

The Solid State

BASICS

Section - 1

1.1 Introduction :

A matter is said to be solid when its constituent particles (atoms, molecules, or ions) are closely packed. A solid is also defined as that form of matter which possesses rigidity and hence possesses a definite shape and a definite volume. Unlike gases and liquids, whose fluidity is determined by the relative free motion of their molecules, in solids, on the contrary, molecules or atoms or ions are not free to move but can oscillate around their fixed positions due to strong intermolecular or inter-atomic or inter-ionic forces. This confers rigidity and long range order in solids.

1.2 Characteristics of Solids :

Some of the common properties of solids, which distinguish them from other two states of matter, are :

- Solids are rigid and have definite shapes.
- Solids have definite volume irrespective of the size or shape of the container in which they are placed.
- Solids are almost incompressible, having compressibility, which is approximately 10^6 times more than gases.
- Many solids have a crystalline appearance and have definite pattern of angles and planes.
- Solids diffuse very slowly as compared to liquids and gases. Constituent particles are very closely packed in solids permitting very little space for their movement.
- Solids have a much higher density (mass to volume ratio) than that of gases and liquids.
- Most solids become liquids when heated. Some undergo sublimation on heating. The temperature at which a solid change into liquid is called the melting point and the process is called as melting. Due to the varying natures of solids their melting temperature vary considerably.

1.3 Classification of Solids :

The properties that different solids have suggest that the behavior of the solids not only depend upon the nature of the constituents, but also on their arrangement.

On the basis of the arrangement of their atoms or ions or molecules, solids are broadly classified into two group :

1. Crystalline Solids

The substances whose constituents are arranged in definite orderly arrangement are called crystalline solids. Many naturally occurring solid substances occur in the crystalline form. Some common examples of crystalline solids are sodium chloride, diamond, sugar, etc.

2. Amorphous Solids

An amorphous solid is a substance whose constituent particles do not possess a regular orderly arrangement e.g. glass, plastics, rubber, starch, and proteins. Though amorphous solids do not possess long range regularity, in some cases they may possess small regions of orderly arrangement. These crystalline parts of an otherwise amorphous solid are known as *crystallites*.

An amorphous solid does not possess a sharp melting point. It undergoes liquefaction over a broad range of temperature. When an amorphous solid is cut with the help of sharp edged knife, it results in an irregular cut.

Amorphous substances are also, sometimes, referred to as super cooled liquids because they possess disorderly arrangement like liquids. In fact many amorphous solids such as glass are capable flowing. Careful examination of the window panes of very old houses reveals that the panes are thicker at the bottom than at the top because the glass has flown under constant influence of gravity

Comparative Study of crystalline and Amorphous Solids

Properties	Crystalline solids	Amorphous solids
Crystal geometry	The internal arrangement of particles is regular so they possess definite and regular geometry. They have long range order.	The internal arrangement of particles is irregular. Thus they do not have any definite geometry. They have short range order.
Melting Point	They have sharp melting points.	They do not have sharp melting points.
External form	There is regularity in the external form when crystals are formed. Crystalline solids give a regular cut when cut with a sharp - edge knife.	There is no regularity in the external form when amorphous solids are formed. Amorphous solids give irregular cut.
Heat of Fusion	They have characteristic heat of fusion.	They do not have characteristic heat of fusion.
Physical state	Crystalline solids are hard and rigid and their shape is not distorted by mild distorting forces.	Amorphous solids are comparatively soft and not very rigid. These can be distorted by bending or compressing forces.
Anisotropic or Isotropic nature	Crystalline solids are anisotropic. This implies that physical properties such as refractive index (e.g. Canada Balsam), conductivity, thermal expansion etc are different in different directions. This is due to orderly arrangement of particles	Amorphous solids are isotropic in nature. This implies that various physical properties are same in all the directions. This is because of random arrangement of particles.
Example	Crystals of NaCl, CsBr, CaF_2 and ZnS	Rubber, glass, plastic etc.

Note : Some substances adopt different structural arrangements under different conditions, Such compounds are called as **polymorphs**. These different structures have different properties such as melting point, density etc.
Example : Diamond and graphite are two different polymorphic forms of carbon.

1.4 Classificaion of Crystalline Solids :

On the basis of the nature of bonding, the crystalline solids have been classified into four main categories viz., Covalent, Ionic, Metallic and Molecular solids.

Different Types of Solids

Type of Solid	Constituent Particles	Bonding/Attractive Forces	Examples	Physical Nature	Electrical Conductivity
Molecular	Molecules	Dispersion Dipole interaction Hydrogen Bonding	Argon, HCl H ₂ O (Ice) Paraffin wax	Soft	Insulator
Metallic	Positive metal ions (kernel s) and mobile electrons	Positive ions and electrons (delocalized electrons)	Ag, Cu, Mg	Ductile & Malleable	Conductor
Covalent	Atoms	Covalent Bonding (Electron sharing)	SiO ₂ , SiC Diamond	Hard	Insulator
Ionic	Ions	Columbic or Electrostatic Forces	NaCl, MgO KCl, BaCl ₂	Hard & Brittle	Conductor (in molten & in aqueous solution)

X-RAY STUDY OF CRYSTALS

Section - 2

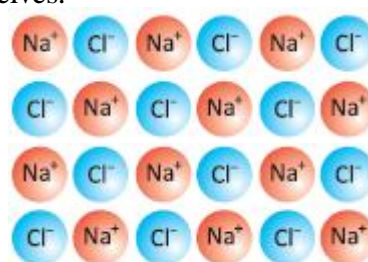
***2.1 X-Ray Diffraction :**

X-ray diffraction (XRD) is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of natural and manufactured materials.

It was suggested by M. Von Laue, in 1913, that it might be possible to diffract X-rays by means of crystals.

The reason for the suggestion was that the wavelength of X-rays was of about the same order (10^{-8} cm) as the inter-atomic distances in a crystal. In fact, Bragg succeeded in diffracting X-ray from Sodium chloride crystals. This observation has proved to be highly useful in determining structure and dimensions of crystals as well as in the study of number of properties of X-rays themselves.

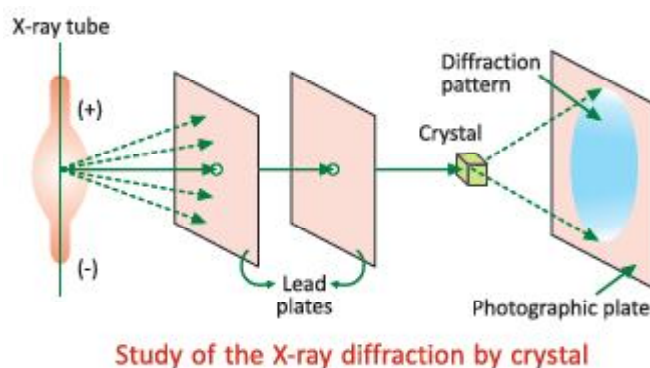
For example, experiments ([X-ray diffraction method](#)) show that in a crystal of sodium chloride, the constituent Na^+ and Cl^- ions are present at alternate sites as shown :



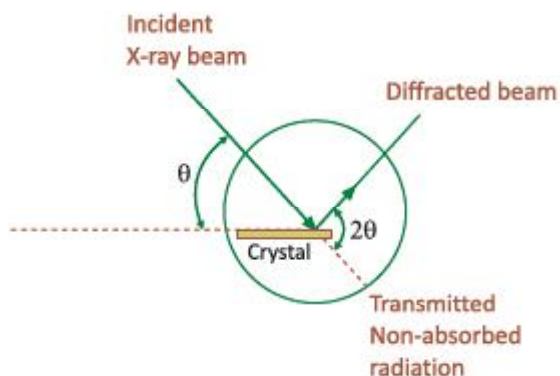
Though shown in two dimensions this systematic long-range order is also found in three dimensions, with each Na^+ surrounded by six Cl^- ions and vice versa. This order is due to strong coulombic forces of attraction between Na^+ and Cl^- ions. Similar regular arrangements are found in other solids too.

In a crystalline solid, the constituent particles ([atoms, ions or molecules](#)) arranged in a regular order. An interaction of a particular crystalline solid with X-rays helps in investigating its actual structure.

Crystals are found to act as diffraction gratings for X-ray and this indicates that the constituent particles in the crystals are arranged in planes at close distances in repeating patterns.



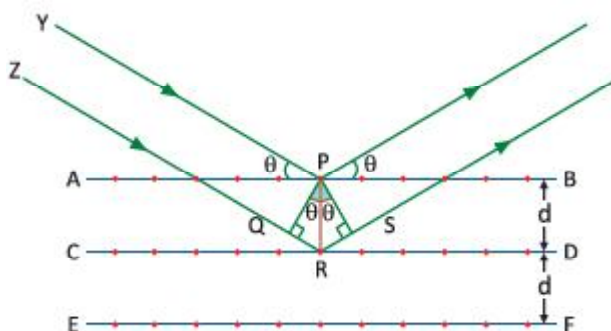
A simple representation of the X-ray diffraction is shown as follows :



*2.2 The Bragg's Equation :

W.H. Bragg pointed out that scattering of X-rays by crystals could be considered as reflection from successive planes of atoms in the crystals.

The process was based upon the principle that a crystal may be considered to be made up of a number of parallel equidistant atomic planes, as represented by line AB, CD and EF in the adjacent figure.



Suppose two waves (Y and Z) of X-ray beams, which are in phase fall on the surface of the crystal. If the ray Y gets reflected from the first layer *i.e.*, AB line and the ray Z is reflected from the second layer of atoms *i.e.*, CD line, then it is evident that as compared to the ray Y, ray Z has to travel a longer distance, equal to QRS in order to emerge out of the crystal. If the waves Y and Z are in-phase (for intensity of the reflected beam to be maximum) after reflection, the difference in distance travelled by the two rays must be equal to an integral multiple of wavelength *i.e.*, $n\lambda$ (for constructive interference).

Thus,

$$\text{Distance QRS} = n\lambda \quad \dots (i)$$

It is obvious from the figure that $QR = RS = PR \sin \theta$

$$\text{Therefore } QRS = 2 PR \sin \theta \quad \dots \text{ (ii)}$$

If the distance between the successive atomic planes is d

$$\text{Then } PR = d \quad \dots \text{ (iii)}$$

So, from equations (i), (ii) and (iii) we have, $n\lambda = 2d \sin \theta$

This is the Bragg's Equation.

Thus, Bragg gave a mathematical equation to establish a relationship between wave length of the incident X-ray, the distance between the layers and the angle of diffraction.

- Here, λ = wavelength of X-ray used.
- θ = Angle between incident X-ray and plane of the crystal. The diffracted beam makes an angle 2θ .
- d = Distance between planes of the constituent particles in a crystal.
- n = An integer (1, 2, 3, 4, etc.) which represents the serial order of diffracted beams.

For a given set of lattice planes, d has a fixed value. Therefore, the possibility of getting maximum reflection (*i.e.*, the possibility of getting reflected waves in phase with one another) depends upon θ . If θ is increased gradually, a number of positions will be found at which the reflections will be maximum. At these positions, n will have values equal to 1, 2, 3, 4, 5 etc. Generally, in experiments on X-ray reflections, n is set equal to 1. If λ is known, it is possible to determine d , the distance between atomic planes in the crystal by determining θ experimentally. Similarly, if interplanar distance are given, the corresponding wavelengths of the incident beam of X-ray can be calculated.

Illustration - 1

A sample of a crystalline solid scatters a beam of X-rays of wavelength 70.93 pm at an angle 2θ of 14.66° . If this is a second order reflection ($n = 2$), calculate the distance between the parallel planes of atoms from which the scattered beam appears to have been reflected. (Use : $\sin 7.33^\circ = 0.1276$)

SOLUTION :

$$\text{We know that : } n\lambda = 2d \sin \theta$$

$$2\theta = 14.66^\circ \text{ or } \theta = 7.33^\circ$$

$$\lambda = 70.93 \text{ pm} = 70.93 \times 10^{-12} \text{ m}$$

$$\text{Therefore, } d = \frac{n\lambda}{2\sin \theta} = \frac{2 \times 70.93 \times 10^{-12}}{2\sin 7.33^\circ} \text{ m} = 556.3 \times 10^{-12} = 556.3 \text{ pm}$$

LATTICE & UNIT CELL

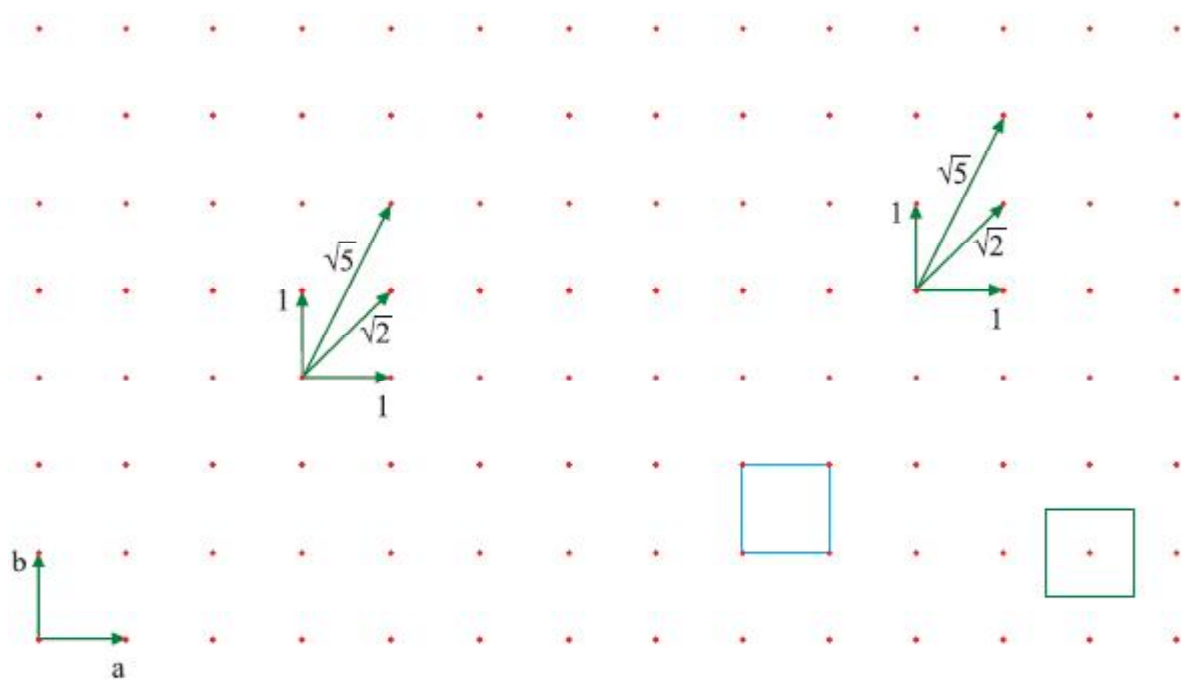
Section - 3

Before discussing the periodic patterns of atomic arrangements in crystals, we need to look into arrangements of points in space in periodically repeating patterns. This leads us to the concept of a space lattice. A space lattice provides the framework with reference to which a crystal structure can be described.

3.1 Definition (Lattice) :

It is the periodic arrangement of the points such that the environment at any point is the same as at any other point. Every point in lattice should have same surroundings.

As an example, consider a two-dimensional square array of points shown in figure. By repeated translation of the two vectors a and b on the plane of the paper, we can generate the square array. The magnitudes of a and b are equal and can be taken to be unity. The angle between them is 90° ; a and b are called the *fundamental translation vectors* that generate the square array. To ignore end effects near the boundary, we will assume that the array can be extended infinitely. If we locate ourselves at any point in the array and look out in a particular direction that lies on the plane of the paper, the scenery is the same, irrespective of where we are.



Consider the immediate surroundings of a point in the array. If we look due north or due east from this point, we see another point at a distance of 1 unit. Along northeast, we see the nearest point at a distance $\sqrt{2}$ units and along north-northeast, the nearest point is at a distance of $\sqrt{5}$ units. As this is true of every point in the array, the array satisfies the definition given above and can be called a *two-dimensional square lattice*.

The main features of a Lattice :

- (i) Lattice should be infinite.
- (ii) Each point in a lattice is called **lattice point**.
- (iii) Lattice points are joined by straight lines to represent the geometry of Lattice.
- (iv) Lattice is different from a crystal. Infact, a Lattice gives to rise to a crystal when points are replaced by particles such as atoms, ion or molecules.

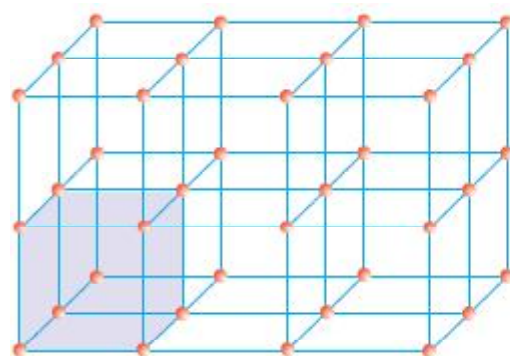
Note :

We can have square lattice, hexagonal lattice but pentagonal lattice is not possible because the interior angle of a regular pentagon is 108° Which is not an integral factor of 360° .

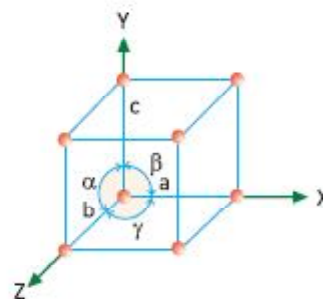
3.2 Space Lattice or 3 -D Lattice :

An array of lattice points showing arrangement of constituent particles in different positions in three dimensional space is known as **space lattice of crystal lattice**. i.e. the constituent particles of a crystalline solid are arranged in a definite fashion in the three dimensional space. Mathematically, a three-dimensional space lattice is generated by repeated translation of three noncoplanar vectors a , b and c .

One such arrangement by representing the particles with points is shown below :



Representation of space
lattice and unit cell



Representation of dimensions
of a unit cell

From the complete space lattice, it is possible to select a smallest three dimensional portion which repeats itself in different directions to generate the complete space lattice. This is called a **Unit Cell**. In the above example of the square lattice, the unit cell is the square obtained by joining four neighbouring lattice points, as shown in figure on last page. Since every corner of this square is common to four unit cell meeting at that corner, the effective number of lattice points in the unit cell is only one. Alternatively, the unit cell can be visualized with one lattice point at the centre of the square and with none at the corners (see figure on previous page)

3.3 Unit cell

The smallest three-dimensional portion of a complete space lattice, which when repeated over and again in different direction produces the complete space lattice.

