nearest neighbouring distance is the distance between the centres of any two touching spheres.

**(a)** In case of SCC (Simple Cubic Lattice)

In a simple cubic lattice the edge length ( $a$ ) = Nearest neighbouring distance

$$a = d = 2r$$

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



**Figure 19.6-a:** Nearest neighbouring distance in case of SCC

**(b)** Body Centred

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

$$\Rightarrow (\text{Body Diagonal})^2 = (\text{Face Diagonal})^2 + (\text{edge})^2$$

$$= 2(\text{edge})^2 + (\text{edge})^2 = 3(\text{edge})^2$$

$$\Rightarrow (\text{Body Diagonal})^2 = 3(\text{edge})^2 = 3a^2$$

$$\therefore \text{body diagonal} = \sqrt{3} a$$

$$\text{Also Body Diagonal} = r + 2r + r = 4r$$

$$\Rightarrow 24r = \sqrt{3}a \Rightarrow r = \frac{\sqrt{3}}{4}a$$

$$d = 2r \Rightarrow d = \frac{\sqrt{3}}{2}a = \text{nearest neighbouring distance}$$

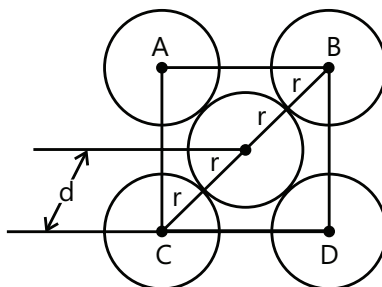


Figure 19.6-b: Nearest neighbouring distance in case of BCC

### (c) Face Centred Cubic Lattice

$$\text{Here } (\text{Face diagonal})^2 = (\text{edge})^2 + (\text{edge})^2$$

$$\therefore (\text{face diagonal})^2 = a^2 + a^2 = 2a^2$$

$$\therefore \text{face diagonal} = \sqrt{2} a$$

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

$$r = \frac{\sqrt{2}}{4}a \Rightarrow r = \frac{1}{2\sqrt{2}}a \Rightarrow d = \frac{\sqrt{2}}{2}a = \frac{1}{\sqrt{2}}a$$

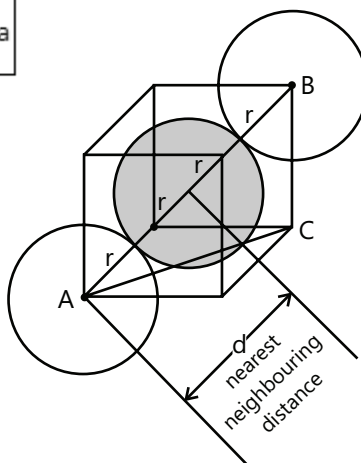


Figure 19.6-c: Nearest neighbouring distance in case of FCC

## 6.6 Packing Fraction

### Packing Fraction in Case of Identical Spheres

Packing fraction is the ratio of volume occupied by sphere to the total volume of the cube

$$\text{Packing Fraction} = \frac{\text{Volume occupied by sphere}}{\text{Total volume of cube}} = \frac{\frac{4}{3}\pi r^3 \times z}{a^3}$$

where  $a$  = edge of cube,  $z$  = number of sphere per unit cell

**Packing fraction of SCC**

$$r = \frac{a}{2}, z = 1; \quad \text{PF} = \frac{\frac{4}{3}\pi\left(\frac{a}{2}\right)^3 \times z}{a^3} = \frac{4\pi}{8 \times 3} = \frac{\pi}{6}$$

$$\Rightarrow \text{PF} = \frac{\pi}{6} = 0.524$$

$$\Rightarrow \% \text{ volume occupied by sphere} = \frac{\pi}{6} \times 100 = 52.4\%$$

$$\Rightarrow \% \text{ Free space} = 100 - 52.4 = 47.6\%$$

**Packing fraction for BCC**

$$r = \frac{\sqrt{3}}{4}a, z = 2; \quad \text{PF} = \frac{\frac{4}{3}\pi\left(\frac{\sqrt{3}}{4}a\right)^3 \times 2}{a^3} = \frac{4}{3} \times \frac{\pi \times 3\sqrt{3} \times 2}{64} = \frac{\sqrt{3}\pi}{8} = 0.68$$

$$\Rightarrow \% \text{ volume occupied} = 100 \times 0.68 = 68\%$$

$$\% \text{ Free space} = 100 - 68 = 32\%$$

**Packing Fraction for FCC**

$$r = \frac{\sqrt{2}}{4}a, z = 4 \quad \text{PF} = \frac{\frac{4}{3}\pi\left(\frac{\sqrt{2}}{4}a\right)^3 \times 4}{a^3} = \frac{4}{3} \times \frac{\pi \times 2\sqrt{2} \times 4}{64} = \frac{\sqrt{2}\pi}{6} = 0.7407$$

$$\Rightarrow \text{PF} = \frac{\sqrt{2}\pi}{6} = 0.740$$

$$\% \text{ volume occupied} = 100 \times 74 = 74 \%$$

$$\% \text{ Free space} = 100 - 74 = 26 \%$$

**MASTERJEE CONCEPTS**

The packing density data reveals that close packing of atoms in cubic structure follow the order, FCC > BCC > SCC, i.e., more closely packed atoms are in FCC structure.

**B Rajiv Reddy (JEE 2012 AIR 11)**

**Table 19.5:** Summary of Various Characteristics of Different Cubic Systems

S. No.	Cubic	Nuber of effective atoms per unit cell ( $Z_{\text{eff}}$ )	Coordination Number (CN)	Atomic radius ( $r$ )	Packing efficiency	Density ( $\rho$ ) ( $\text{g cm}^{-3}$ )	Nearest neighbour distance ( $d$ )
1.	Simple cube (sc)	1	6	$r = \frac{a}{2}$	$\text{PE} = \frac{\pi}{6} \times 100 = 52.4\%$	$\rho = \frac{Z_{\text{eff}} \times \text{Mw}}{N_A \times a^3 \times 10^{-30}}$ $= \frac{1 \times \text{Mw}}{N_A \times a^3 \times 10^{-30}}$	a

2.	Body centred cubic (bcc)	2	8	$r = \frac{\sqrt{3}a}{4}$	$PE = \frac{\sqrt{3}}{8} \pi \times 100$ = 68%	$\rho = \frac{2 \times Mw}{N_A \times a^3 \times 10^{-30}}$	$\frac{\sqrt{3}}{2} a$
3.	Face centred cubic (fcc)	4	12	$r = \frac{a}{2\sqrt{2}}$	$PE = \frac{\sqrt{2}}{6} \pi \times 100$ = 74.04%	$\rho = \frac{4 \times Mw}{N_A \times a^3 \times 10^{-30}}$	$\frac{a}{\sqrt{2}}$

**Illustration 8:** The density of solid Argon is 1.65 g/mL at  $-233^\circ\text{C}$ . If the Argon atom is assumed to be sphere of radius  $1.54 \times 10^{-8}$  cm. What percentage of solid Argon is apparently empty space? ( $A_r = 40$ ) **(JEE ADVANCED)**