The size and shape of a unit cell is determined by the lengths of the edges of the unit cell (a , b and c) and by the angles α , β and γ between the edges b and c , c and a , and a and b respectively.

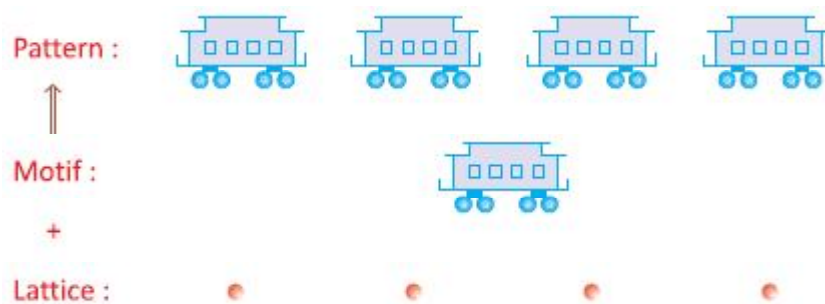
If we take into consideration, the symmetry of the axial distances (a , b , c) and also the axial angles between the edges (α , β and γ), the various crystals can be divided into seven crystal systems. These are also called *crystal habits*.

3.4 Difference between Crystal and Lattice :

A space lattice is combined with basis/motif to generate a crystal structure.

$$\text{Space lattice} + \text{Basis} \longrightarrow \text{Crystal Structure}$$

The regular pattern of wagons below can be described by placing a lattice point at the same place in each wagon. The arrangement of dots is the lattice, which has a given repeat distance. The motif is the wagon. The pattern is recovered by stamping the motif on each lattice point.



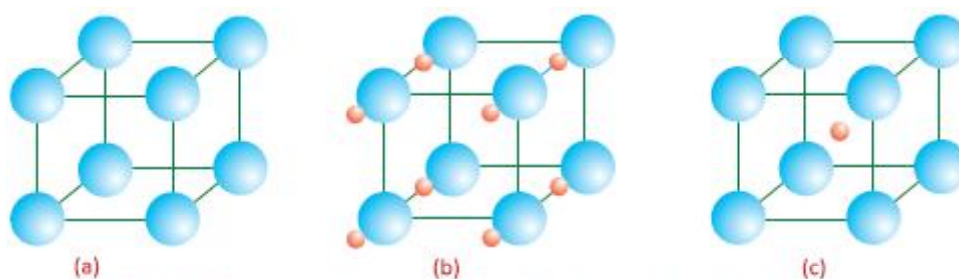
The motif/basic can be single atom or groups of atoms. But in many elemental crystals, the basis is simple and consists of one atom per lattice point. In such cases, the crystal is generated by just positioning one atom of the element at each lattice point. For example, the crystal structure of chromium and copper are generated as :

$$\text{BCC space lattice} + 1 \text{ Cr atom per lattice point} \longrightarrow \text{BCC crystal of Cr}$$

$$\text{FCC space lattice} + 1 \text{ Cu atom per lattice point} \longrightarrow \text{FCC crystal of Cu}$$

These crystals are called *monoatomic crystals*, to denote the fact that the basis is one atom per lattice point. ABCC crystal means a monoatomic BCC crystal, unless otherwise stated.

In principle, an infinite number of crystal structure can be generated by combining different bases and different lattice parameters with the same space lattice. In figure, three different base are combined with the simple cubic lattice. In figure (a), the crystal is monoatomic, with just one atom at each lattice point. For clarity, neighbouring atoms are shown separately. Figure (b) illustrates a *molecular crystal*, with a diatomic molecule at each lattice point. The centre of the larger atom of the molecule coincides with a lattice point, while the smaller atom is not at a lattice point. In molecular crystals, the basis is fully defined by giving the number and types of atoms, the internuclear distance of separation between neighbours molecule and the orientation of the molecule in relation to the unit cell. In figure (c), the corner atoms of the cube are of one type, but the atom at the body centre is of different type. The basis is two atoms, the larger one in this case at a lattice point and the smaller one positioned half-way along the body diagonal, at the body centre, which is not a lattice point. In the crystal, of course, the unit cell can be shifted such that the body centre becomes a lattice point and the body corners are no longer lattice points. This crystal should not be confused with monoatomic BCC crystal, where the body corner and the body centre atom are of the same type.

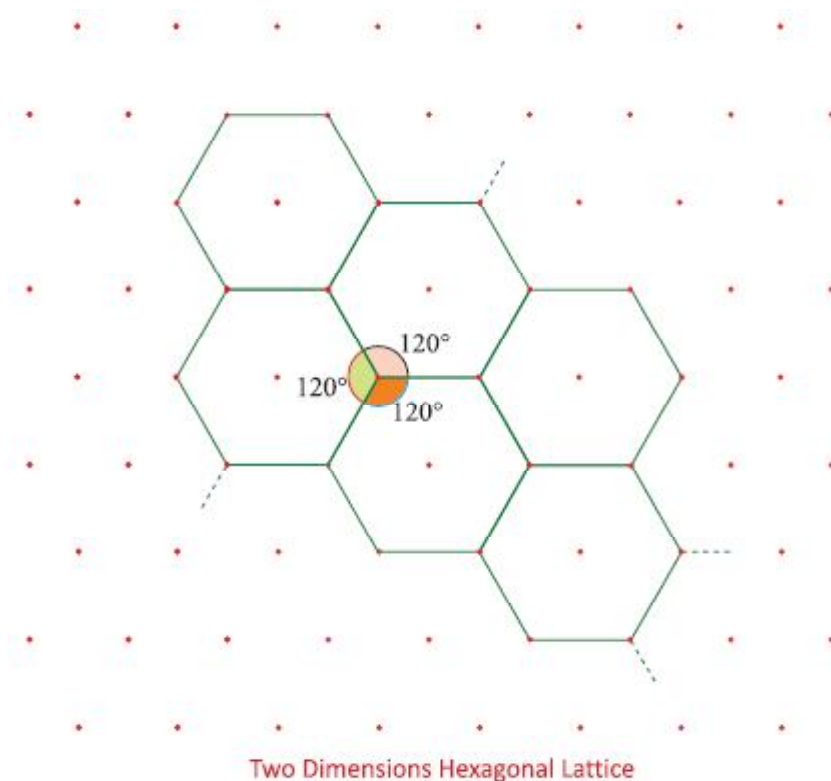


Three different crystal structures referred to the same simple cubic lattice.
(For clarity, neighbouring atoms or molecules are shown separated)

Illustration - 2 Draw two dimensional Hexagonal Lattice. Try to visualize the possibility of pentagonal two dimensional lattice.

SOLUTION :

Three regular hexagons intersect at one point. So, in this two-dimensional lattice, this lattice point is shared by three unit cells.



So, effective no. of lattice points per unit cell = $6 \times \left(\frac{1}{3}\right) + 1 \times (1) = 3$

A regular pentagon has an interior angle of 108° . As 360° is not an integral multiple of 108° , pentagons cannot be made to meet at a point bearing a constant angle to one another. Hence, a pentagonal lattice is not possible. On the other hand, a square or a hexagonal two-dimensional lattice is possible as their internal angles add up to give 360° .

Note : You are advised to read this section again after Section – 5 and then proceed further.

TYPES OF SYMMETRY IN CRYSTALS

Section - 4

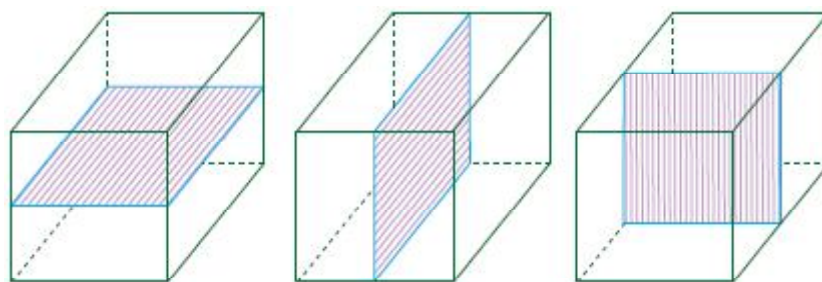
4.1 Definition

Crystals possess a regular, repetitive internal structure. The concept of **symmetry** describes the repetition of structural features. Crystals therefore possess symmetry, and crystallography is basically concerned with describing different types of symmetry. Broadly, two general types of symmetry exist. These consist of **translational symmetry** and **point symmetry**. Translational symmetry describes the periodic repetition of a structural feature across a length or through an area or volume. The concept of a lattice is directly related to the idea of a translational symmetry. Point symmetry, on the other hand describes the periodic repetition of a structural feature around a point. Reflection, rotation, and inversion are all point symmetries.

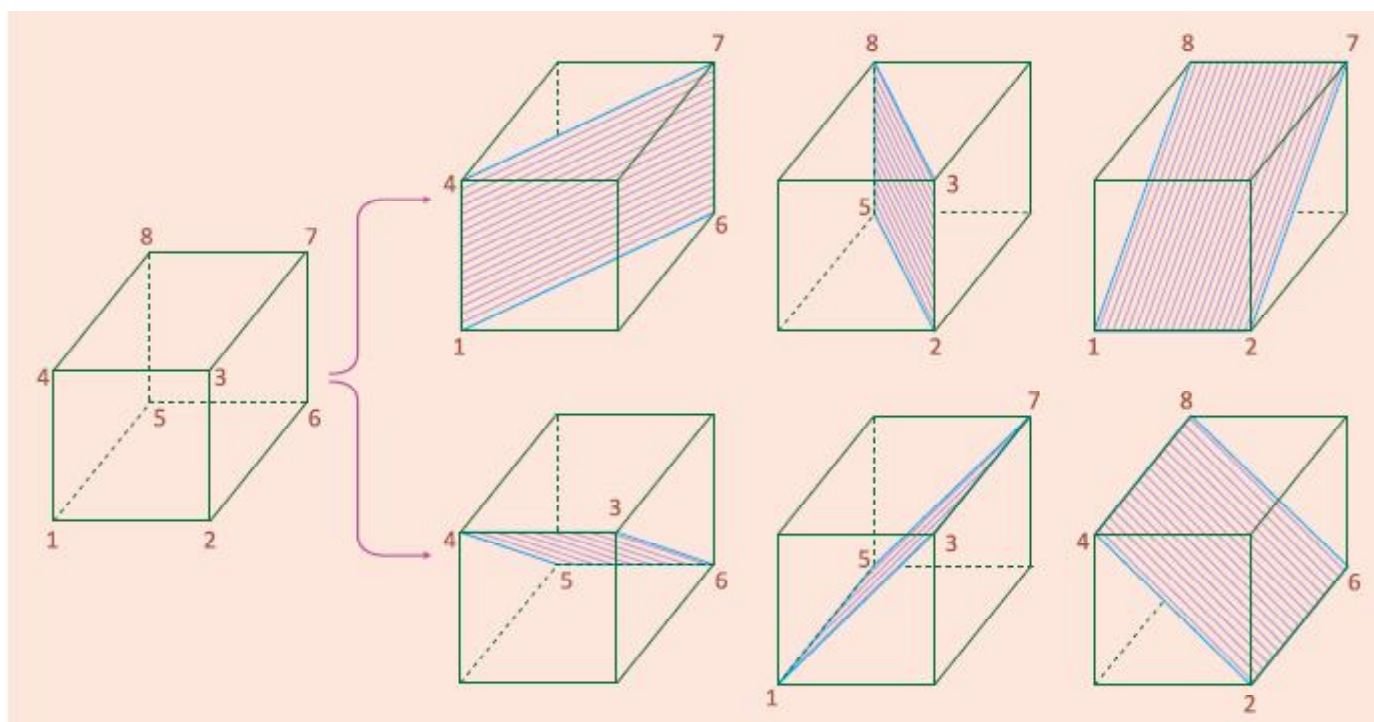
These are explained in detail as below :

(a) Reflection/plane of symmetry :

A **reflection** occurs when a motif on one side of a plane passing through the center of crystal is the mirror image of a motif which appears on the other side of the plane. The motif is said to be reflected across the mirror plane which divides the crystal. In other terms, it is an imaginary plane which passes through the centre of crystal and divides it into two equal portions such that one part is exactly the mirror image of the other. A cubic crystal like NaCl possesses, in all, nine planes of symmetry: three rectangular planes of symmetry and six diagonal planes of symmetry.



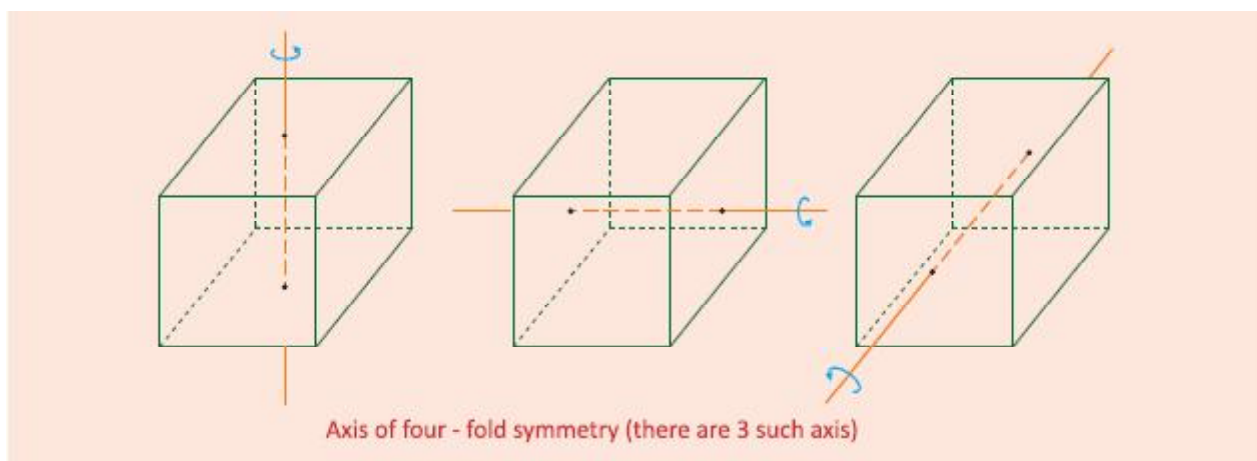
Rectangular planes of symmetry (there are 3 such planes)



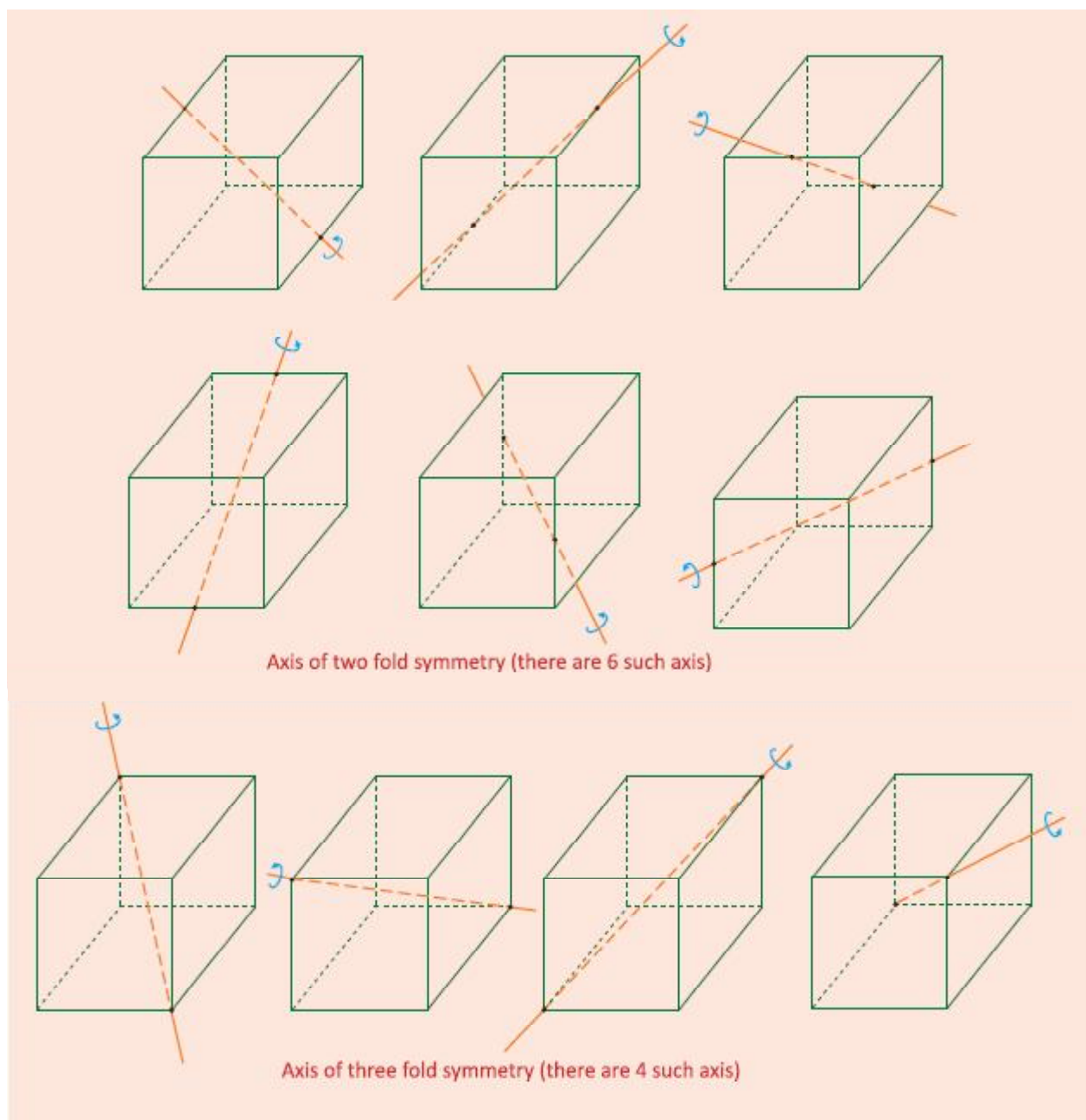
Diagonal planes of symmetry (there are 6 such planes)

(b) Rotational symmetry/ Axis of symmetry :

It arises when a structural element is rotated a fixed number of degrees about a central axis before it is repeated. In other terms, it is an imaginary straight line about which, if the crystal is rotated, it will present the same appearance more than once during the complete revolution.



Axis of four - fold symmetry (there are 3 such axis)

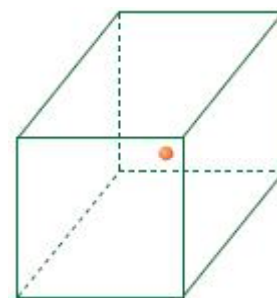


The axes of symmetry are called *diad*, *triad*, *tetrad* and *hexad*, respectively, if the original appearance is repeated twice (after an angle of 180°), Thrice (after an angle of 120°), four times (after an angle of 90°) and six times (after an angle of 60°) in one rotation. These axes of symmetry are also called *two-fold*, *three-fold*, *four-fold* and *six-fold*, respectively.

In general, if the same appearance of a crystal is repeated on rotating through an angle $\frac{360}{n}$, of around an imaginary axis, the axis is called an *n-fold axis*.

(c) Inversion symmetry/Centre of Symmetry :

If a crystal possesses **inversion symmetry**, then every line drawn through the center of the crystal will connect two identical features on opposite sides of the crystal. In other terms, it is such an imaginary point within the crystal that any line drawn through it intersects the surface of the crystal at equal distances in both directions. A crystal always possesses only one centre of symmetry.

**4.2 Elements of symmetry :**

The total number of planes, axes and centre of symmetry possessed by a crystal are termed as **elements of symmetry**. A cubic crystal possesses a total of 23 elements of symmetry.

$$\text{Planes of symmetry} = (3 + 6) = 9$$

$$\text{Axes of symmetry} = (3 + 6 + 4) = 13$$

$$\text{Centre of symmetry} = 1$$

$$\text{Total number of symmetry elements} = 23$$

CRYSTAL SYSTEM AND BRAVAIS LATTICES**Section - 5**

On the basis of symmetry, viz., Translational, Rotational and Reflection, in total only fourteen 3-D lattices are possible. These are called **Bravais Lattices**. These are categorized under 7 crystal systems. Before going into their detail, let's take a look at the types of unit cells.

5.1 Types of Unit Cells :

Unit cells in which the particles are present only at the corners are called '**Simple Unit Cells**' or '**Primitive Unit Cells**'.

However it has been observed that the particles may be present not only at the corners but may also be present at some other special positions with the unit cells. Such unit cells are called '**Non-primitive Unit Cells**' or '**Centred Unit Cells**'.

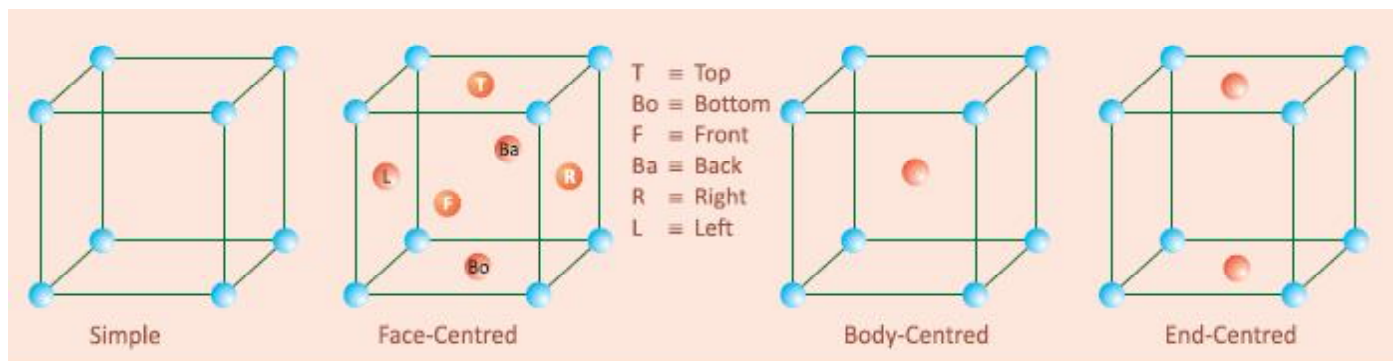
There are different types of non - primitive unit cells as follows :

(a) Face centred unit cell

When the particles are present not only at the corner but also at the centre of each of the unit cell, is called **Face Centred Unit cell**.

(b) Body centred unit cell

When in addition to the particles at the corner of the cube, there is one present at the body Centre position of the unit cell, then the unit cell is called **Body Centred Unit cell**.

**(b) End centred unit cell**

Another type of unit cell, called **End centered unit cell**, is possible for orthorhombic and monoclinic crystal types. In an end centered unit cell, there are lattice points in the face centers of only one set of opposite faces, in addition to the lattice points at the corners of the unit cell.

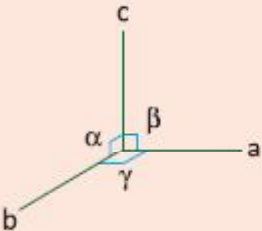
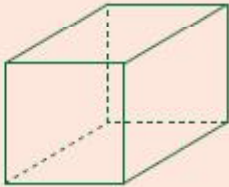
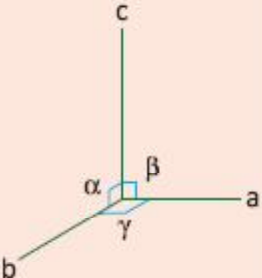
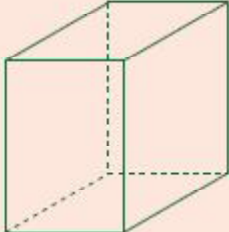
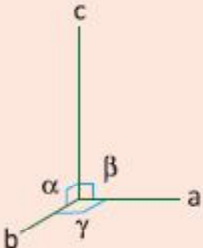
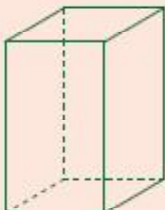
It may be noted that all the four types of unit cells are not possible for each crystal system *i.e.*, simple, face centered, end centered and body centered.

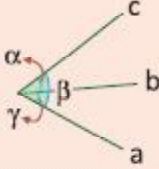
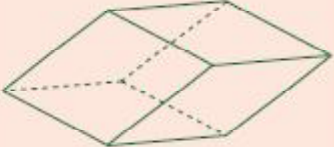
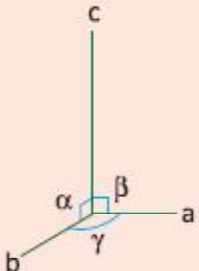
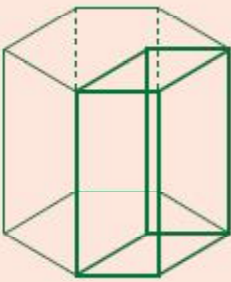
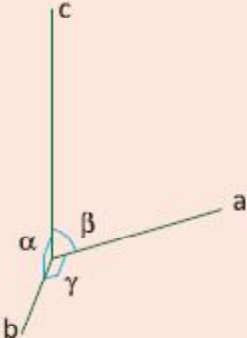
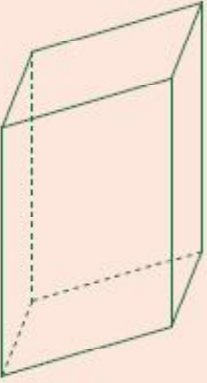
A three-dimensional space lattice is generated by repeated translation of three non coplanar vectors a, b and c . It so turns out that there are only 14 distinguishable ways of arranging points in three-dimensional space such that each arrangement conforms to the definition of a space lattice. These 14 space lattices are known as **Bravais Lattices** according to the arrangement of the points in the different unit cells involved. They belong to seven **Crystal systems**.

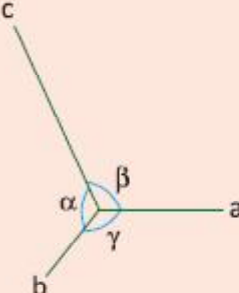
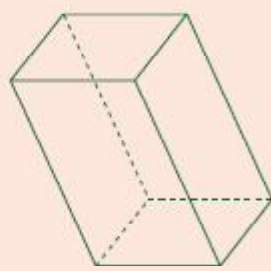
Crystal system and their features with some examples

S.No.	System	Axial Lengths	Axial Angles	Examples
1.	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	NaCl, KCl, ZnS, Diamond
2.	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	NH_4Br , SnO_2 , TiO_2
3.	Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	K_2SO_4 , BaSO_4 , KNO_3
4.	Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	NaNO_3 , CaCO_3 , ICl
5.	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	HgS , CdS , ZnO
6.	Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
7.	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{K}_2\text{Cr}_2\text{O}_7$

Type of unit cells in the crystal system

Crystal	Space Lattice	Unit Cell
I. Cubic $a = b = c$ $\alpha = \beta = \gamma = 90^\circ$ 	<ol style="list-style-type: none"> Simple (Lattice points at the eight corners of the unit cell) Body centered (Points at the eight corners and at the body centre) Face centered (Points at the eight corners and at the six face centres) 	
II. Tetragonal $a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$ 	<ol style="list-style-type: none"> Simple (Points at the eight corners of the unit cell) Body centered (Points at the eight corners and at the body centre) 	
III. Orthorhombic $a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$ 	<ol style="list-style-type: none"> Simple (Points at the eight corners of the unit cell) Body centered (Points at the eight corners and at the body centre) Face centered (Points at the eight corners and at the six face centres) End centered (Also called side centered or base centered) (Points at the eight corners and at two face centres opposite to each other) 	

Crystal	Space Lattice	Unit Cell
IV. Rhombohedral $a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$ 	10. Simple (Points at the eight corners of the unit cell)	
V. Hexagonal $a = b \neq c$ $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$ 	11. Simple [(i) Points at the eight corners of the unit cell outlined by thick lines or (ii) Points at the twelve corners of the hexagonal prism and at the centres of the two hexagonal faces]	
VI. Monoclinic $a \neq b \neq c$ $\alpha = \gamma = 90^\circ \neq \beta$ 	12. Simple (Points at the eight corners of the unit cell) 13. End centered (Points at the eight corners and at two face centres opposite to each other.)	

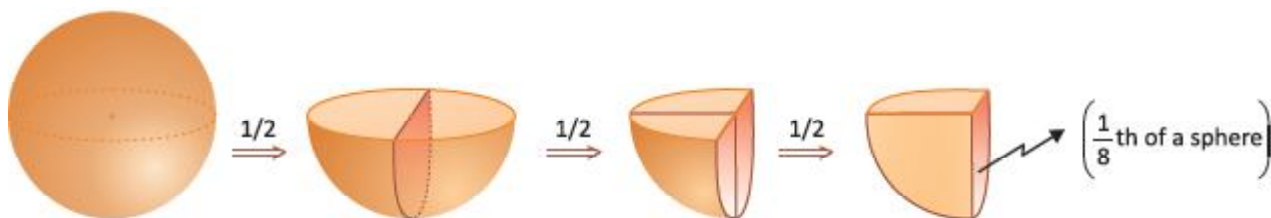
Crystal	Space Lattice	Unit Cell
VII. Triclinic $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$ 	14. Simple (Points at the eight corners of the unit cell)	

EFFECTIVE NUMBER OF ATOMS IN A UNIT CELL

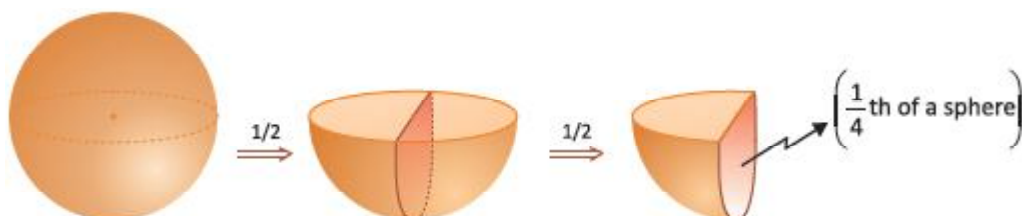
Section - 6

It can be determined by the simplest relation :

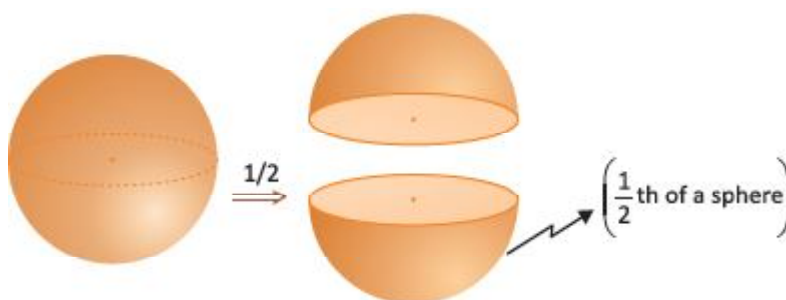
1. A point that lies at the corner of a unit cell is shared among eight unit cell and, therefore, only one-eighth of each such point lies within the given unit cell.



2. A point along an edge is shared by four unit cells and only one-fourth of it lies within any one cell.



3. A face-centred point is shared by two unit cell and only one half of it is present in a given unit cell.



4. A body-centred point lies entirely within the unit cell and contributes one complete point to the cell.

$$\text{Total number of atoms in unit cell} = \frac{n_e}{8} + \frac{n_f}{2} + \frac{n_i}{1} + \frac{n_e}{4}$$

When n_c : Number of atom at the corners of the unit cell

n_f : Number of atoms at six faces of the unit cell

n_i : Number of atoms completely inside the unit cell

n_e : Number of atoms at the edge centres of the unit cell

Effective number of atoms per unit cell

S.No.	Cubic Unit Cell	n_c	n_f	n_i	Total Atoms per Unit Cell
1.	Simple Cubic	8	0	0	1
2.	Body Centred Cubic	8	0	1	2
3.	Face Centred Cubic	8	6	0	4

ATOMIC RADIUS & SHORTEST DISTANCE IN CUBIC SYSTEM

Section - 7

7.1 Definition :

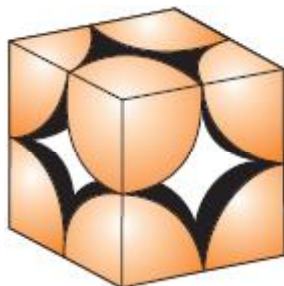
The atomic radius is defined as half the distance (centre to centre) between neighbouring atoms in a crystal. It is expressed in terms of edge 'a' of the unit cell of the crystal.

7.2 Detailed View :

(a) Simple Cubic (SC)

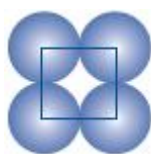
1. Crystal System : Cubic
2. Lattice Points Occupied : Only all corners of cube are occupied and each corner atom is in contact with adjacent corner atoms.

3. Arrangement of constituent particles in simple cubic.



Note : Neighbouring atoms are in contact with each other.

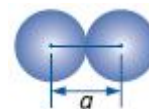
4. Top View of Unit Cell :



5. Relation between edge length of unit cell and radius of constituent particles.

Each corner atom is in contact with its adjacent corner atom such that

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



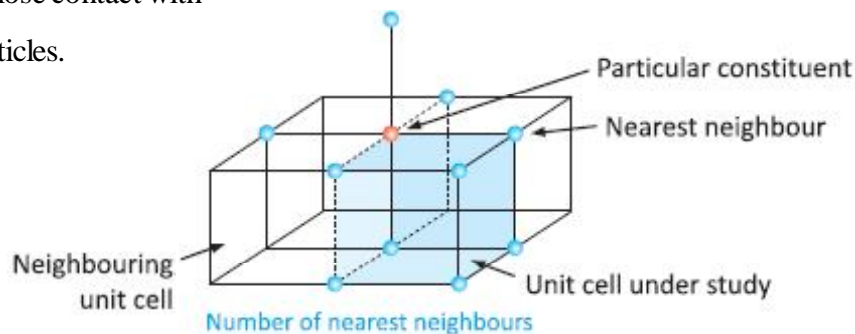
6. Rank of the unit cell (z) : Effective number of constituent particles per unit cell.

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

7. Number of nearest neighbours or Co-ordination number.

(i) Number of nearest neighbours (NNs) :

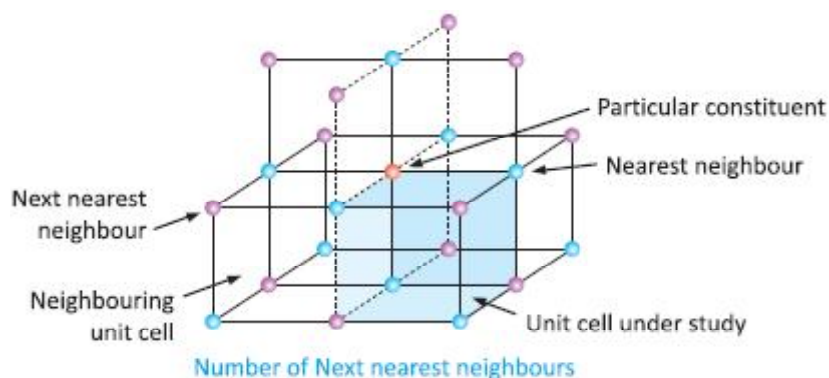
It is number of neighbouring constituent particles that are in close contact with given constituent particles.