**Sol:** First determine the no. of atoms of Ar present in 1.65 g from this calculate the total volume occupied by all atoms of Ar. we can determine % empty space by subtracting the volume of solid Ar taken and volume occupied by Ar,

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

$$\text{Also, number of atoms in 1.65 g or one cm}^3 = \frac{1.65}{40} \times 6.023 \times 10^{23} = N$$

$$\therefore \text{Total volume of all atoms of Ar in solid state} = \frac{4}{3} \pi r^3 N = \frac{4}{3} \times \frac{22}{7} \times (1.54 \times 10^{-8})^3 \times \frac{1.65}{40} \times 6.023 \times 10^{23} = 0.380 \text{ cm}^3$$

As the volume of solid argon taken =  $1 \text{ cm}^3$

$$\therefore \% \text{ empty space} = \frac{[1 - 0.380]}{1} \times 100 = 62\%$$

## 7. CLOSED PACKING OF CONSTITUENTS

**(a) Close Packing in One Dimension:** Here, spheres are arranged in a row, touching each other, in a one-dimensional close packed structure as shown below,

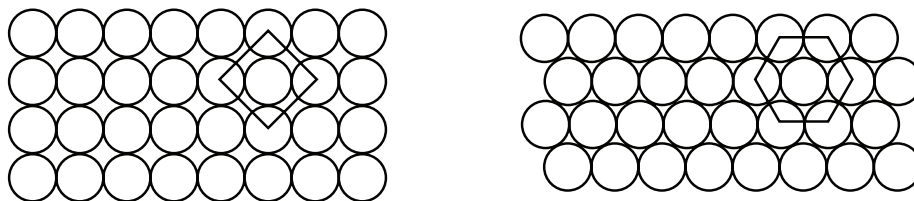


**Figure 19.7-a:** Close packing of spheres in one dimension

**(b) Close Packing in Two Dimensions:** Two-dimensional close packed structure can be produced by stacking the rows of close packed spheres. This can be done in two different ways as shown in figures (a) and (b).

**(i)** Square close packing

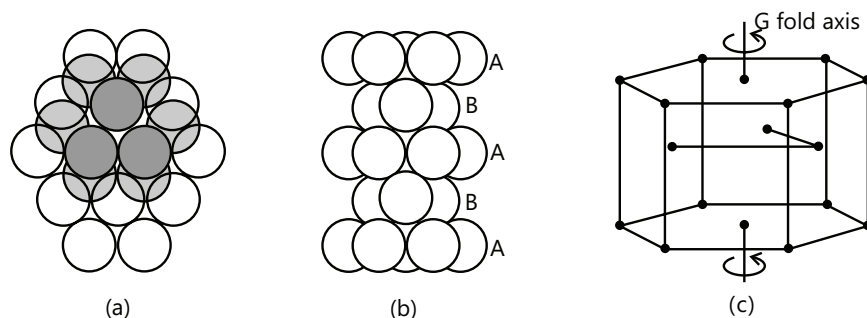
**(ii)** Hexagonal close packing



**Figure 19.7-b:** Close packing of spheres in two dimension

**(c) Close Packing in Three Dimensions:**

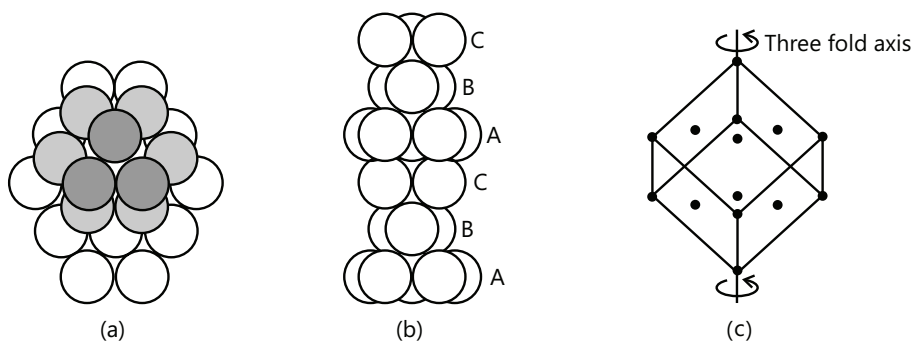
- (i) **Hexagonal Close Packing (HCP):** While forming the first layer, minimum space is wasted by utilizing the maximum space possible. In every second row the particles occupy the depressions (also called voids) between the particles of the first row. In the third row, the particles are vertically aligned with those in the first row giving AB AB AB ... type of arrangement. This structure has hexagonal symmetry and is known as hexagonal close packing (HCP). In HCP, the coordination number is 12 and only 26% space is free. A single unit cell has 4 atoms.



**Figure 19.7-c:** Hexagonal close packing of spheres in three dimension

- (ii) **Cubic Close Packing (CCP):** If we start with hexagonal layer of spheres and second layer of spheres is arranged by placing the spheres over the voids of the first layer, half of these holes can be filled by these spheres. Presume that spheres in the third layer are arranged to cover octahedral holes. When organized this way, the third layer does not resemble either the first or second layer; but the fourth layer is similar to the first layer, fifth layer to second, sixth to third and so on giving pattern ABCABCABC ... . This arrangement has cubic symmetry and is known as cubic closed packed (CCP) arrangement. This is also called face-centred cubic (FCC) arrangement.

The free space available in this packing is 26% and coordination number is 12.



**Figure 19.7-d:** Cubic close packing of spheres in three dimension

- (iii) **Body Centred Close Packing (BCP):** In B.C.P. arrangement, 8 particles are present at the corners and 1 particle is present at the body centre. The coordination number of central sphere is 8. The efficiency of this type of packing is less, only 68% space is occupied and 32% remains unoccupied. A single unit cell has 2 atoms.

### MASTERJEE CONCEPTS

- In two dimensional hexagonal close packing, there is less free space between sphere than two dimensional square close packing. Thus, hexagonal close packing is denser than square close packing.
- In hexagonal close packing about 60.4% of available space is occupied by spheres whereas square close packing occupies only 52.4% of the space by spheres.
- If only one layer of spheres is to be packed, the spheres arrange themselves in hexagonal close packing.
- In both CCP and HCP, the co-ordination number of spheres remain twelve.

Rohit Kumar (JEE 2012 AIR 79)

**Illustration 9:** A hexagonal close-packed structure and a cubic close-packed structure for a given element would be expected to have the same density. Explain. **(JEE MAIN)**

**Sol:** In both the structures, the fraction of the total volume occupied is 0.74. The two structures have the same co-ordination number of 12.

## 8. VOIDS OR HOLES

The voids/holes are the empty spaces in between closed packed spheres.

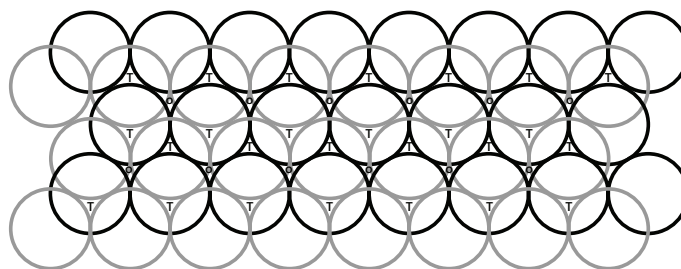


Figure 19.8-a: Representation of a Void

### Types of Voids:

- (a) **Octahedral Voids:** This void is surrounded by six spheres and formed by a combination of two triangular voids of the first and second layer. There is one octahedral void per atom in a crystal. The radius ratio ( $r_{\text{void}}/r_{\text{sphere}}$ ) is 0.414.

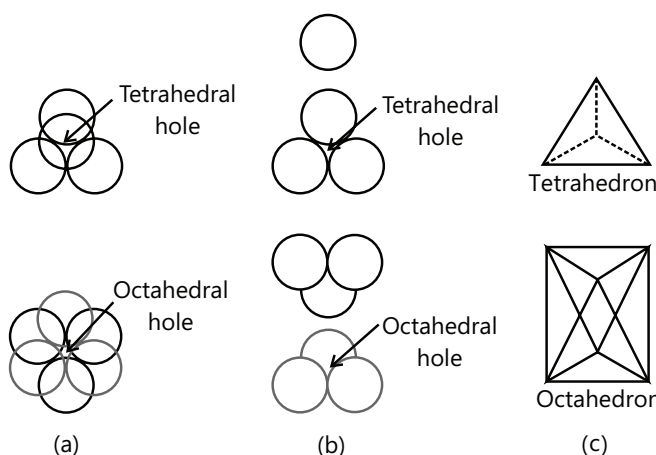


Figure 19.8-b: Tetrahedral and Octahedral Voids (a) top view, (b) exploded side view, and (c) Geometrical shape of the void

- (b) **Tetrahedral Voids:** These voids are surrounded by four spheres, which lie at the vertices of a regular tetrahedron. There are 2 tetrahedral voids per atom in a crystal and the radius ratio is 0.225.
- (c) **Trigonal Voids:** The void enclosed by three spheres in contact is called a trigonal void. There are 8 trigonal voids per atom in a crystal and the radius ratio is 0.155.

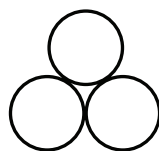


Figure 19.8-c: Trigonal void

**Locating Tetrahedral and Octahedral Voids:** Both octahedral and tetrahedral voids are present in all closed packed structures. In a CCP pattern, there is one octahedral void at the centre of body and 12 octahedral voids in each of the 12 edges of the cube. Each void on the edge is shared by four other unit cells.

### MASTERJEE CONCEPTS

The co-ordination number of a tetrahedral void is four. The co-ordination number of an octahedral void is six.

Krishan Mittal (JEE 2012, AIR 199)

Table 19.6: Summary of the Main Characteristics and Examples of Some Simple Ionic Solids

Crystal Structure	Brief description	Examples	Coordination number	Number of formula unit/ units cell	Coordination number
Type AB: Rock salt (NaCl) type	It has fcc arrangement in which $\text{Cl}^-$ ion occupy the corners and face centres of a cube while $\text{Na}^+$ ions are present at the body and edge centres.	Halides of Li, Rb, AgF, AgBr, $\text{NH}_4\text{Cl}$ , $\text{NH}_4\text{Br}$ , $\text{NH}_4\text{I}$	Each $\text{Na}^+$ is surrounded by 6 $\text{Cl}^-$ . Each $\text{Cl}^-$ is surrounded by 6 $\text{Na}^+$ ; occupy all OVs	General formula $\text{A}_4\text{B}_4$ or AB $Z_{\text{eff}} = 4$	6: 6
Radius for fcc	$(r^+ + r^-) = \frac{a}{2}$				
Cesium Chloride (CsCl) type	It has bcc arrangement with $\text{Cs}^+$ at the body centre and $\text{Cl}^-$ ions at the corners of a cube or vice versa.	CsCl, CsBr, CsI, CsCN, TlCl, TlBr, TlI and TICN	Each $\text{Cs}^+$ is surrounded by 8 $\text{Cl}^-$ . Each $\text{Cl}^-$ is surrounded by 8 $\text{Cs}^+$ .	General formula AB $Z_{\text{eff}} = 1$	8: 8
Radius for bcc type	$(r^+ + r^-) = \frac{\sqrt{3}a}{2}$				
Zinc blende (ZnS) (sphalerite) type	It has ccp arrangement in which $\text{S}^{2-}$ ions form fcc and each $\text{Zn}^{2+}$ ion is surrounded tetrahedrally by $\text{S}^{2-}$ ion vice versa.	CuCl, CuBr, CuI, AgI	Each $\text{Zn}^{2+}$ is surrounded by 4 $\text{S}^{2-}$ . Each $\text{S}^{2-}$ is surrounded by 4 $\text{Zn}^{2+}$ . $\text{Zn}^{2+}$ are in alternate TVs.	General formula $\text{A}_4\text{B}_4$ or AB $Z_{\text{eff}} = 4$	4: 4



Crystal Structure	Brief description	Examples	Coordination number	Number of formula unit/ units cell	Coordination number
Type AB <sub>2</sub> Fluorite (CaF <sub>2</sub> ) type	It has ccp arrangement in which Ca <sup>2+</sup> ions form fcc with each Ca <sup>2+</sup> ions surrounded by 8 F <sup>-</sup> ions and each F <sup>-</sup> by 4 Ca <sup>2+</sup> ions	BaF <sub>2</sub> , BaCl <sub>2</sub> , SrF <sub>2</sub> , SrC <sub>2</sub> , CdF <sub>2</sub> , PbF <sub>2</sub>	Each Ca <sup>2+</sup> is surrounded by 8 F <sup>-</sup> . Each F <sup>-</sup> is surrounded by 4 Ca <sup>2+</sup> . F <sup>-</sup> ions occupy all the 8 TVs.	General formula A <sub>4</sub> B <sub>4</sub> or AB Z <sub>eff</sub> = 4	8: 4
Type A <sub>2</sub> B Antifluorite Type	Here O <sup>2-</sup> form the ccp arrangement so that each Na <sup>+</sup> ion is surrounded by four O <sup>2-</sup> ions and each O <sup>2-</sup> ion is surrounded by 8 Na <sup>+</sup> ions.	Na <sub>2</sub> O, Li <sub>2</sub> O	Each Na <sup>+</sup> is surrounded by 4 O <sup>2-</sup> . Each O <sup>2-</sup> is surrounded by 8 Na <sup>+</sup> . Na <sup>+</sup> ions occupy all the TVs	General formula A <sub>4</sub> B <sub>4</sub> or AB Z <sub>eff</sub> = 4	4: 8

**Illustration 10:** In a cubic lattice, the closed packed structure of mixed oxides of the lattice is made up of oxide ion; one eighth of the tetrahedral voids are occupied by divalent ions (A<sup>2+</sup>) while one half of the octahedral voids are occupied by trivalent ions (B<sup>3+</sup>). What is the formula of the oxides? **(JEE ADVANCED)**

**Sol:** Let there be n no. of O<sup>2-</sup> in the crystal.

∴ Octahedral voids = n

Tetrahedral voids = 2n

$$A^{2+} \text{ ions} = \frac{1}{8} \times 2n = \frac{n}{4}, \quad B^{3+} \text{ ions} = \frac{1}{2} \times n = \frac{n}{2}$$

$$A^{2+} : B^{3+} : O^{2-} = \frac{n}{4} : \frac{n}{2} : n = 1 : 2 : 4$$

∴ Formula is **AB<sub>2</sub>O<sub>4</sub>**.