(ii) Number of next nearest neighbours (NNNs)

It is neighbours at second shortest distance (NNNs = 12)

Four in every plane

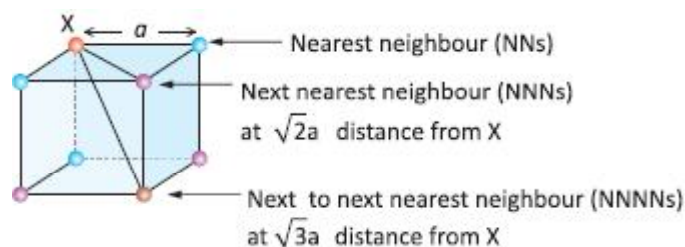


NNs is at 'a' distance from 'X' (NNs = 3)

NNNs is at $\sqrt{2}a$ distance from 'X' (NNNs = 3)

NNNNs is at $\sqrt{3}a$ distance from X (NNNNs = 1)

In a simple cubic system for particle 'X'



8. Packing Efficiency :

$$\text{Packing efficiency} = \frac{\text{volume occupied by all constituent}}{\text{Volume of unit cell}}$$

For cubic unit cell

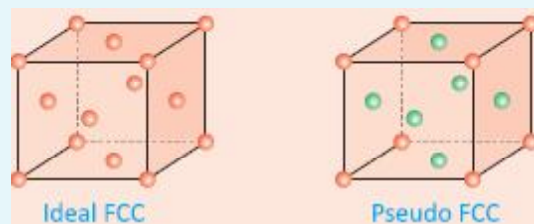
$$\text{Packing efficiency} = \frac{z \times \frac{4}{3} \pi r^3}{a^3} = \frac{1 \times \frac{4}{3} \pi r^3}{a^3} = \frac{1 \times \frac{4}{3} \pi r^3}{(2r)^3} = 0.52$$

(b) Face Centred Cubic (FCC)

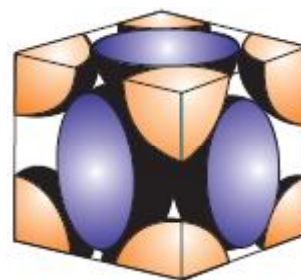
1. Crystal system : Cubic
2. Lattice point occupied : Two types of lattice points are occupied and these are

- (i) All corners (ii) All face centres

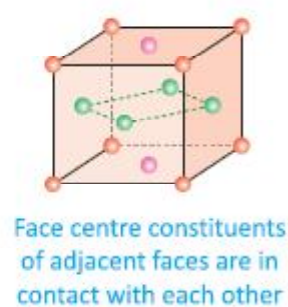
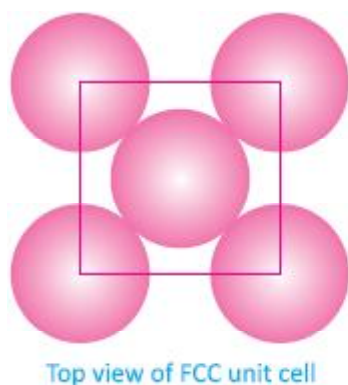
Note : FCC unit cell can be ideal FCC and pseudo FCC. In pseudo FCC constituents at corner lattice points are different from the face centre lattice points.



3. Arrangement of constituent particles in FCC unit cell.



4. Top view of unit cell

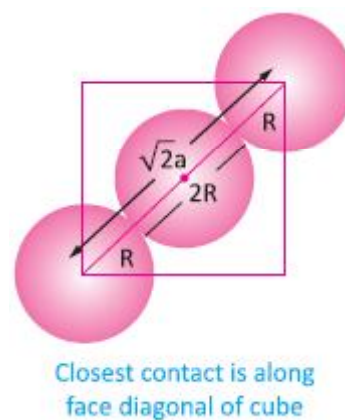


Note : Face centre constituent particle is in close contact with constituent particle at corners. Face centre constituent of adjacent faces are in contact with each other.

5. Relation between radius of constituent particles and edge length of unit cell

Closest contact is along face diagonal of cube. Each corner of a particular face centre atom touches the face centre atom such that :

$$2R = \frac{a}{\sqrt{2}} \Rightarrow R = \frac{a}{2\sqrt{2}} \text{ or } \sqrt{2}a = 4R$$



Note : Each face centre touches other face centre atoms (at a distance of $\frac{a}{\sqrt{2}}$) provided they are not the centres of opposite faces.

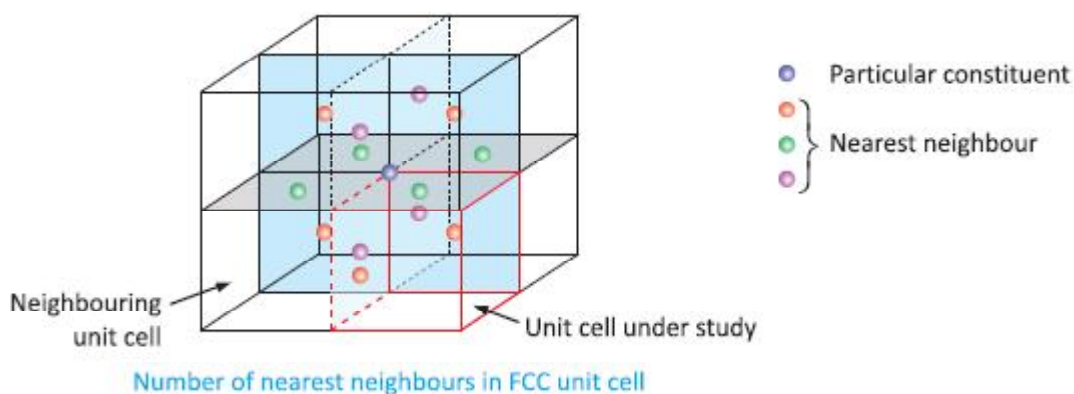
6. Rank of the unit cell (z) : Effective number of constituent particles per unit cell.

$$Z = \frac{1}{8} \times (\text{No. of corner}) + \frac{1}{2} \times (\text{No. of face centres})$$

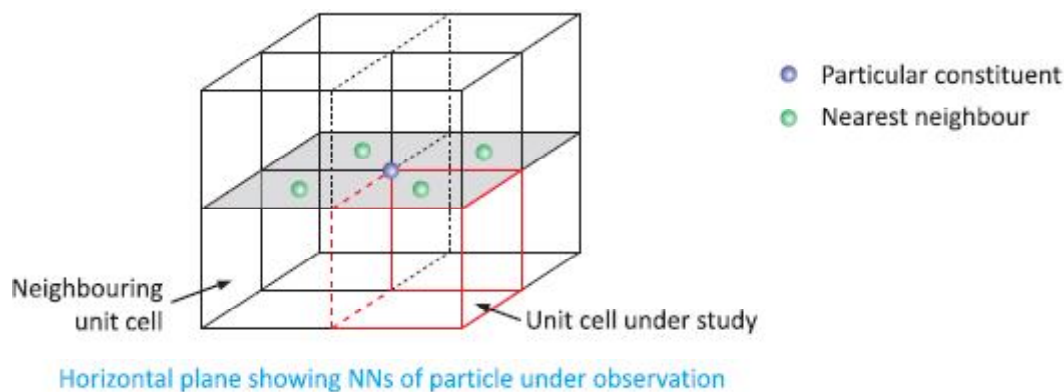
$$= \frac{1}{8} \times 8 + \frac{1}{2} \times 6 = 1 + 3 = 4$$

7. Number of nearest neighbours (Co-ordination Number)

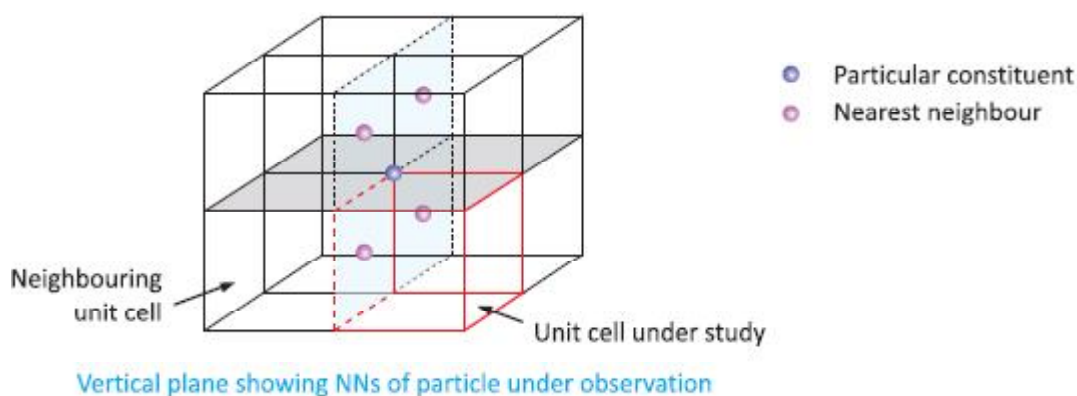
Constituent particles at corners are nearest neighbours of the constituent particle at face centre of the FCC unit cell.



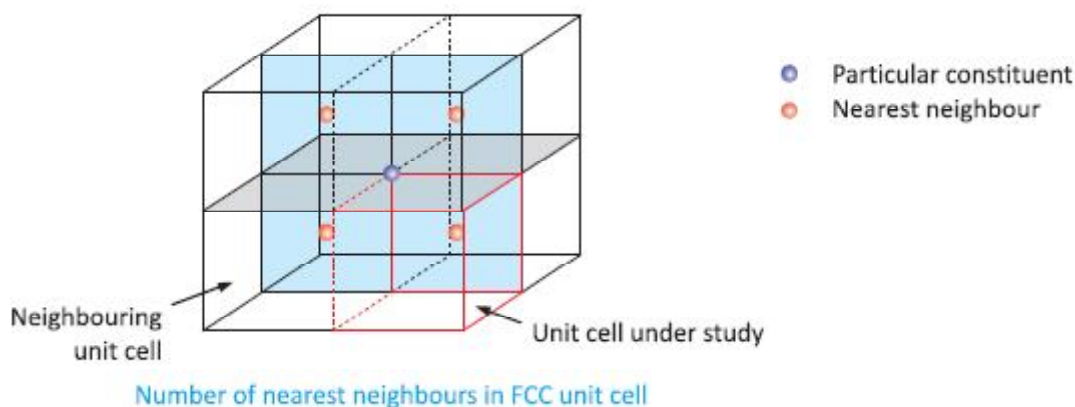
Horizontal plane showing NNs of particle under observation



Vertical plane showing NNs of particle under observation



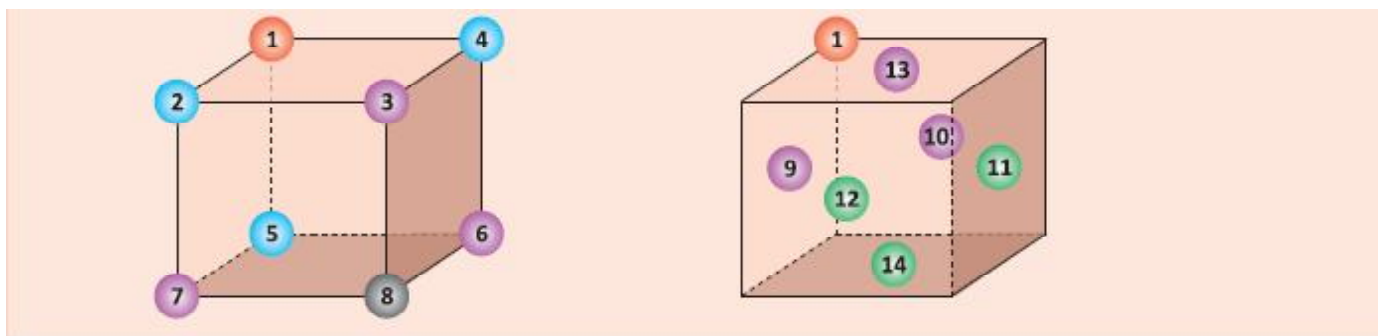
Vertical plane showing NNs of particle under observation.



$$8. \quad \text{Packing efficiency} = \frac{Z \times \frac{4}{3} \pi r^3}{a^3} = \frac{4 \times \frac{4}{3} \pi r^3}{\left(\frac{4r}{\sqrt{2}}\right)^3} = 0.74$$

Note : In single FCC unit cell there are total 14 constituent particles present at different lattice points.

- (i) No. of nearest neighbours (NNs) at $\frac{\sqrt{2}}{2} a$ distance from particles under observation are three.
- (ii) No. of next nearest neighbor (NNNs) at a distance from particle under observation are three.
- (iii) No. of next to next nearest neighbours (NNNNs) at $\sqrt{\frac{3}{2}} a$ distance from particle under observation are three.



Reference Atom/Constituent Particle is 1.

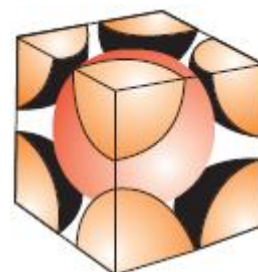
- No of atoms at distance $\frac{\sqrt{2}a}{2}$ (NNs) are 3. [9, 10, 13]
- No. of atoms at distance a (NNNs) are 3 [2, 4, 5]
- No. of atoms at distance $\frac{\sqrt{3}}{2}a$ (NNNNs) are 3 [11, 12, 14]
- No. of atom at distance $\sqrt{2}a$ are 3 [3, 6, 7]
- No. of atoms at distance $\sqrt{3}a$ is 1 [8]

Total No. of atoms for reference atom = $3 + 3 + 3 + 3 + 1 = 13$

(c) Body Centred Cubic (BCC)

Each corner of the unit cell touches the body centre atom such

$$\text{that } 2R = \frac{\sqrt{3}}{2}a \Rightarrow R = \frac{\sqrt{3}}{4}a$$



NOW ATTEMPT IN-CHAPTER EXERCISE-A BEFORE PROCEEDING AHEAD IN THIS EBOOK

VOIDS

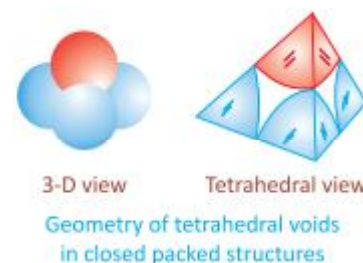
Section - 8

In close packing of spheres, there is always some empty space left. The empty space is called **hole** or **void** or **interstitial site**. There are two main types of interstitial voids in closely packed structures :

- (a) Tetrahedral voids (b) Octahedral voids

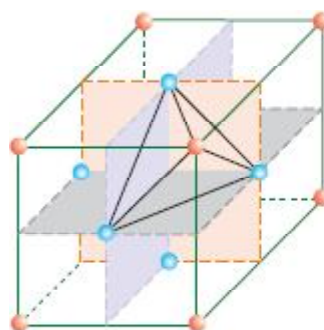
Tetrahedral void : When one sphere is placed upon the three other spheres which are touching each other, tetrahedral structure results. The name 'tetrahedral void' comes from the regular tetrahedron obtained by joining the centres of four spheres. The four spheres leave a small space between them which is smaller than the size spheres.

However, when the spheres are bigger in size, the tetrahedral site becomes larger. In HCP and FCC, each sphere is in contact with three spheres above and three spheres below (see adjacent fig). Thus, there are two tetrahedral sites associated with each sphere.



For example, in the FCC unit cell, the centres of the tetrahedral voids lie quarter - way and three - quarter - way along the four nonparallel body diagonals of the cube (at a distance of $\sqrt{3}a/4$ from every corner along body diagonal). There are thus eight tetrahedral voids in the unit cell. As the effective number of atoms in the unit cell is 4, this works out to a ratio 2 : 1 for the tetrahedral void to the atoms.

Figure show 8 Tetrahedral voids per FCC unit cell :

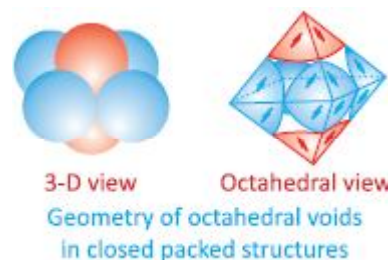


(A FCC unit cell has been divided into 8 sub-cubes such that centre of each sub-cube is the location of tetrahedral void.

Note : For HCP unit cell, refer to the Section - 10.

Octahedral void : An octahedral void is formed with three spheres on a close packed plane and three more spheres on an adjacent close packed plane. Note that the three spheres of the adjacent plane are positioned such that the centres of the three spheres are directly over the three triangular valleys surrounding the central valley of the first plane, with no sphere over the central valley. The given figure is tilted view of the octahedral arrangement, showing the square base with one sphere each on top and at the bottom.

The name comes from the regular octahedron (a polyhedron with six corners and eight faces, the face being equal and equilateral triangles) formed by joining the centres of the six spheres. There is one octahedral void per sphere in the three dimensional array.



For example, in the FCC unit cell, the centres of the octahedral voids fall at the body centre and the middle of the 12 cube edges. the effective number of octahedral voids per unit cell is then $(1 \times 1) + \left(\frac{1}{4} \times 12\right) = 4$. As the effective number of atoms in the unit cell is 4, this work out to a ratio 1 : 1 for the octahedral void to the atoms.

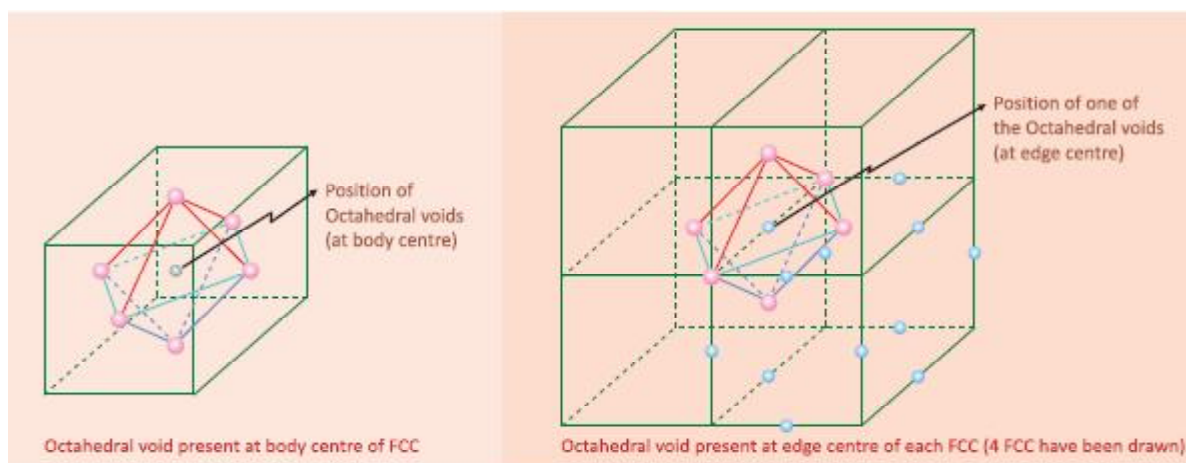


Figure shows 1 octahedral void at the body centre (with probability 1) and 12 octahedral sites (with probability 1/4) are at edge centres in FCC unit cell.

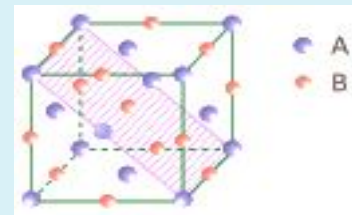
(Note : Only required atoms are shown in figure)

Note : For HCP unit cell, refer to the Section – 10.