## 9. RADIUS RATIO

The ratio of radius of cation to anion is known as radius ratio of ionic solids, i.e.,

$$\text{Radius ratio} = \frac{\text{Radius of cation (or } r^+)}{\text{Radius of anion (or } r^-)}$$

Following important conclusions can be drawn from radius ratio of ionic solids.

- If the radius ratio ( $r^+/r^-$ ) = 0.225, the cation would fit exactly into the tetrahedral voids and have co-ordination number four.
- If the radius ratio ( $r^+/r^-$ ) = 0.414, the cation would fit exactly into the octahedral voids and have co-ordination number six.

**Illustration 11:** If the radius of the bromide ion is 0.182 nm, how large a cation can fit in each of the tetrahedral hole? **(JEE MAIN)**

**Sol:** Radius ratio =  $\frac{\text{Radius of cation (or } r^+)}{\text{Radius of anion (or } r^-)}$

For tetrahedral voids ( $r^+/r^-$ ) = 0.414

From the given value of radius of the bromide ion determine the radius for cation. Depending upon the size of the cation predict the answer.

For tetrahedral voids  $(r^+/r^-) = 0.414$  (for maximum value of  $r^+$ )

$$r^+ = 0.414 \times 0.182 = \mathbf{7.53 \times 10^{-2} \text{ nm}}$$

Thus, cation of  $7.53 \times 10^{-2} \text{ nm}$  will fit exactly in tetrahedral voids.

**Illustration 12:** In the cubic crystal of CsCl ( $d = 3.97 \text{ g cm}^{-3}$ ) the eight corners are occupied by  $\text{Cl}^-$  with a  $\text{Cs}^+$  at the centre and vice versa. Calculate the distance between neighbouring  $\text{Cs}^+$  and  $\text{Cl}^-$  ions. What is the radius ratio of the two ions? (At. wt. of Cs = 132.91 and Cl = 35.45) **(JEE ADVANCED)**

**Sol:** In a unit cell,  $n = 1$  for cubic crystal

$$\therefore \text{density} = \frac{n \times \text{mol.wt.}}{V \times \text{Av.No.}} = \frac{n \times \text{mol.wt.}}{a^3 \times \text{Av.No.}}$$

$$\therefore 3.97 = \frac{1 \times 168.36}{a^3 \times 6.023 \times 10^{23}}$$

$$a = 4.13 \times 10^{-8} \text{ cm}$$

$$a = 4.13 \text{ \AA}$$

For a cube of side length 4.13 Å.

$$\text{Diagonal} = \sqrt{3} \times 4.13 = 7.15 \text{ \AA}$$

As it is a bcc with  $\text{Cs}^+$  at centre (radius  $r^+$ ) and  $\text{Cl}^-$  corners (radius  $r^-$ ) so,

$$2r^+ + 2r^- = 7.15 \text{ or } r^+ + r^- = 3.57 \text{ \AA}$$

i.e., distance between neighbouring  $\text{Cs}^+$  and  $\text{Cl}^- = 3.57 \text{ \AA}$

Now assume two  $\text{Cl}^-$  ions touching each other

So, Length of unit cell =  $2r^- = 4.13 \text{ \AA}$

$$\therefore r^- = 2.06 \text{ \AA}$$

$$\therefore r^+ = 3.57 - 2.06 = 1.51$$

$$\therefore \frac{r^+}{r^-} = \frac{1.51}{2.06} = 0.73$$

## 10. DEFECTS

**Atomic Imperfection:** Atomic imperfections are the defects that arise due to irregularity in the arrangement of atoms or ions. These are of following types:

**Point Defects:** These are caused by missing or misplaced atoms or ions. These involve:

**(a) Vacancy defect:** If an atom or ion is missing from the lattice site, the defect is known as vacancy defect.

**(b) Impurity defect:** If a foreign atom or ion occupies a lattice site as an impurity, the defect is called impurity defect. If the foreign atom or ion occupies voids in the structure, the defect is called **interstitial impurity**.

**Point Defects:** These are caused by a departure from the periodic arrangement in the vicinity of an atom or a group of atoms. Point defects in crystals may be classified as:

**(a)** Defects in stoichiometric solids, also called as stoichiometric defects.

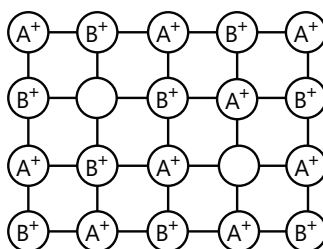
**(b)** Defects in non-stoichiometric solids, also called as non-stoichiometric defects.

**(c)** Impurity defects.

**Defects in Stoichiometric Solids:** Stoichiometric solids are those in which the number of positive and negative ions are exactly in the ratio indicated by their chemical formulae. These are of 2 types (i) Schottky defect, (ii) Frenkel defect

**(i) Schottky Defect:** A pair of 'holes' or vacancies exists in the crystal lattice due to one cation and one anion missing from the normal lattice sites. As the number of missing cations and anions remain the same, the crystal as a whole remains the same. This sort of defect occurs in highly ionic compounds with a high coordination number and where the ions (both cations and anions) are of similar size. Alkali metal halides such as NaCl, KCl, KBr, AgBr and CsCl show this defect. In NaCl crystal, at room temperature, there will be one Schottky defect per  $10^{16}$  ions.

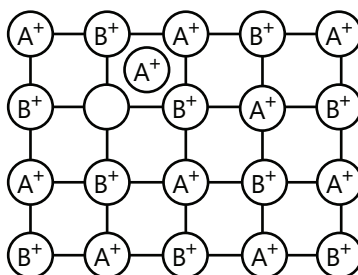
Since the presence of large number of Schottky defects in a crystal leads to decrease in the number of ions in the lattice, this results in lowering the density of the solid markedly.



**Figure 19.9-a:** Schottky defect in a crystal

**(ii) Frenkel Defect:** When a 'hole' or 'vacancy' exists in the crystal lattice because an ion occupies an interstitial lattice site, it gives rise to Frenkel defect. The crystal remains neutral. The defect occurs more frequently in solids which have low coordination number and possess ions (cations and anions) of different sizes. Since cations are generally smaller than anions, it is more common to find the cations occupying the interstitial sites. For example, in AgBr and ZnS crystals.  $\text{Ag}^+$  ions and  $\text{Zn}^{2+}$  ions are missing from their normal lattice sites and are present in the interstitial positions. AgBr, AgCl and AgI are special cases which show both Schottky and Frenkel defects.

However, the density of the solid remains the same as the presence of Frenkel defect does not change the number of ions in the lattice. The defect causes increase in dielectric constant of the crystals as similar charges come closer.

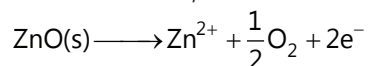


**Figure 19.9-b:** Frenkel defect observed in a crystal

**Illustration 13:** Explain, why ZnO becomes yellow on heating?

**(JEE ADVANCED)**

**Sol:** Due to Frenkel defect, when ZnO is heated, it loses oxygen reversibly and turns yellow in colour.



The  $\text{Zn}^{2+}$  ions formed enter the vacant voids in the crystal to form non-stoichiometric solid. The released electrons are trapped in its neighbourhood. It is therefore, non-stoichiometric ZnO is yellow and shows increased conductivity.

**Table 19.7:** Difference between frenkel and schottky defects

S.No.	Frenkel Defects	Schottky Defects
1.	The ion occupies an interstitial position than its actual lattice position.	Both cations and anions are missing from their lattice positions in the crystal (vacancy defect).

2.	There is no change in the density of the crystal.	The defect decreases the density of the crystal.
3.	It occurs in ionic compounds with low coordination number and with a large difference in the size of cations and anions.	It occurs in compounds with high coordination number and with ions of similar sizes.

**Illustration 14:** Calculate the concentration of cation vacancies if NaCl is doped with  $10^{-3}$  mole % of  $\text{SrCl}_2$ .

**(JEE ADVANCED)**

**Sol:** Doping of  $\text{SrCl}_2$  to NaCl brings in replacement of two  $\text{Na}^+$  ion by each  $\text{Sr}^{2+}$  ion, but each  $\text{Sr}^{2+}$  occupies only one lattice point. This produces one cation vacancy.

Thus, doping of  $10^{-3}$  moles of  $\text{SrCl}_2$  in 100 mole NaCl will produce cation vacancies =  $10^{-3}$  moles.

$\therefore$  100 mole NaCl will have cation vacancies after doping =  $10^{-3}$  moles.

$\therefore$  1 mole of NaCl will have cation vacancies =  $\frac{10^{-3}}{100} = 10^{-5}$

$\therefore$  Total cationic vacancies =  $10^{-5} \times N_A = 6.02 \times 10^{18}$

## 11. MAGNETIC PROPERTIES OF SOLIDS

On the basis of their magnetic properties, substances can be classified into five categories.

**Table 19.8:** Magnetic properties of crystals

Sr. No	Properties	Information	Magnetic Alignment	Example	Application
1.	Diamagnetic	Repelled weakly in magnetic field. Such solids have only paired electrons.	$\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$	Benzene, NaCl, $\text{TiO}_2$ , $\text{V}_2\text{O}_5$ , etc.	Insulators
2.	Paramagnetic	Have unpaired electrons; weakly attracted in magnetic field. They cannot be permanently magnetised.	$\uparrow\downarrow \rightarrow \uparrow\downarrow$	$\text{O}_2$ , VO, CuO, TiO	Electronic devices
3.	Ferromagnetic	Also, have unpaired electrons. Strongly attracted in magnetic field. Such solids can be permanently magnetised. On heating to a temperature called Curie Point, these solids change to paramagnetic solid.	$\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow$	Fe, Ni, Co, $\text{CrO}_2$	$\text{CrO}_2$ is used in audio, video tapes.
4.	Antiferromagnetic	In these solids changes electrons align themselves in such a way that resultant magnetic moment is zero.	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$	$\text{Cr}_2\text{O}_3$ , CoO, $\text{Co}_3\text{O}_4$ , $\text{Fe}_2\text{O}_3$ , MnO, $\text{MnO}_2$	Used in the instruments of magnetic susceptibility measurement
5.	Ferrimagnetic	unpaired electrons align themselves in such way that there is a net magnetic moment.	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$ or $\uparrow\uparrow \downarrow\downarrow \uparrow\uparrow$ $\downarrow\downarrow \uparrow\uparrow$ and so on	$\text{Fe}_3\text{O}_4$	–

**Curie Temperature:** The temperature at which a ferromagnetic substance loses its ferromagnetism and attains paramagnetism only is called Curie temperature. For iron, the Curie temperature is 1033 K, for Ni it is 629 K and for  $\text{Fe}_3\text{O}_4$  it is 850 K. Below this temperature, paramagnetic substances behave as ferromagnetic substances.

## 12. ELECTRICAL PROPERTIES OF SOLIDS

Solids are classified into three groups on the basis of their electrical conductivities:

- 1. Conductors:** These generally include metals. Their conductivity is of the order of  $10^7$ -  $10^4 \text{ ohm}^{-1} \text{ m}^{-1}$ .
- 2. Semiconductors:** Those solids which have intermediate conductivities ranging from  $10^{-6}$  to  $10^4 \text{ ohm}^{-2} \text{ m}^{-1}$  are classified as semiconductors. As the temperature rises there is a rise in conductivity because electrons from the valence band jump to conduction band.
- 3. Insulators:** These are solids which have very low conductivity values ranging from  $10^{-10}$  to  $10^{-20} \text{ ohm}^{-1} \text{ m}^{-1}$ .

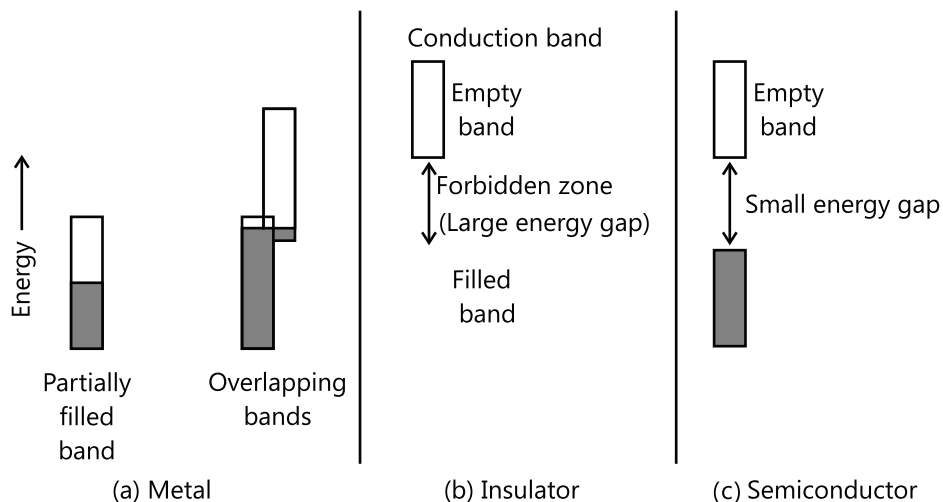
### Causes of conductance in solids:

In most of the solids, conduction takes place due to migration of electrons under the influence of electric field. However, in ionic compounds, the movement of the ion is responsible for their conducting behavior. In metals, conductivity strongly depends upon the number of valence electrons available in an atom.

A band is formed due to closeness of molecular orbitals which are formed from atomic orbital.

If this band is partially filled or it overlaps the unoccupied higher energy conduction band, the electrons can flow easily under an applied electric field and the solid behaves as conductor.

If the gap between valence band and next higher unoccupied conduction band is large, electrons cannot jump into it and such a substance behaves as insulator.