In general, if in a Close Packed crystal (CCP or HCP), there are N spheres (atoms or ions) in the packing, then Number of Octahedral voids = N and Number Tetrahedral voids = 2N

Illustration - 3

A crystal is made of particles A and B. A forms FCC packing and B occupies all the octahedral voids. If all the particles along the plane as shown in figure are removed, then the formula of the crystal would be :



- (A) AB (B) A_5B_7 (C) A_7B_5 (D) None of these

SOLUTION : (A)

$$\text{No. of A atoms Left} = 4 - \left(\frac{1}{8} \times 4 \right) - \left(\frac{1}{2} \times 2 \right) = \frac{5}{2}$$

(corner atoms) (face center atoms)

$$\text{No. of B atoms Left} = 4 - \left(\frac{1}{4} \times 2 \right) - (1 \times 1) = \frac{5}{2}$$

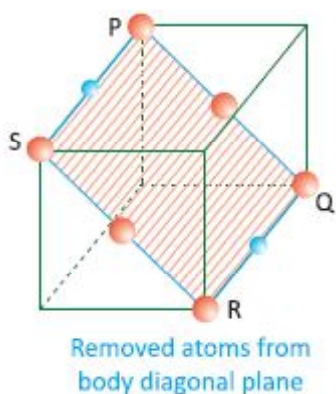
(edge center atoms) (body center atoms)

This simplest formula of crystal is AB

Illustration - 4

In a solid AB having rock salt structure, if all the atoms touching 1 body diagonal plane are removed (except at body centre), then the formula for the left unit cell is :

- (A) A_7B_3 (B) A_5B_3 (C) A_5B_3 (D) $A_{7/2}B_{5/2}$

SOLUTION : (D)

PQRS is the body diagonal plane

'B' atoms are at corners and face centres

$$\text{No. of B atoms left} = 4 - \left(\frac{1}{8} \times 4 \right) - \left(\frac{1}{2} \times 2 \right) = \frac{5}{2}$$

'A' are at edge centres and body centre

$$\text{No. of 'A' atoms left} = 4 - \left(\frac{1}{4} \times 2 \right) = \frac{7}{2}$$

The formula of the compound is : $A_{7/2}B_{5/2}$

CO-ORDINATION NUMBER (C.N.)

Section - 9

The number of atoms in a crystal which surrounds particular atom as its nearest neighbour atoms in its neighbourhood is called **co-ordination number**.

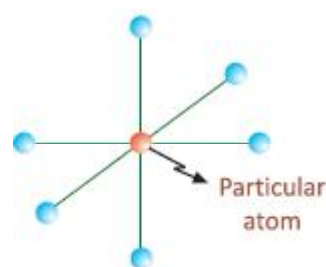
- Note :**
- (i) For diatomic atoms, co-ordination no. of a cation is the no. of surrounding anions of vice – versa.
 - (ii) In crystals with directional bonds, co-ordination number is lower than that of crystals with non-directional bond such as metals and ionic compounds.

The coordination no. of Monoatomic crystals is discussed below :

(A) Simple Cubic (SC)

No. of atoms surrounding the (touching) the body centre atom = 6

Hence, Co-ordination No. = 6

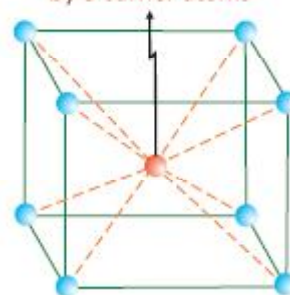


(B) Body Centred Cubic (BCC)

No. of atoms surrounding the (touching) the body centre atom = 8

Hence, Co-ordination No. = 8

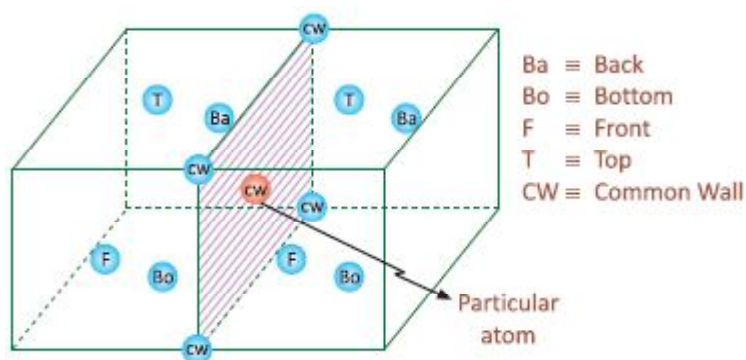
Body Centred Atom is surrounded by 8 corner atoms



(C) Face Centred Cubic (FCC)

No. of atoms surrounding (touching) the face centre of any face = 12

Hence, co-ordination No. = 12.



PACKING OF CONSTITUENT PARTICLES IN CRYSTALS

Section - 10

In the formation of crystals, the constituent particles, atoms or ions or molecules, may be different sizes and so it may give different mode of packing of particles in the crystal. The actual mode of packing of the particles in the crystal is determined experimentally by the **X-ray diffraction method**. However, in order to understand the packing of the constituent particles in a crystal, it is assumed that these particles are hard spheres of identical size. The packing of these spheres takes place in such a way that they occupy the maximum available space and hence the crystal has maximum density. This type of packing is called closed packing in **crystals**. The packing of spheres of equal size takes place as follows :

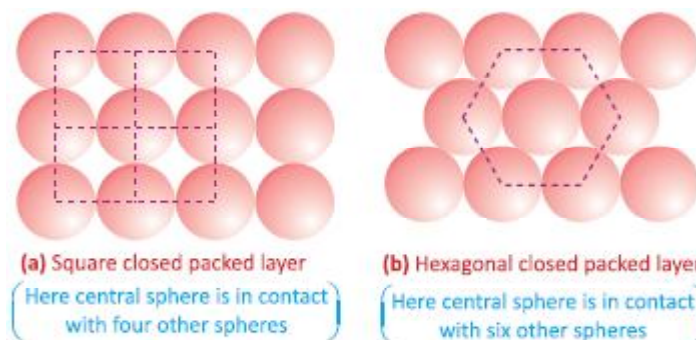
One Dimensional Packing :

When the spheres are placed in a horizontal row, touching each other, an edge of the crystal is formed.

**Two dimensional Packing :**

When the rows are combined touching each other, crystal plane is obtained. The rows can be combined in two different ways :

- (a) **Square Packing :** The particles when placed in the adjacent row, show a horizontal as well as vertical alignment and form squares. This type of packing is called **Square Close Packing**.



- (b) **Hexagonal Packing :** The particles in every next row are placed in the depression between the particles of the first row. The particles in the third row will be vertically aligned with those in the first row. This type of packing gives a hexagonal pattern and is called **Hexagonal Close Packing (HCP)**.

Note : (i)

The second mode of packing (*i.e.*, **HCP**) is more efficient as more space is occupied by the sphere in this arrangement.

(ii)

In Square Close Packing, a central sphere is in contact with four other spheres whereas in Hexagonal Close Packing a central sphere is in contact with six other spheres.

Three Dimensional close packing :

In three dimension packing of spheres, the two dimensional close packed layers can be stacked in two different arrangements :

- (a) When the spheres of the second layer are placed on the spheres of the first layer and the spheres of the third layer on the spheres of second layer and so on. In this form of packing, the spheres are vertically aligned and the voids are also vertically overlapping. It results in an inefficient way of three dimensional packing. This leads to simple cubic packing with a packing efficiency of 52% (It has been discussed in section 14)
- (b) When the second layer is placed in such a way that its spheres find place in the 'a' voids of the first layer, then 'b' voids will be left unoccupied since under this arrangement no sphere can be placed in them. Similarly there are two types of voids in the second layer. When both layers are considered together, we have two type of voids marked as voids 'c' and voids 'd'.

The voids 'c' are ordinary voids which lie above the spheres of the first layer whereas voids 'd' lie on the voids of the first layer and hence are combination of two voids ; one of the first layer and other of the second layer with the vertex on one triangle upwards and the vertex of the other triangle downwards which leads to an octahedral void.

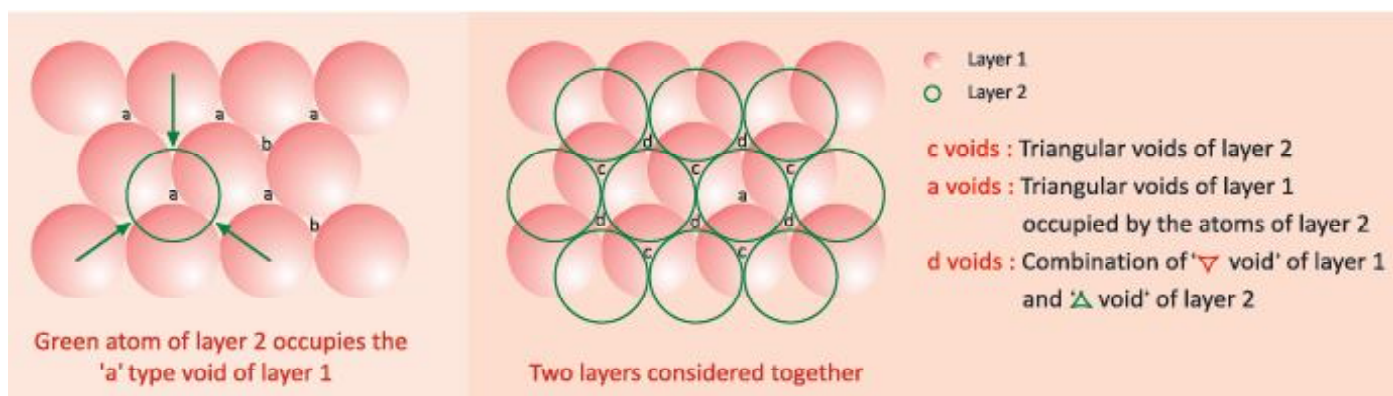
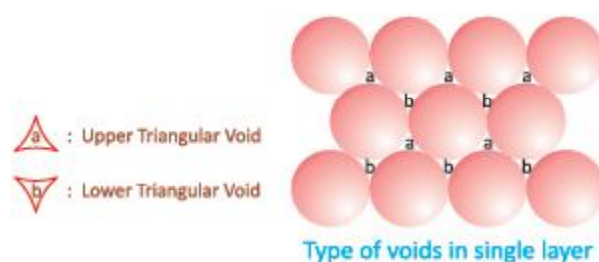


Figure shows the type of voids when two layers are considered

Now there are two way to build up the third layer :

- (i) When a third layer is placed over to second layer in such a way that the spheres cover the tetrahedral or 'c' voids, a three dimension closest packing is obtained where the spheres in every third of alternate layer are vertically aligned (i.e., the third layer is directly above the first, the fourth above the second layer and so on). Calling the first layer as layer A and second layer as layer B, the arrangement is called ABAB.....pattern or Hexagonal Closed Packing (HCP). Molybdenum, Magnesium and Beryllium crystallise in HCP structure.

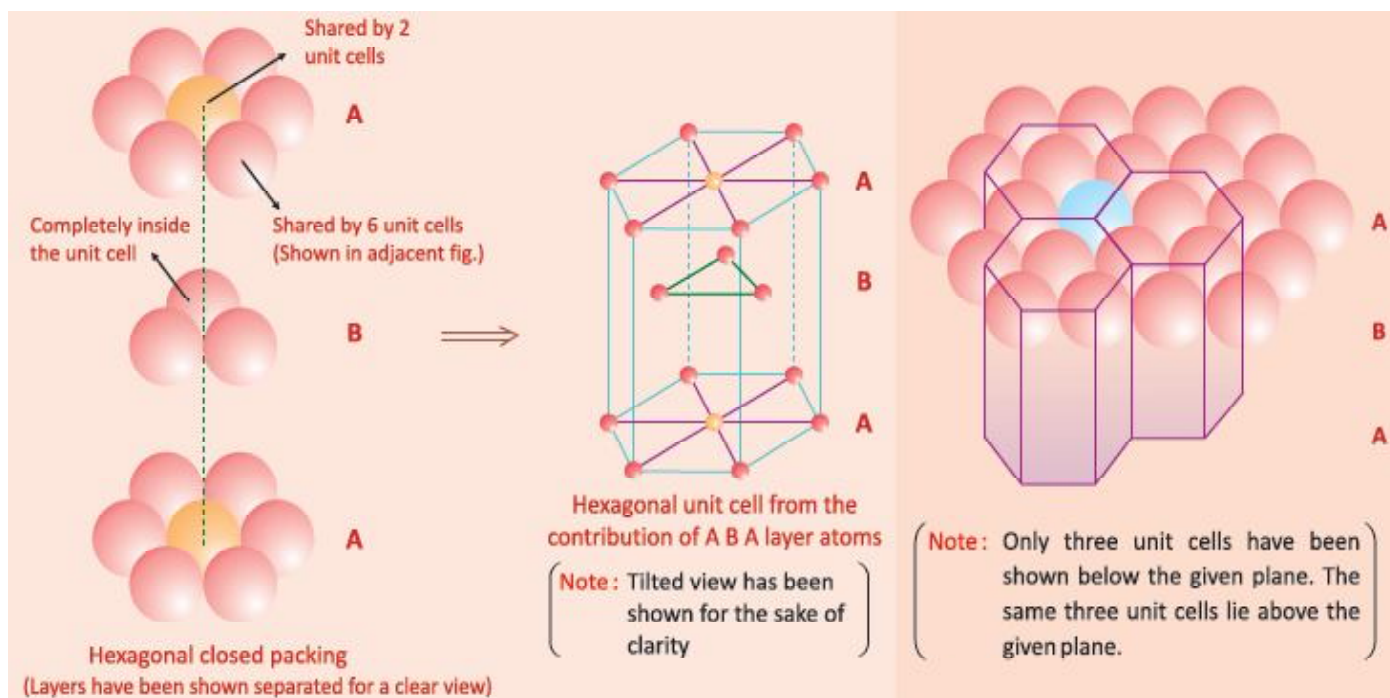
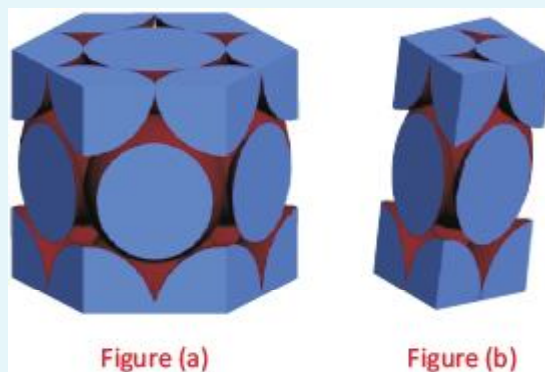


Figure shows Hexagonal Closed Packing

Figure shows 'e' is shared by six unit cells

$$\text{Effective number of atoms per HCP unit cell} = \left(\frac{1}{6} \times 12 \right) + \left(\frac{1}{2} \times 2 \right) + (1 \times 3) = 6$$

Note : 11.51% of the total volume of the middle layer sphere extends out of one side of the parallelepiped. Another 11.51% of this sphere extends out of an adjacent face of the unit cell, leaving 76.98% enclosed within the unit cell boundary. The excluded portions are precisely matched by portions of two other middle layer spheres extending from adjacent unit cells into the first unit cell toward the center of the equilateral triangle centered over the unoccupied hole in the bottom layer [See figure (a) and (b)].



- (ii) When the third layer is placed over the second layer in such a way that spheres cover the octahedral of 'd' voids, a layer different from layers A and B is produced. Let us call it as layer C. Continuing further a packing is obtained where the spheres in every fourth layer will be vertically aligned. This pattern of stacking spheres is called ABCABC.....pattern or **Cubic Close Packing (CCP)**. It is similar to **Face-Centred Cubic (FCC)** packing.

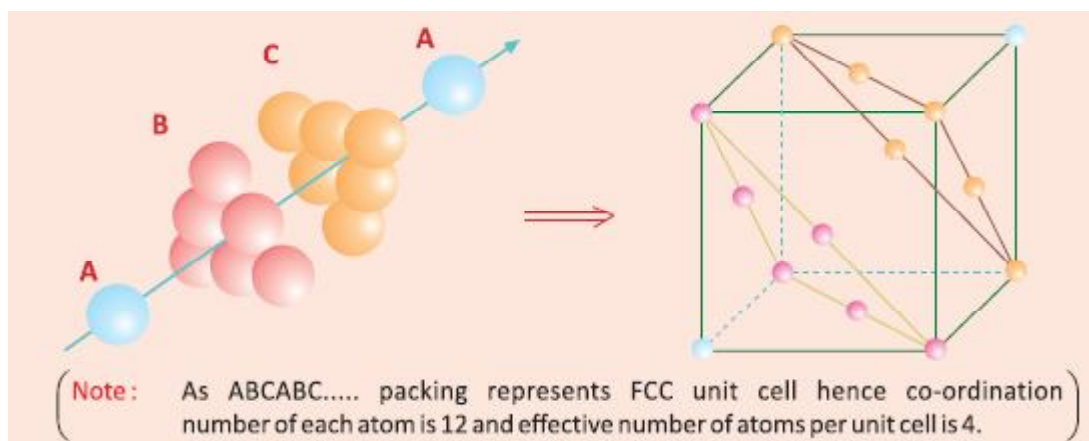


Figure show ABCABC.....packing can be represented in FCC unit cell

Note : In both HCP and CCP the coordination number is 12 because a sphere is in contact with 6 spheres in its own layer. It touches three spheres in the layer above and three in the layer below.

Comparison of Various Type of Views of HCP & FCC Unit Cell :

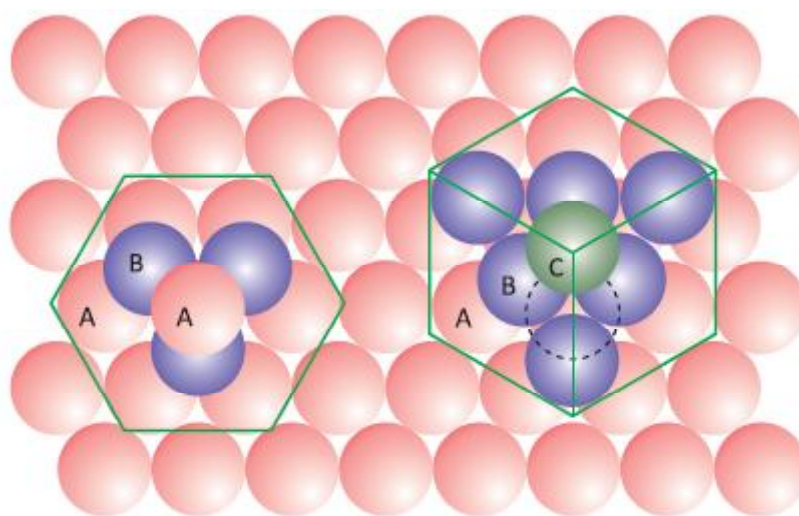


Figure showing Comparison between HCP & FCC

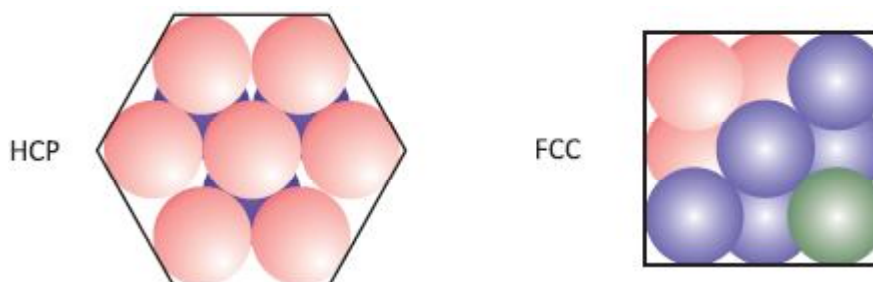


Figure showing Comparison of Top view of unit cells

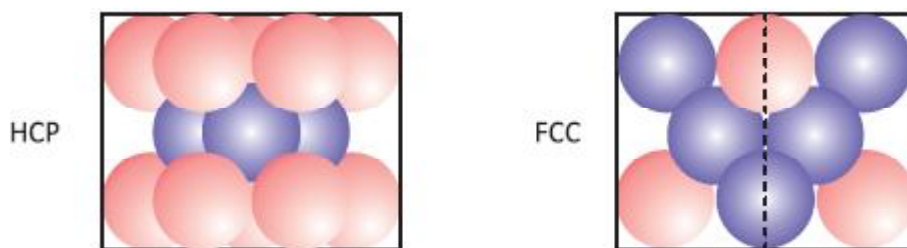
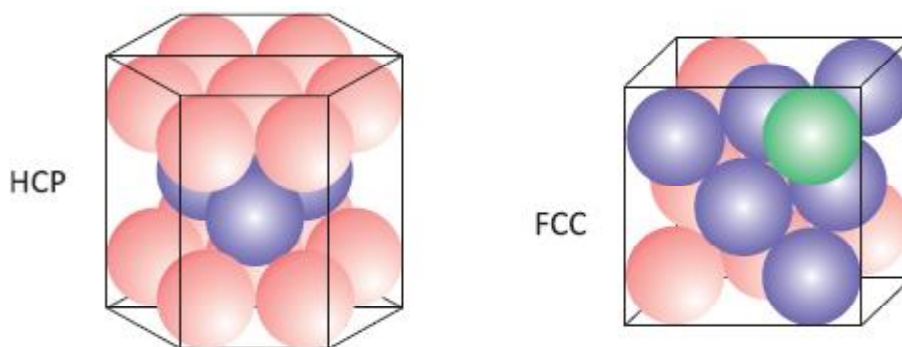


Figure showing comparison of Front view of unit cells

**Illustration - 5**

When over a 2 dimensional square packing same layers are kept in the way so that the centres are aligned in all 3 dimensions, coordination number of each sphere is :

- (A) 6 (B) 8 (C) 12 (D) 10

SOLUTION : (A)

The co-ordination number is 6. ("4 atoms" in the plane + 1 atom above + 1 atom below the particular atom).

Illustration - 6

In an FCC crystal, which of the following shaded planes contains the given (\rightarrow) type of arrangement of atoms ?

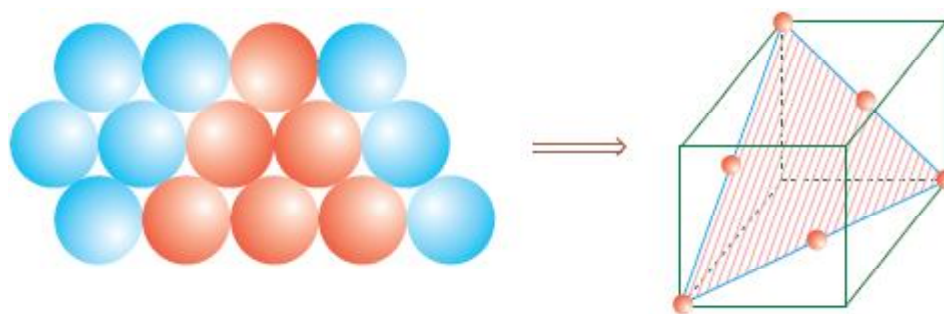
**SOLUTION : (A)**

Illustration - 7

In hexagonal close packing of sphere in three dimensions.

- (A) In one unit cell there are 12 octahedral voids and all are completely inside the unit cell
 (B) In one unit cell there are six octahedral voids and all are completely inside the unit cell
 (C) In one unit cell there are six octahedral void and of which three are completely inside the unit cell and other three are from contributions of octahedral voids which are partially inside the unit cell
 (D) In one unit cell there are 12 tetrahedral voids, all are completely inside the unit cell

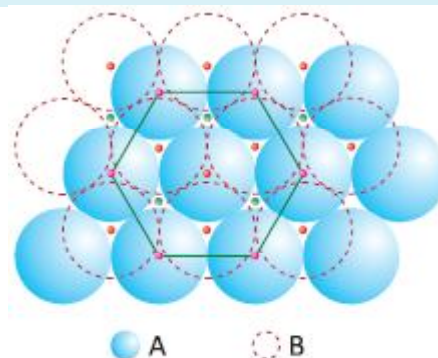
SOLUTION : (B)

HCP \equiv AB AB AB pattern repeat

For calculating voids between two layers A and B.

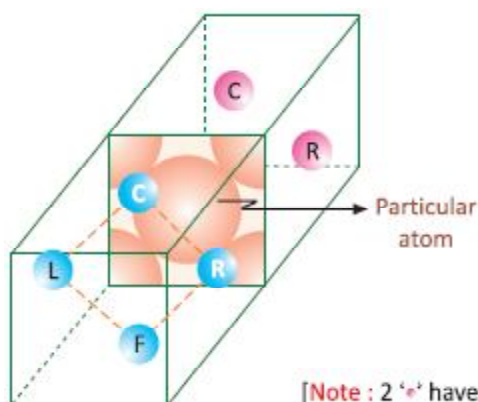
Total tetrahedral voids = 12 (represented by '•' and '•') out of which 8 are completely inside ('•') and ('•') are shared by other unit cells (each shared in 3 unit cells)

Total octahedral voids = 6 (represented by '•'). All are completely inside.

**Illustration - 8**

The co-ordination number of fcc structure for a metal is 12, since

- (A) each atom touches 4 others in same layer, 2 in layer above and 6 in layer below
 (B) each atom touches 4 others in same layer, 4 in layer above and 4 in layer below
 (C) each atom touches 6 others in same layer, 5 in layer above and 1 in layer below
 (D) each atom touches 8 others in same layer, 2 in layer above and 2 in layer below

SOLUTION : (B)

C \equiv Ceiling
 R \equiv Right
 F \equiv Floor
 L \equiv Left

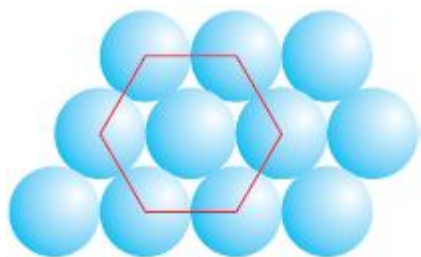
Each atom touches 4 atoms in same layer,
 4 in above layer and 4 in layer below.

[Note : 2 '•' have not been shown in the figure]

Illustration - 9 Which of the following statements is correct for a two-dimensional hexagonal close-packed layer ?

- (A) Each sphere is surrounded by six spheres (B) Each sphere is surrounded by six voids
(C) Each sphere has three voids (D) Each void is surrounded by three spheres

SOLUTION : (ABD)



- (A) Each sphere is surrounded by six spheres
(B) Each sphere is surrounded by six voids

(C) Effective number of atoms in a hexagonal unit cell

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

Effective no. of voids in a hexagonal unit cell = 6

Hence, each sphere has 2 voids

(D) Each void is surrounded by 3 spheres

Illustration - 10 Calculate the c/a ratio for an ideally close packed HCP crystal.

SOLUTION :

The...ABA...type of stacking represents the HCP structure joining the centres of the three neighbouring atoms of the middle plane to the centres of the atoms of the top and the bottom planes results in two tetrahedra with a common base. The top and bottom atoms are centred at two lattice points, one above the other on the two hexagonal basal planes of the unit cell. So, the distance between them is the unit distance along the c -axis. The distance between any two adjacent atoms of a plane is unit distance along the a -axis. Unit of c is equal to twice the normal from the apex of a tetrahedron to its base. Unit of a is equal to the side of the tetrahedron.

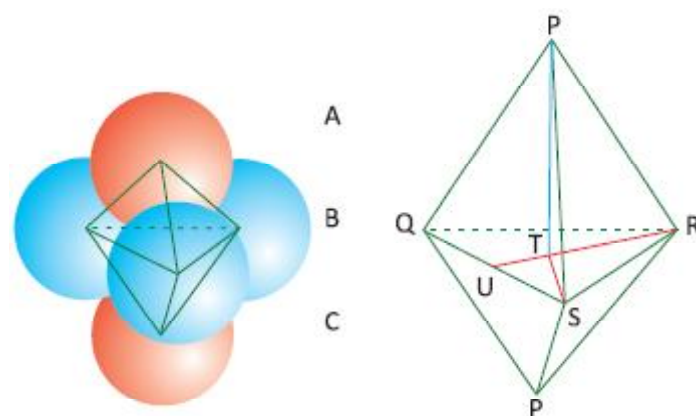
$$\frac{c}{a} = \frac{2PT}{RS}$$

$$RU = \sqrt{RS^2 - SU^2} = \sqrt{a^2 - a^2/4} = \sqrt{3}a/2$$

$$RT = \frac{2}{3} RU = \frac{a}{\sqrt{3}}$$

$$PT = \sqrt{PR^2 - RT^2} = \sqrt{a^2 - a^2/3} = a\sqrt{2}/\sqrt{3}$$

$$\frac{c}{a} = \frac{2\sqrt{2}}{\sqrt{3}} = 1.633$$



In the ... ABA ... packing, which is HCP, the centres of three atoms Q, R and S on plane B are joined to the centres of P atoms in plane A above and below.

Note : You are advised to learn it as a result.

STACKING SEQUENCE

Section - 11

11.1 Definition

It is the sequence in which closest packing can exist. In stacking sequence, the same layer can not repeat just after a layer i.e. A after A is restricted.

If carefully observed, stacking sequence has FCC, HCP and combination of FCC and HCP such that all are closely packed with packing efficiency of 74% (P.E. has been discussed in Section – 14)

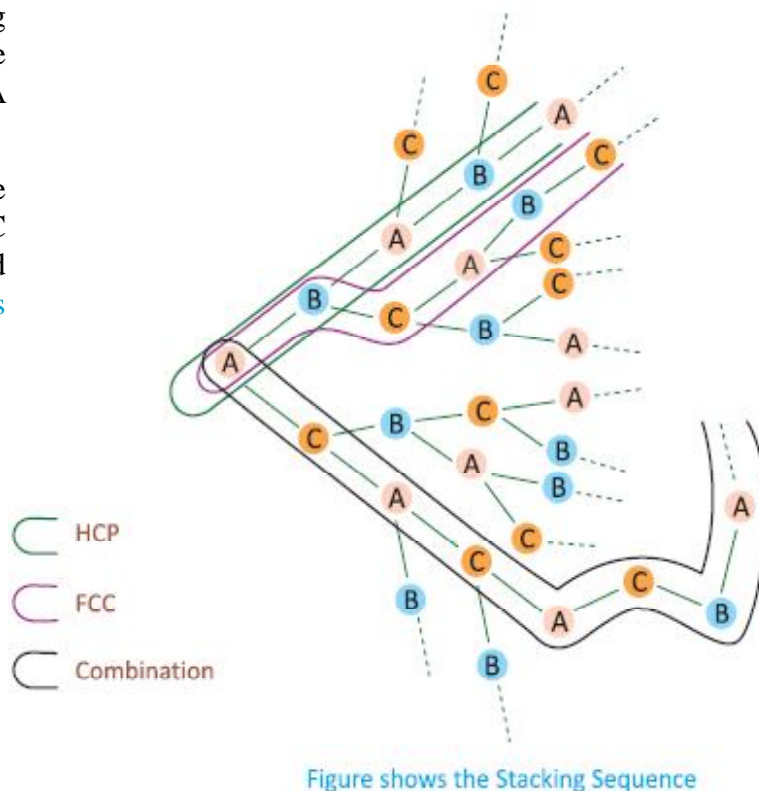


Illustration - 11

Tick the close – packing arrangements in the following :

(A) ABABABA

(B) ABCABCABCA

(C) ABABCBCABC

(D) ACCBCABCABC

SOLUTION : (ABC)

HCP, CCP and their combination (HCP + CCP) are the close – packed arrangement with packing efficiency = 74%

IN-CHAPTER EXERCISE-B

1. Sapphire is aluminium oxide. It crystallises with aluminium ions in two-thirds of octahedral holes in a closest packed array of oxide ions. What is the formula of aluminium oxide ?

NOW ATTEMPT IN-CHAPTER EXERCISE-B FOR REMAINING QUESTIONS

FAMILIES OF CRYSTALS

Section - 12

Main Characteristics and Examples of some Ionic Solid families

S.No.	Crystal Structure	Brief Description	Examples	Co-ordination Number	Number of units per cell
1.	Type AB Rock salt (NaCl) type	It has FCC arrangement in which Cl^- ions occupy the corners and face centres of a cube while Na^+ ions are present at the body centre and edge centres.	Halides of Li, Na, K, Rb, Ag, NH_4^+ , etc.	$\text{Na}^+ = 6$ $\text{Cl}^- = 6$	4
2.	Type AB Cesium chloride (CsCl) type	It has the SC arrangement with Cs^+ at the body centre and Cl^- ions at the corners of a cube or vice versa.	CsCl, CsBr, CsI, CsCN, TiCl, TiBr, TiI	$\text{Cs}^+ = 8$ $\text{Cl}^- = 8$	1
3.	Type AB Zinc blende (ZnS) type	It has FCC arrangement in which S^{2-} ions form FCC and each Zn^{2+} ion is surrounded tetrahedrally by four S^{2-} ions and vice versa. Zn^{2+} ions occupy alternate tetrahedral voids.	CuCl, CuBr, CuI, AgI, BeS	$\text{Zn}^{2+} = 4$ $\text{S}^{2-} = 4$	4
4.	Type AB₂ Fluorite (CaF ₂) type	It has FCC arrangement in which Ca^{2+} ions form FCC with each Ca^{2+} ion is surrounded by 8 F^- ions and each F^- ions by 4 Ca^{2+} ions. F^- ions occupy all tetrahedral voids.	BaF ₂ , BaCl ₂ , SrF ₂ , SrCl ₂	$\text{Ca}^{2+} = 8$ $\text{F}^- = 4$	4
5.	Type A₂B Antifluorite (Na ₂ O) type	Here negative ions form the FCC arrangement so that each positive ion is surrounded by 4 negative ions and each negative ion by 8 positive ions.	Na ₂ O	$\text{Na}^+ = 4$ $\text{O}^{2-} = 8$	4

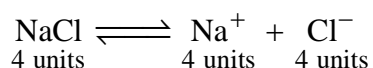
These are discussed in detail as follows :

(i) **Rock Salt (NaCl) type :**

The chloride ions form a FCC lattice and sodium ions are present in octahedral voids i.e. at body centre and edge centre of the chloride lattice.