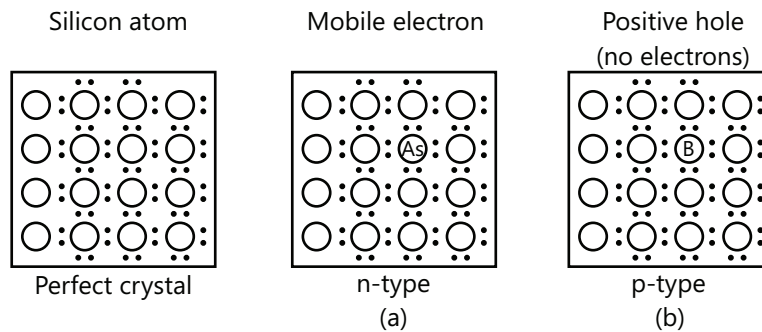
**Figure 19.10-a:** Distinction among metals, insulators and semiconductors

If the gap between the valence band and conduction band is small, some electrons may jump from valence band to the conduction band. Such a substance shows some conductivity and it behaves as a semiconductor [Fig(c)]. An increase in temperature will increase the electrical conductivity of semiconductors as more electrons can jump from valence to conduction band. Silicon and germanium show this type of behaviour and are called intrinsic semiconductors.

**Doping:** The process of introducing an impurity into semi-conductors to enhance their conductivity is called doping.

**n-type semiconductor:** When silicon or germanium crystal is doped with a group 15 element like P or As, the dopant atom forms four covalent bonds like a Si or Ge atom but the fifth electron, not used in bonding, becomes delocalised and contributes its share towards electrical conduction. Thus, silicon or germanium doped with P or As is called n-type semiconductor, n indicative of negative since it is the electron that conducts electricity.

**p-type semiconductor:** When silicon or germanium is doped with a group 13 element like B or Al, the dopant atom forms three covalent bonds like a B or Al atom, but in place of the fourth electron, a hole is created. This hole moves through the crystal like a positive charge giving rise to electrical conductivity. Thus, Si or Ge doped with B or Al is called p-type of semiconductor (p stands for positive hole), since it is the positive hole that is responsible for conduction.



**Figure 19.10-b:** Distinction among perfect crystal, n-type and p-type semiconductor

**Diode:** When n-type and p-type semiconductors are combined, what results, is known as a diode. These diodes are used as rectifiers.

**Transistors:** These are used to detect or amplify radio or audio signals. They consist of pnp or npn Sandwich semiconductors.

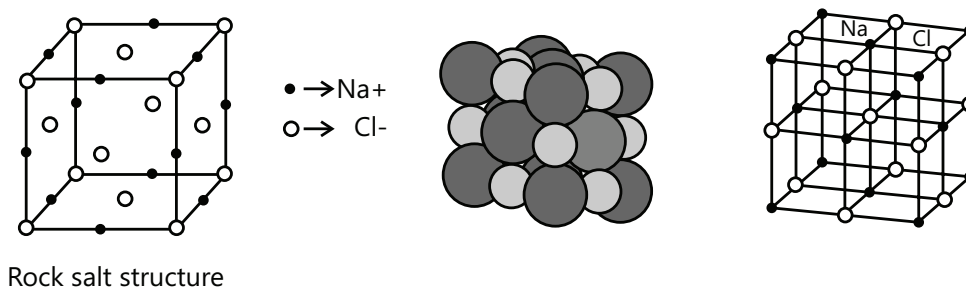
**Photodiode:** These are diodes which are capable of converting light energy into electrical energy and are used in solar cells.

**Table 19.9:** Electrical properties of crystals

	Properties	Information	Dipolar Property	Example	Application
1.	Piezoelectricity	When a crystal of dielectrics is subjected to mechanical stress, then small magnitude current is produced. It is called direct Piezoelectric effect.	Development of charge in some part of crystal	Quartz and Rochelle salt	–
2.	Anti piezoelectricity	In some solids, electric field develops mechanical effect.	Crystal suffers elastic deformation in an electric field	–	
3.	Ferroelectricity	Piezoelectric crystals having permanent dipoles are said to possess ferroelectricity	↑↑↑↑↑↑	BaTiO <sub>3</sub> , KH <sub>2</sub> PO <sub>4</sub> , Rochelle salt	Electromagnetic appliances
4.	Anti ferroelectricity	Piezoelectric crystals with zero dipole are said to possess anti ferroelectricity.	↑↓ ↑↓ ↑↓ ↑↓	PbZrO <sub>3</sub> , Lead zirconate	
5.	Pyroelectricity	Some polar crystals produce electric impulse on heating.	–	Crystals of tartaric acid	Used in fire alarms, thermostat

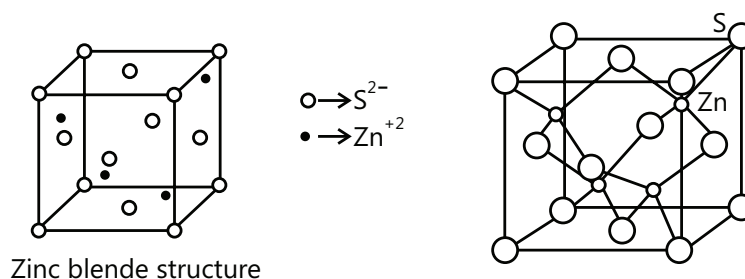
### 13. TYPES OF IONIC STRUCTURES

(a) **Rock Salt Structure:** (NaCl) Larger atoms form ccp arrangement and smaller atoms fill all octahedral voids.



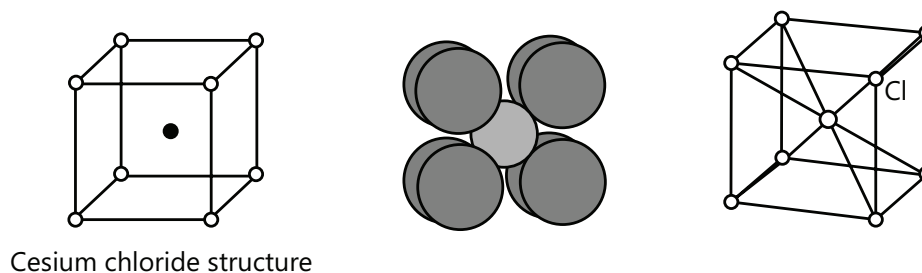
**Figure 19.11-a:** Arrangement of atoms in rock salt type structure

(b) **Zinc Blende (Sphalerite) Structure:** (ZnS) Larger atoms form ccp arrangement and smaller atoms fill half of alternate tetrahedral voids.



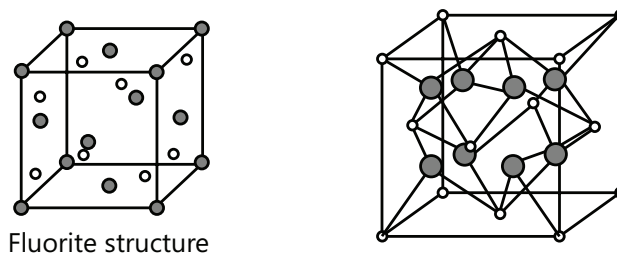
**Figure 19.11-b:** Arrangement of atoms in Zinc blende type structure

(c) **Cesium Halide Structure:** (CsCl) Cl<sup>-</sup> at the corners of cube and Cs<sup>+</sup> in the centre.



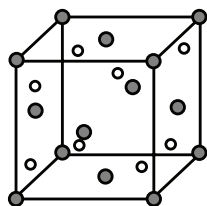
**Figure 19.11-c:** Arrangement of atoms in cesium chloride type structure

(d) **Fluorite Structure:** (CaF<sub>2</sub>) Ca<sup>2+</sup> form ccp arrangement and F<sup>-</sup> fill all tetrahedral voids.



**Figure 19.11-d:** Arrangement of atoms in fluorite type structure

(e) **Antifluorite Structure:** ( $\text{Li}_2\text{O}$ )  $\text{O}^{2-}$  ion form ccp and  $\text{Li}^+$  take all tetrahedral voids.



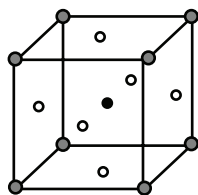
Antifluorite structure

**Figure 19.11-e:** Arrangement of atoms in antifluorite type structure

(f) **Corundum Structure:** ( $\text{Al}_2\text{O}_3$ )  $\text{O}^{2-}$  form hcp and  $\text{Al}^{3+}$  fill  $2/3$  octahedral voids.

(g) **Rutile Structure:** ( $\text{TiO}_2$ )  $\text{O}^{2-}$  form hcp while  $\text{Ti}^{4+}$  ions occupy half of the octahedral voids.

(h) **Pervoskite Structure:** ( $\text{CaTiO}_3$ )  $\text{Ca}^{2+}$  in the corner of cube,  $\text{O}^{2-}$  at the face centre and  $\text{Ti}^{4+}$  at the centre of cube.



Pervoskite structure

**Figure 19.11-f:** Arrangement of atoms in pervoskite type structure



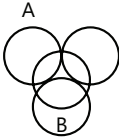
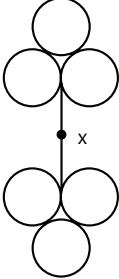
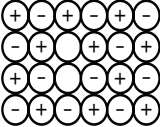
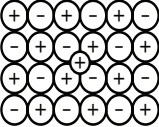
**Table 19.10:** Summary of some characteristic of some closest and non-closest packed structure

S. No.	Formula	Type of lattice	Type of structure	$Z_{\text{eff}}$	Radius	Packing factor (PF)	TV occupied	OV occupied	Ligancy
1.	AB	Rock salt (NaCl)*	fcc	4	$(r_{A^{\circ}} + r_{B^{\circ}}) = \frac{\pi}{2} a$	$PF = \frac{\left[ 4 \times \frac{4}{3} \pi r_{A^{\circ}}^2 \right] + \left[ 4 \times \frac{4}{3} \pi r_{B^{\circ}}^2 \right]}{a^2}$	None	All by $\text{Na}^+$ ions	6 : 6
2.		ZnS (Zinc blende)	ccp	4	$(r_{A^{\circ}} + r_{B^{\circ}}) = \frac{\sqrt{3}}{4} a$	$PF = \frac{\left[ 4 \times \frac{4}{3} \pi r_{A^{\circ}}^2 \right] + \left[ 4 \times \frac{4}{3} \pi r_{B^{\circ}}^2 \right]}{a^2}$	Half by $\text{Zn}^{2+}$ ions (Alternate TV)	None	4 : 4
3.		CaCl	hcp	1	$2(r_{A^{\circ}} + r_{B^{\circ}}) = \sqrt{3}a$	$PF = \frac{\left[ 1 \times \frac{4}{3} \pi r_{A^{\circ}}^2 \right] + \left[ 1 \times \frac{4}{3} \pi r_{B^{\circ}}^2 \right]}{a^2}$	None	Only one by $\text{Cs}^+$	8 : 8
4.	$\text{AB}_2$	$\text{CaF}_2^*$	ccp	4	$(r_{A^{\circ}} + r_{B^{\circ}}) = \frac{\sqrt{3}}{4} a$	$PF = \frac{\left[ 4 \times \frac{4}{3} \pi r_{A^{\circ}}^2 \right] + \left[ 8 \times \frac{4}{3} \pi r_{B^{\circ}}^2 \right]}{a^2}$	All by $\text{Na}^+$ ions	None	8 : 4
<b>Note:</b> Here radius rule will change. Now $r/r$ lies in 0.225 – 0.414 as anion lies in TV. 4 : 8									
5.	$\text{A}_2\text{B}$	$\text{Na}_2\text{O}$ (Antifluorite)	ccp	4	$(r_{A^{\circ}} + r_{B^{\circ}}) = \frac{\sqrt{3}}{4} a$	$PF = \frac{\left[ 8 \times \frac{4}{3} \pi r_{A^{\circ}}^2 \right] + \left[ 4 \times \frac{4}{3} \pi r_{B^{\circ}}^2 \right]}{a^2}$ $PF = \frac{8 \times \frac{4}{3} \pi r_{A^{\circ}}^2}{a^2} = \frac{\sqrt{3}}{16} \pi = 0.34$	All by $\text{Na}^+$ ions	None	4 : 8
6.		Diamond Cubic (DC)	fcc	8	$r = \frac{\sqrt{3}}{8} a$	$PF = \frac{8 \times \frac{4}{3} \pi r_{A^{\circ}}^2}{a^2} = \frac{\sqrt{3}}{16} \pi = 0.34$ Height $c = 4 r \frac{\sqrt{2}}{3}$	4 more C – atoms are present in alternate TVs	None	4