Effective no. of Cl^- per NaCl unit cell = 4 [Cl^- being present at corners and face centres of the unit cell]

Effective no. of Na^+ per NaCl unit cell = 4 [Na^+ being present in octahedral voids of the unit cell]



No. of NaCl formula units per FCC unit cell = 4

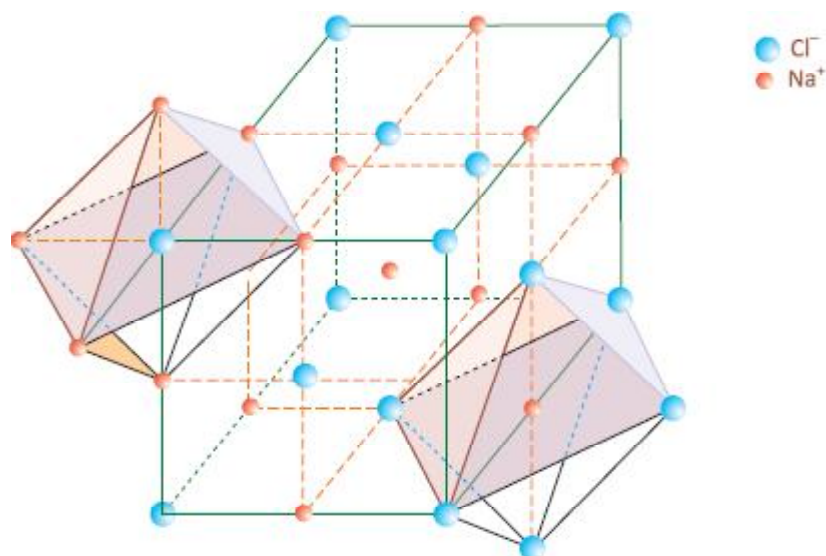


Figure shows the concept of reversibility in the case of NaCl crystal

Co-ordination no. of Na^+ = 6

[Na^+ is present in octahedral void formed by six Cl^- ions]

Co-ordination no. of Cl^- = 6

[Cl^- is present in octahedral void formed by six Na^+ ions using reversibility principle]

(ii) Cesium chloride (CsCl) type :

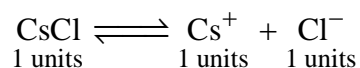
The chloride ions form a SC lattice and cesium ions are present in the cubic void (or body centred void)

Effective no. Cl^- of ions per CsCl unit cell = 1

[Cl^- being present at the corners of the unit cell]

Effective no. Cs^+ of ions per CsCl unit cell = 1

[Cs^+ being present at the body centre of the unit cell]



No. of CsCl formula units per SC unit cell = 1

Co-ordination no. of Cs^+ = 8

[Cs^+ touches eight corner (Cl^-) atoms of the unit cell]

Co-ordination no. of Cl^- = 8

[Cl^- touches eight corner (Cs^+) atoms of the unit cell using reversibility principle]

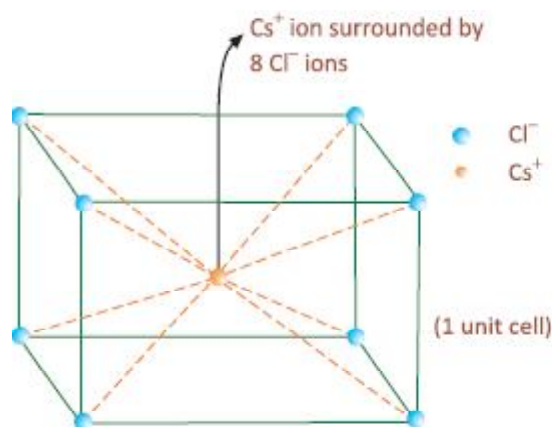


Figure shows Cs⁺ at body centre of CsCl unit cell is surrounded by 8 Cl⁻

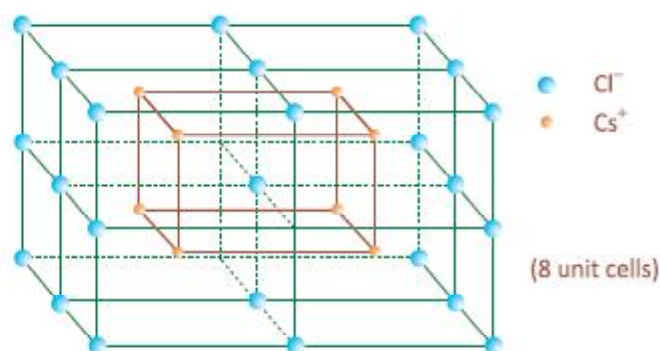


Figure shows the concept of reversibility in the case of CsCl crystal such Cl⁻ lies in the simple cubic of Cs⁺

(Note : Some Cl⁻ have not been shown for the sake of clarity)

(iii) Zinc Blend (ZnS) type :

Lets first know about the structure of diamond. Diamond has FCC structure with four more carbon atoms are found to be present in the alternate tetrahedral voids. So, effective no. of carbon atoms in diamond cubic unit

$$\text{cell} = \underbrace{\frac{1}{8} \times 8 + \frac{1}{2} \times 6}_{\text{FCC unit cell}} + \underbrace{(1 \times 4)}_{\text{Alternate tetrahedral}} = 8$$

The carbon atom in tetrahedral voids touches its 4 surrounding atoms (nearest neighbours), so the co-ordination no. is 4.

Note :

Carbon atoms in the FCC lattice do not touch at all (But carbon atoms which are present in the tetrahedral voids touch the surrounding 4 atoms. So, centre to centre distance between two carbon

atoms is $2r = \frac{\sqrt{3}a}{4}$ where a is the length of the unit cell and r is the radius of the carbon atom.

Solids which follow the structure of diamond are called “Diamond cubic”

Zinc blende (ZnS) is a member of diamond cubic family where sulphide (S²⁻) ions form a FCC lattice with zince (Zn²⁺) ions present in alternate tetrahedral voids i.e. 4 out of 8 tetrahedral voids are unoccupied.

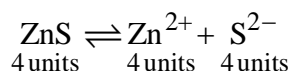
We have two tetrahedral voids per body diagonal out of which one is filled but in alternate fashion with other boyd diagonls.

No. of S^{2-} ions per ZnS unit cell = 4

[S^{2-} being present at corners and face centres of the unit cell]

No. of Zn^{2+} ions per ZnS unit cell = 4

[Zn^{2+} being present in 4 out of 8 tetrahedral voids of the unit cell]



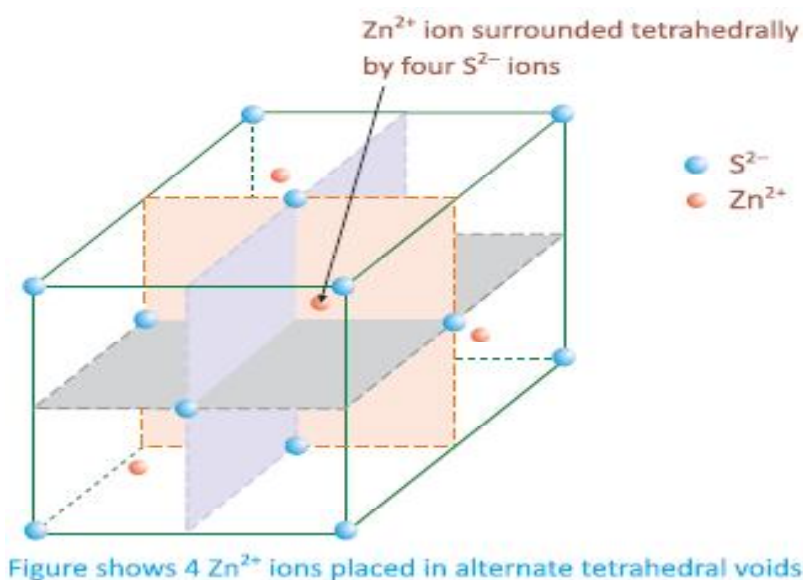
No. of ZnS formula units per FCC unit cell = 4

Co-ordination no. of Zn^{2+} = 4

[Zn^{2+} is present in the tetrahedral void formed by 4 S^{2-} ions]

Co-ordination no. of S^{2-} = 4

[One S^{2-} supports 8 tetrahedrons out of which 4 are filled with Zn^{2+}]



(iv) Fluorite (CaF_2)

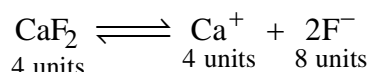
In the fluorite structure, calcium (Ca^{2+}) ions form a FCC and Fluorite (F^-) ions are present in all the tetrahedral voids.

No. of Ca^{2+} ions per CaF_2 unit cell = 4

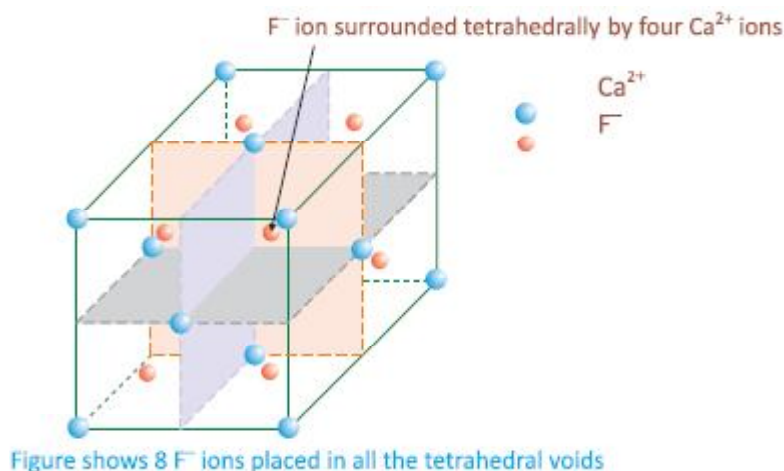
[Ca^{2+} being present at the corners and face centres of the unit cell]

No. of F^- ions per CaF_2 unit cell = 8

[F^- being present in all 8 tetrahedral voids of the unit cell]



No. of CaF_2 formula units per FCC unit cell = 4



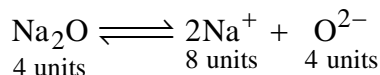
Co-ordination no. of F⁻ = 4 [F⁻ is present in the tetrahedral void formed by 4 Ca²⁺ ions]

Co-ordination no. of Ca²⁺ = 8 [One Ca²⁺ supports 8 tetrahedral voids and all are filled with F⁻]

(v) **Antifluorite (Na₂O) type** : It is just opposite to the fluorite structure where role of cations and anions is interchanged. So, oxide (O²⁻) ions form a FCC unit cell and sodium (Na⁺) ions are present in all the tetrahedral voids

No. of oxide (O²⁻) ions per FCC unit cell = 4

No. of (Na⁺) sodium ions per FCC unit cell = 8



Co-ordination no. of Na⁺ = 4 Co-ordination no. of O²⁻ = 8

Illustration - 12

Diamond has face-centred cubic lattice. There are two atoms at (0, 0, 0) and $\left(\frac{a}{4}, \frac{a}{4}, \frac{a}{4}\right)$ coordinates. The ratio of the carbon-carbon bond distance to the edge of the unit cell is :

- (A) $\sqrt{\frac{3}{16}}$ (B) $\sqrt{\frac{1}{4}}$ (C) $\frac{1}{4}$ (D) $\frac{1}{\sqrt{2}}$

SOLUTION : (A)

$$\text{Distance between } (0, 0, 0) \text{ and } \left(\frac{a}{4}, \frac{a}{4}, \frac{a}{4}\right) = 2r$$

$$\Rightarrow 2r = \frac{\sqrt{3}a}{4} \Rightarrow \frac{2r}{a} = \sqrt{\frac{3}{16}} \quad \text{where } 2r = \text{bond distance}$$

Illustration - 13 Which of the following statements is (are) correct for the diamond structure ?

- (A) Each atom has 4 nearest neighbours and 12 next-nearest neighbours
- (B) It is relatively empty
- (C) The maximum proportion of the available volume which may be filled by hard spheres is only 0.34
- (D) The maximum proportion of the available volume which may be filled by hard spheres is only 0.46

SOLUTION : (ABC)

Atom (carbon) lying in the tetrahedral voids touches the surrounding 4 atoms at a distance of $\frac{\sqrt{3}a}{4}$

And the face centre atom has 12 next nearest neighbours at a distance of $\frac{a}{\sqrt{2}}$

$$\text{The packing efficiency (P.E.)} = \frac{8 \times \frac{4}{3} \pi R^3}{a^3} \quad \text{where} \quad 2R = \frac{\sqrt{3}a}{4} \Rightarrow \frac{R}{a} = \frac{\sqrt{3}}{8}$$

$$\text{Hence P.E. is :} \quad \frac{32}{3} \pi \left(\frac{3\sqrt{3}}{8 \times 64} \right) = \frac{\sqrt{3}\pi}{16} \sim 0.34$$

Note : You will be able to understand P.E. in [Section - 14](#).

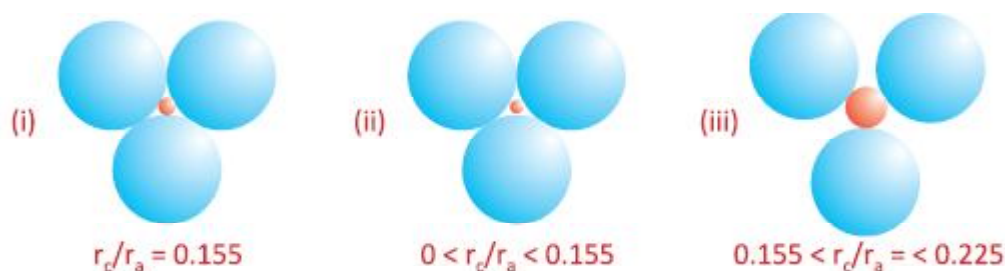
RADIUS RATIO RULES

Section - 13

Consider first the local packing geometry of one type of cation and one type of anion. The cation is assumed to be the smaller ion. The number of anions surrounding a central cation is called the coordination number or ligancy. The ligancy is function of the ion sizes and can be worked out from spaced filling geometry when the following conditions corresponding to a stable configuration are satisfied simultaneously :

- (a) An anion and a cation are assumed to be hard spheres always touching each other.
- (b) Anions generally will not touch, but may be close enough to be in contact with one another in a limiting situation.
- (c) Cation should surround itself with as many anions as possible. Each ion tends to surround itself with as many ions of opposite sign as possible to reduce the potential energy. This tendency promotes the formation of close packed structures.

When the cation is very small compared to the anion, it is easily seen that only two anions can be neighbours to the cation in order to satisfy all the above three conditions. Consider the configuration as shown in the figure (i) below. Here, the three surrounding anions are touching one another and also the central cation.



Triangular coordination of anions around a central cation :

(i) the critical configuration, (ii) the unstable configuration; and (iii) stable (but not critical) configuration.

The ratio of the cation to anion radius r_c / r_a for this configuration is 0.155, which can be worked out from the simple geometry (see Illustration- 14). The triangular arrangement in (i) is one of the limiting situations.

The radius ratio is said to be a critical value because for value of r_c / r_a smaller than 0.155, the central cation will rattle in the hole and not touch all the three anions at the same time, as illustrated in (ii). This violates condition (a) above and leads to instability. When the radius ratio is less than 0.155, then only way to satisfy all three conditions is to reduce the number of anions to 2. For values of r_c / r_a slightly greater than 0.155, all the anions touch the central cation but do not touch one another, as shown in (iii). All three conditions of stability are still satisfied. This situation will prevail till the radius ratio increases to 0.225, the next higher critical value corresponding to tetrahedral (four) coordination. At $r_c / r_a = 0.225$, the four surrounding anions touch one another and also the central cation. This configuration is the same as that obtained by fitting the largest possible sphere in the tetrahedral void of a close packed structure, (See Illustration- 15).

A ligancy of five does not satisfy all the three conditions for stable configuration because it is always possible to have six anions as an alternative to any arrangement that contains five anions, without a change in the radius ratio. The critical condition for octahedral (six) coordination occurs at $r_c / r_a = 0.414$, which is the same as the size of the octahedral void in a close packed structure. Ligancies of 7, 9, 10 and 11 are again not permissible.

The radius ratio ranges in which different values of ligancy are obtained are summarized in the given table. At the end of the table, the limiting case of $r_c / r_a = 1$ is identified with configurations of close packing of equal sized spheres.

Ligancy as Function of Radius Ratio

S.No.	Ligancy	Range of radius ratio	Configuration	S.No.	Ligancy	Range of radius ratio	Configuration
1.	2	$0.0 < \frac{r}{R} < 0.155$	Linear	4.	6	$0.414 \leq \frac{r}{R} < 0.732$	Octahedral
2.	3	$0.155 \leq \frac{r}{R} < 0.225$	Triangular	5.	8	$0.732 \leq \frac{r}{R} < 1.0$	Cubic
3.	4	$0.225 \leq \frac{r}{R} < 0.414$	Tetrahedral	6.	12	$\frac{r}{R} = 1.0$	"FCC" or "HCP"

Illustration - 14 Find the critical radius ratio for triangular coordination.

SOLUTION :

The critical condition for triangular coordination is shown in the adjacent figure.

The three anions touch one another as well as the central cation. From the simple geometry, we can write :

$$(R + r) \cos 30^\circ = r \Rightarrow R + r = \frac{2}{\sqrt{3}} R$$

$$\frac{r}{R} = \frac{2}{\sqrt{3}} - 1 = 0.155$$

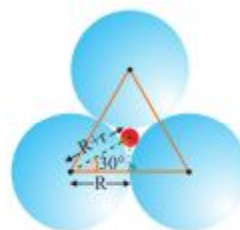


Illustration - 15 Find the critical radius ratio for tetrahedral co-ordination.

SOLUTION :

The critical condition for tetrahedral co-ordination is shown in the adjacent figure. Then anions touch one another as well as the central cation. From the simple geometry, we can write :

$$\ell = 2R \text{ and } \frac{3}{4}h = R + r \text{ where } h = \frac{\sqrt{2}}{\sqrt{3}} \ell$$

$$\Rightarrow \frac{3}{4} \times \frac{\sqrt{2}}{\sqrt{3}} \times 2R = R + r$$

$$\frac{r}{R} = \frac{\sqrt{3}}{\sqrt{2}} - 1 = 0.225$$

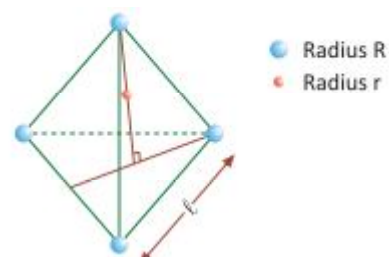


Figure shows 'r' is present in tetrahedral void 'R' atoms
(Note : Atoms have been shown separated for clarity)

Note : The centre of tetrahedron is at distance of 3/4th of 'h' from the apex. Also, height of regular tetrahedron is $\sqrt{2} / \sqrt{3}$ times is side of the tetrahedron.

Illustration - 16 Find the critical radius ratio for octahedral co-ordination.

SOLUTION :

The critical condition for octahedral co-ordination is shown in the adjacent figure. The anions touch one another as well as the central. From the simple geometry, we can write :

$$(2r + 2R) \cos 45^\circ = 2R$$

$$\Rightarrow \frac{r}{R} = \sqrt{2} - 1 = 0.414$$

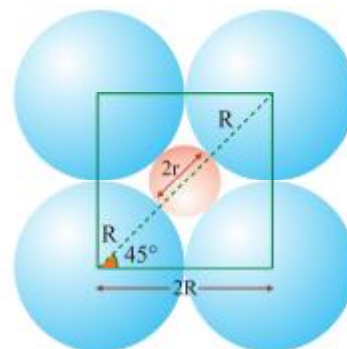


Figure shows '●' is present in octahedral void of '●' atoms
(Note : Only square plane has been shown)

Illustration - 17 Find the critical radius ratio for body-centered co-ordination.