S. No.	Formula	Type of lattice	Type of structure	$Z_{\text{eff}}$	Radius	Packing factor (PF)	TV occupied	OV occupied	Ligancy
7.		Hexagonal closed packed (AB AB... packing)	hcp	6	$2r = 4$ Height (c) = $4r \frac{\sqrt{2}}{3}$ Base area, $A = 6\sqrt{3} r^2$ Volume = $24\sqrt{2} r^3$	$\text{PF} = \frac{\left(\frac{4}{3} \pi r^3\right)}{24\sqrt{2} r^3} = \frac{\pi}{3\sqrt{2}} = 0.74$ $\text{PF} = \frac{\left(\frac{4}{3} \pi r^3\right)}{24\sqrt{2} r^3} = \frac{\pi}{3\sqrt{2}} = 0.74$	-	-	-
8.	$\text{AB}_2\text{O}_4$	Spinel ( $\text{ZnAl}_2\text{O}_4$ )	fcc	4 $\text{Al}^{3+} = 2$ $\text{Zn}^{2+} = 1$ $\text{O}^{2-} = 4$	Volume = $a^3 = 16\sqrt{2} r_{\text{O}^{2-}}^3$ For TV, $\frac{r_{\text{Zn}^{2+}}}{r_{\text{O}^{2-}}} = 0.225$ For OV, $\frac{r_{\text{Al}^{3+}}}{r_{\text{O}^{2-}}} = 0.414$	$\text{PF} = \frac{\left[2 \times \frac{4}{3} \pi r_{\text{Al}^{3+}}^3\right] + \left[1 \times \frac{4}{3} \pi r_{\text{Zn}^{2+}}^3\right] + \left[4 \times \frac{4}{3} \pi r_{\text{O}^{2-}}^3\right]}{16\sqrt{2} r_{\text{O}^{2-}}^3}$ $= \frac{\pi}{3\sqrt{2}} \left[ \frac{1}{2} \left( \frac{r_{\text{Al}^{3+}}}{r_{\text{O}^{2-}}} \right)^3 + \frac{1}{4} \left( \frac{r_{\text{Zn}^{2+}}}{r_{\text{O}^{2-}}} \right)^3 + 1 \right]$ $= \frac{\pi}{3\sqrt{2}} \left[ \frac{1}{2} (0.414)^3 + \frac{1}{4} (0.225)^3 + 1 \right] = 0.77$	$\text{Zn}^{2+} = \frac{1}{8} \text{TV}$	$\text{Al}^{3+} = \frac{1}{2} \text{OV}$ $\text{Al}^{3+} = \frac{2}{3} \text{OV}$	-
9.	$\text{Al}_2\text{O}_3$	Correndum ( $\text{Al}_2\text{O}_3$ )	Hcp	6 $\text{O}^{2-} = 6$ $\text{Al}^{3+} = 4$	Volume of hcp = $24\sqrt{2} r^3$ For OV, $\frac{r_{\text{O}^{2-}}}{r_{\text{Al}^{3+}}} = 0.414$	$\text{PF} = \frac{\left[6 \times \frac{4}{3} \pi r_{\text{O}^{2-}}^3\right] + \left[4 \times \frac{4}{3} \pi r_{\text{Al}^{3+}}^3\right]}{24\sqrt{2} r_{\text{O}^{2-}}^3}$ $= \frac{\pi}{3\sqrt{2}} \left[ \frac{2}{1 + \frac{2}{3}} \left( \frac{r_{\text{Al}^{3+}}}{r_{\text{O}^{2-}}} \right)^3 \right]$ $= \frac{3.1416}{3 \times 1.414} \left[ \frac{2}{1 + \frac{2}{3}} (0.414)^3 \right] = 0.7756$		$\text{Al}^{3+} = \frac{2}{3} \text{OV}$	6 : 4

## POINTS TO REMEMBER

<p><b>Radius Ratio:</b> In a given coordination number, radius ratio has fixed value in the limiting case:</p>	<table border="1" data-bbox="961 254 1263 548"> <thead> <tr> <th>C.N</th> <th><math>r^+/r</math></th> </tr> </thead> <tbody> <tr> <td>3</td> <td>0.155</td> </tr> <tr> <td>4(<math>T_d</math>)</td> <td>0.225</td> </tr> <tr> <td>4(SP)</td> <td>0.414</td> </tr> <tr> <td>6</td> <td>0.414</td> </tr> <tr> <td>8</td> <td>0.732</td> </tr> </tbody> </table>	C.N	$r^+/r$	3	0.155	4( $T_d$ )	0.225	4(SP)	0.414	6	0.414	8	0.732
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3	0.155												
4( $T_d$ )	0.225												
4(SP)	0.414												
6	0.414												
8	0.732												
<p><b>Packing fraction [<math>\phi</math>]:</b> It is the maximum fractional volume of unit cell which can be occupied by atoms or ions. In case of atomic solids of like atoms, following are the values of packing fractions</p>	<table border="1" data-bbox="821 581 1404 827"> <thead> <tr> <th>Typing of unit cells</th> <th>Packing fractions</th> </tr> </thead> <tbody> <tr> <td>Simple cubic</td> <td>0.53</td> </tr> <tr> <td>Body centred cubic</td> <td>0.68</td> </tr> <tr> <td>Fcc</td> <td>0.74</td> </tr> <tr> <td>Hcp</td> <td>0.74</td> </tr> </tbody> </table>	Typing of unit cells	Packing fractions	Simple cubic	0.53	Body centred cubic	0.68	Fcc	0.74	Hcp	0.74		
Typing of unit cells	Packing fractions												
Simple cubic	0.53												
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Hcp	0.74												
<p><b>Relationship between radius and sides of unit cells in atomic solids (<math>a</math> = edge length, <math>r</math> = atomic radius):</b></p>	<table border="1" data-bbox="958 858 1268 1199"> <tbody> <tr> <td>SC</td> <td><math>A=2r</math></td> </tr> <tr> <td>Bcc</td> <td><math>\sqrt{3}a = 4r</math></td> </tr> <tr> <td>Fcc</td> <td><math>\sqrt{2}a = 4r</math></td> </tr> <tr> <td>Hcp</td> <td><math>h = \left( 4\sqrt{\frac{2}{3}} \right) r</math></td> </tr> </tbody> </table>	SC	$A=2r$	Bcc	$\sqrt{3}a = 4r$	Fcc	$\sqrt{2}a = 4r$	Hcp	$h = \left( 4\sqrt{\frac{2}{3}} \right) r$				
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Fcc	$\sqrt{2}a = 4r$												
Hcp	$h = \left( 4\sqrt{\frac{2}{3}} \right) r$												
<p><b>Bravias lattices:</b></p>	<p>Based on the arrangement of atoms or ions, the seven crystal systems are further classified into 14 types known as the bravias lattices.</p>												
<p><b>Primitive cell:</b></p>	<p>A primitive cell is a bravias lattice that homes only one atom (effectively) in one unit cell.</p>												
<p><b>Density of solid [<math>\rho</math>]:</b></p>	$\rho = \frac{\text{Mass of atoms / ions in one unit cell}}{\text{volume of an unit cell}}$												
<p><b>Cubic System :</b></p>	$\rho = \frac{NM}{N_A} \left( \frac{1}{a^3} \right) \text{gcm}^{-3}$ <p><math>N</math>=number of atoms per unit cell,  <math>M</math>=molar mass,  <math>N_A</math> =Avogadro's number  <math>a^3</math>=volume of unit cell in <math>\text{cm}^3</math></p>												

<p><b>Tetrahedral and Octahedral void (Holes) :</b></p>	<p>(i) Number of tetrahedral voids = <math>2 \times</math> effective number of atoms/unit cell.</p> <p>(ii) Number of octahedral voids = Number of atoms (effectively) per unit cell.</p> <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">  <p>The interstices below B is tetrahedral void</p> </div> <div style="text-align: center;">  <p>x is the central of octahedral void</p> </div> </div>
<p><b>Crystal defects :</b></p>	<p><b>A) Point Defects \ Stoichiometric defects</b></p> <p>Two types:-</p> <p><b>(i) Schottky Defect</b> – Atoms or ions absent from their normal lattice sites. Observed in NaF, KCl etc.</p> <p><b>(ii) Frenkel Defect</b> - Smaller cation leaves its normal lattice, occupies the interstitial site. Observed in solids with smaller cations like LiI.</p> <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">  <p>Schottky defect</p> </div> <div style="text-align: center;">  <p>Frenkel defect</p> </div> </div> <p><b>B) F-center defect</b> - Alkali metal vapours passed on an ionic solid lets out electrons which substitute some anions leading to trapped electrons.</p>

Based on the geometry of unit cells, solids are divided into seven crystal systems as:

System	Parameters	Interaxial angle
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma$
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = \beta \neq 90^\circ$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ \neq \gamma = 120^\circ$
Rhombohedral (or) (Trigonal)	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$