SOLUTION :

The critical condition for cubic void shown in the adjacent figure. The anions touch one another as well as the central cation. From the simple geometry, we can write :

$$a = 2R \text{ and } \sqrt{3}a = 2R + 2r$$

$$\Rightarrow \frac{r}{R} = \sqrt{3} - 1 = 0.732$$

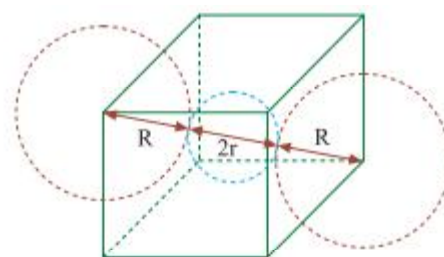


Figure shows '●' is present in the cubic void of '●' atoms

The ligancy rules outlined above are obeyed in a number of cases. for example, in the NaCl crystal, the ratio $r_{\text{Na}^+} / r_{\text{Cl}^-} = 0.54$, which lies between 0.414 and 0.732. As listed in the previous table, the predicated ligancy is six. The octahedral geometry of six chlorine ions surrounding a central cation is experimentally observed. In MgO, $r_{\text{Mg}^{2+}} / r_{\text{O}^{2-}} = 0.59$ and again the octahedral coordination is observed. In CsCl,

$r_{\text{Cs}^+} / r_{\text{Cl}^-} = 0.73$, it is difficult to predict whether a six – fold or an eight – fold coordination will occur. It so turns out that the eight coordination is observed. In this case, that is, every cesium cation is surrounded by eight chlorine anions.

The Si – O bond in silica as well as in silicates is about 50% ionic and 50% covalent. Here, the central silicon cation is surrounded by four oxygen anions located at the corners of a regular tetrahedron. This arrangement satisfies both the ligancy rules (as $r_c / r_a = 0.29$, then tetrahedral coordination is predicted from the previous table, as well as the orientation relationships of (sp^3) bonds).

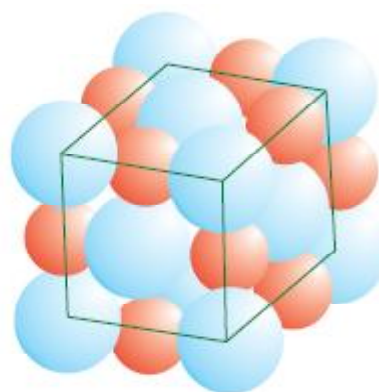
The stability criteria listed above for predicting the ligancy may not always be valid. If directional characteristics of bonding persist to any significant degree, the considerations based on the radius ratio alone will not lead to the correct prediction of ligancy. In the above-discussed example of Si – O coordination, the radius ratio criterion and the bond angle requirements happen to coincide. In ZnS, where the bond is more covalent than ionic, the ligancy predicated from $r_{\text{Zn}^{2+}} / r_{\text{S}^{2-}} = 0.48$ is octahedral. Yet the four-fold coordination characteristic of (sp^3) bonding is what is observed.

In the formation of ionic crystals, the ligancy rules described above determine the local packing around a cation. The long-range arrangement of ions in the crystal is dependent on the following factors :

- (i) In the crystal, the **overall electrical neutrality** should be maintained, whatever be the net charge on a local group of a cation and surrounding anions. For example, in NaCl, where a cation is surrounded by six anions, the net charge on (NaCl_6) is five. Evidently, this has to be neutralized in the long range arrangement.
- (ii) The ionic bond being nondirectional, the ions are packed as closely as possible in the crystal, consistent with the local coordination.

When the cation charge is not more than two or at best three and when the radius ratio is in the range 0.414-0.732, the crystal structure can be described as a FCC or HCP packing of anions with the cations occupying all or part of the octahedral voids in the structure. The fraction of octahedral voids that are filled depends on the number of cations to anions in the chemical formula. Thus, for the rock salt (NaCl) structure, adopted by hundreds of binary ionic compounds, $r_{\text{Na}^+} / r_{\text{Cl}^-} = 0.54$, and the anion packing is FCC with all octahedral voids filled with sodium cations. Recall that there is one octahedral void per sphere in a close packed array. A unit cell of NaCl crystal is shown in fig. below, with the large chlorine ions occupying the corner and facecentred cubic positions and the sodium ions in the octahedral voids. The octahedral positions are at the body centre and the midpoints of the cube edges. Note that, unlike in the monoatomic FCC crystal, the chlorine ions do not touch one another along the face diagonal. This is so because the radius ratio of 0.54 is greater than the size of the octahedral void in a close packed structure, which is 0.414. The FCC close packing is 'opened up' here to the extent necessary to accommodate the sodium cations in the octahedral voids.

Figure shows unit cell of NaCl with chlorine ions at the FCC positions and the sodium ions in the octahedral voids.



As the FCC positions and the octahedral void centre are interchangeable like the body centre and the body corners in the BCC cell, the NaCl structure can also be described as two interpenetrating monoatomic FCC cells, one corresponding to the anions and the other to the cations. The sum of their radii, r_c / r_a
 $r_{\text{Na}^+} + r_{\text{Cl}^-} = a / 2$, where a is the lattice parameter.

When r_c / r_a is in the range $0.7312 - 1$, the eight-fold coordination is observed. CsCl with $r_{\text{Cs}^+} + r_{\text{Cl}^-} = 0.91$ is a typical example of this structure. The cesium ions are at the body centre and the chlorine ions are at the body corners. The space lattice is simple cubic, with a basis of one cesium ion plus one chlorine ion per lattice point.

As an example of an ionic crystal with more than two types of ions, consider the crystal structure of **spinel**. Spinel is a compound with two different cations A^{2+} and B^{3+} and oxygen as the anion, with general formula, AB_2O_4 . Here, the oxygen anions form the FCC packing. For every four oxygen anions, there are four octahedral sites and eight tetrahedral sites. Out of these twelve, only three are needed to fill the cations of the above formula. In the **normal spinel structure**, the A cations are in the tetrahedral voids and the B cations are in the octahedral voids. Alternatively, half of the B cations can occupy the tetrahedral voids while the remaining half of the B cations and all the A cations are randomly distributed in octahedral voids, resulting in the **inverse spinel structure**. In both normal and inverse spinels, only half of the octahedral sites and 1/8 of the tetrahedral sites are filled.

Note : When $B_2O_3 = Fe_2O_3$, we have a series of compounds called **ferrites**, where different cations can be present in varying proportions. Ferrites have the inverse spinel structure.

PACKING EFFICIENCY

Section - 14

$$\text{Packing Fraction} = \frac{\text{volume occupied by atoms}}{\text{volume of unit cell}}$$

$$\text{Packing Efficiency} = \frac{\text{volume occupied by atoms}}{\text{volume of unit cell}} \times 100$$

We will discuss it for monoatomic and diatomic cases separately.

(A) Monoatomic unit cells :

For monoatomic unit cells, packing efficiency is given as :

$$\text{Packing Efficiency} = \frac{(\text{No. of atoms per unit cell}) \times (\text{volume of one atom})}{\text{volume of unit cell}} \times 100$$

(i) Simple Cubic (SC)

$$\text{P.E.} = \frac{(1) \times \frac{4}{3} \pi r^3}{a^3} \times 100$$

Where $2r = a$ [a \equiv length of unit cell]

$$\text{P.E.} = \frac{4}{3} \pi \left(\frac{1}{2}\right)^3 \times 100 = \frac{\pi}{6} \times 100 = 52\%$$

(ii) Body Centred cubic (BCC)

$$\text{P.E.} = \frac{(2) \times \frac{4}{3} \pi r^3}{a^3} \times 100$$

Where $2r = \frac{\sqrt{3}a}{2}$ [a \equiv length of unit cell]

$$\text{P.E.} = \frac{8}{3} \pi \left(\frac{\sqrt{3}}{4}\right)^3 \times 100 = \frac{\sqrt{3}\pi}{8} \times 100 = 68\%$$

(iii) Face centred Cubic (FCC)

$$\text{P.E.} = \frac{(4) \times \frac{4}{3} \pi r^3}{a^3} \times 100$$

where $2r = \frac{a}{\sqrt{2}}$ [a \equiv length of unit cell]

$$\text{P.E.} = \frac{16}{3} \pi \left(\frac{1}{2\sqrt{2}}\right)^3 \times 100 = \frac{\pi}{3\sqrt{2}} \times 100 = 74\%$$

(iv) Diamond Cubic (DC)

$$\text{P.E.} = \frac{(8) \times \frac{4}{3} \pi r^3}{a^3} \times 100$$

where $2r = \frac{\sqrt{3}a}{4}$ [a \equiv length of unit cell]

$$= \frac{32}{3} \pi \left(\frac{\sqrt{3}}{8}\right)^3 \times 100 = \frac{\sqrt{3}\pi}{16} \times 100 = 34\%$$

(v) Hexagonal Crystal Closed Packed (HCP)

$$\text{P.E.} = \frac{(6) \times \frac{4}{3} \pi r^3}{6 \times \frac{\sqrt{3}}{4} a^2 \times c} \times 100$$

where $c = \frac{2\sqrt{2}}{\sqrt{3}} a$ and $2r = a$

[a \equiv length of unit cell]

$$\text{P.E.} = \frac{\pi}{3\sqrt{2}} \times 100 = 74\%$$

(B) Diatomic unit cells :

For diatomic unit cells, packing efficiency is given as :

$$\text{P.E.} = \frac{\sum (\text{no. of atoms of each kind}) \times (\text{volume of atom of each kind}) \times 100}{\text{volume of unit cell}}$$

(i) Rock Salt (NaCl) type :

$$\text{If AB crystallizes in the same way as NaCl, then P.E.} = \frac{4 \times \frac{4}{3} \pi r_{A^+}^3 + 4 \times \frac{4}{3} \pi r_{B^-}^3}{a^3} \times 100$$

$$\text{such that } 2r_{A^+} + 2r_{B^-} = a \quad [a \equiv \text{length of unit cell}]$$

Note :

If nothing is mentioned, we consider the limiting case i.e. anions-anions are also contact at the same time when cation-anion contact is always present. So, we can always have cation-anion contact equation but anion-anion contact equation is possible for limiting case only.

(ii) Cesium Chloride (CsCl) type :

$$\text{If AB crystallizes in the same way as CsCl, then P.E.} = \frac{1 \times \frac{4}{3} \pi r_{A^+}^3 + 1 \times \frac{4}{3} \pi r_{B^-}^3}{a^3} \times 100$$

$$\text{Such that } 2r_{A^+} + 2r_{B^-} = \sqrt{3}a \quad [a \equiv \text{length of unit cell}]$$

(iii) Zinc Blende (ZnS) type :

$$\text{If AB crystallizes in the same way as ZnS, then P.E.} = \frac{4 \times \frac{4}{3} \pi r_{A^+}^3 + 4 \times \frac{4}{3} \pi r_{B^-}^3}{a^3} \times 100$$

$$\text{Such that } r_{A^+} + r_{B^-} = \frac{\sqrt{3}a}{4} \quad [a \equiv \text{length of unit cell}]$$

(iv) fluorite structure type :

$$\text{If AB}_2 \text{ crystallizes in the same way as CaF}_2, \text{ then P.E.} = \frac{4 \times \frac{4}{3} \pi r_{A^+}^3 + 8 \times \frac{4}{3} \pi r_{B^-}^3}{a^3} \times 100$$

$$\text{Such that } r_{A^+} + r_{B^-} = \frac{\sqrt{3}a}{4} \quad [a \equiv \text{length of unit cell}]$$

Note : Here radius ratio rules will change. Now, $\frac{r_-}{r_+}$ lies in 0.225 – 0.414 as anion lies in tetrahedral void.

(v) Anti-fluorite structure type :

If A_2B crystallizes in the same way as Na_2O , P.E. = $\frac{8 \times \frac{4}{3} \pi r_{A^+}^3 + 4 \times \frac{4}{3} \pi r_{B^-}^3}{a^3} \times 100$

Such that $r_{A^+} + r_{B^-} = \frac{\sqrt{3}a}{4}$ [a \equiv length of unit cell]

DENSITY

Section - 15

It is defined as the ratio of mass of the unit cell and volume of unit cell.

$$\text{Density} = \frac{\text{mass of atoms present in unit cell}}{\text{volume of unit cell}}$$

$$= \frac{(\text{No. of atoms}) \times (\text{Molecular weight in a.m.u.}) \times 1.67 \times 10^{-27} \text{ kg}}{\text{volume of unit cell}} \quad [\text{For monoatomic crystal}]$$

In general,

$$\text{Density} = \frac{\sum (\text{No. of atoms of each kind}) \times (\text{Molecular weight of each kind in a.m.u.}) \times 1.67 \times 10^{-27} \text{ kg}}{\text{volume of unit cell}}$$

or $\text{Density} = \frac{(\text{No. of formula units}) \times (\text{Molecular weight of compound}) \times 1.67 \times 10^{-27} \text{ kg}}{\text{volume of unit cell}}$

Illustration - 18 Al crystallises in cubic shape unit cell and with edge length 405pm and density 2.7g/cc. Predict the type of crystal lattice.

SOLUTION :

$$\text{Density} = \frac{(\text{No. of atoms}) \times (\text{Molecular weight}) \times 1.67 \times 10^{-27} \text{ kg}}{\text{volume of unit cell}}$$

$$2.7 \times 10^3 \text{ kg/m}^3 = \frac{(n) \times 27 \times 1.67 \times 10^{-27}}{(4.05 \times 10^{-10})^3} \Rightarrow n \sim 4$$

Hence, the possible crystal lattice is FCC.

Illustration - 19 *CdO has NaCl structure with density 8.27 g/cc. If the ionic radius of O^{2-} is 1.24 \AA , determine ionic radius of Cd^{2+} .*

SOLUTION :

$$\text{Density} = \frac{(\text{No. of formula units}) \times (\text{Molecular weight of compound}) \times 1.67 \times 10^{-27} \text{ kg}}{\text{volume of unit cell}}$$

$$8.27 \times 10^3 \text{ kg/m}^3 = \frac{(4) \times 128.41 \times 1.67 \times 10^{-27}}{a^3} \Rightarrow a = 4.70 \text{ \AA}$$

$$\text{We have, } 2(r_{Cd^{2+}} + r_{O^{2-}}) = a$$

$$\Rightarrow r_{Cd^{2+}} + 1.24 = 2.35 \Rightarrow r_{Cd^{2+}} = 1.11 \text{ \AA}$$

NOW ATTEMPT IN-CHAPTER EXERCISE-C BEFORE PROCEEDING AHEAD IN THIS EBOOK

DEFECTS IN CRYSTALS

Section - 16

According to third law of thermodynamics, it is only at 0 K that true crystals pass perfect order of arrangement of atoms in pure crystals. But with rise in temperature, some deviations from complete order take place. Presence of impurities also adds to disorder.

“Any departure from perfectly ordered arrangement of atoms/ions in a crystal is called imperfection or crystal defect”.

These imperfections modify the properties of the crystal and also sometimes impart new properties to the solids.

There are two types of imperfections :

- Electronic imperfections
- Atomic or point imperfections

16.1 Electronic Imperfections

At zero K (**absolute zero**), electrons in covalent or ionic crystals (e.g., Si or NaCl) occupy the lowest energy level. Above zero K in pure silicon or germanium, electrons are released thermally from the covalent bonds. This leads to the presence of free electrons and electron deficient bonds called **holes**, which are responsible for intrinsic conduction. These free electrons and the holes in solids give rise to electronic imperfections.

(a) **Hole :** The electron deficient bond formed by the release of an electron.

(b) **Intrinsic conduction :** Conduction which is caused in crystal due to heating, leading to the formation of free electrons and holes. e.g., crystal of Si or Ge.

(c) **n :** Concentration of electrons (e)

(d) **p :** Concentration of holes (h)

16.2 Atomic or Point imperfections

The defects which arise due to the irregularity in the arrangement of atoms or ions are called point defects. Point defects in crystal may be classified into the following three types :

- Stoichiometric defects
- Non-stoichiometric defects
- Impurity defects

16.2.1 Stoichiometric Defect

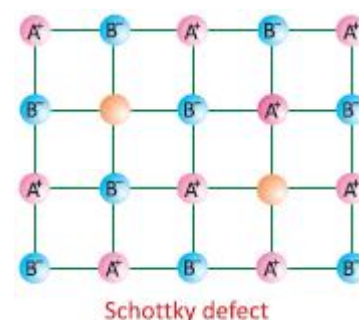
If imperfections in the crystal are such that the ratio between the anions and cations remain same as represented by the molecular formula, the defect is called a **stoichiometric defect**.

There are three types of stoichiometric defects :

- Schottky defect
- Frenkel defect
- Interstitial defect

(a) Schottky defect

In ionic crystals of the type $A^+ B^-$, equal number of anions and cations are missing from the lattice sites so that electrical neutrality is maintained. This type of defect is called **Schottky defect**



Types of compound exhibiting Schottky defect

This type of defect is shown by highly ionic compounds which have

- High coordination number
- Cations and anions of similar size

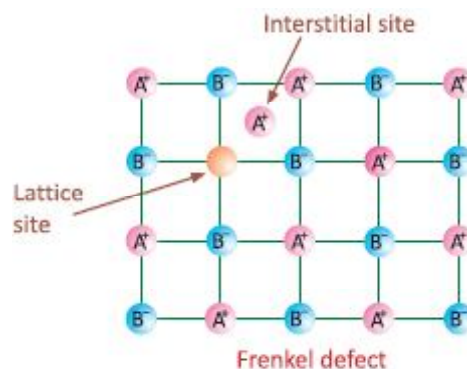
Examples : KCl, NaCl, AgBr, KBr and CsCl.

Consequences of Schottky Defect

- As the number of ions decrease, volume is the same, so density decreases.
- Crystals with Schottky defect conduct electricity to a small extent. This is because if an ion moves from its lattice site to occupy a 'hole', it creates a new 'hole'. In this way, a hole moves across the crystal which as a result moves the charge in the opposite direction.
- Due to the presence of holes, the stability (or lattice energy) of the crystal decreases.

(b) Frenkel Defect

If an ion is missing from its lattice site (causing a vacancy or a hole there) and it occupies an interstitial site so that electrical neutrality as well as stoichiometry of the compound are maintained. This type of defect is called **Frenkel defect**. Since the size of cation is generally smaller it is more likely that cations occupy interstitial sites.

**Types of compounds exhibiting Frenkel defect**

This type of defect is present in those compound which have

- Low co-ordination number
- Large difference in size of anion and cation e.g., AgCl, AgBr, AgI and ZnS

Consequences of Frenkel Defect

- Solids with this defect conduct electricity to a small extent
- The density of the solid is unchanged
- The dielectric constant of the crystal increases.
- Due to the presence of holes, the stability of the crystal decreases.

Note 1 :

(i) The above two defects are intrinsic defects, or thermodynamic defects.

(ii) AgBr is a compound in which both Schottky and Frenkel defects are found because AgBr is highly ionic but there is a great difference in the size of Ag^+ and Br^- .

Note 2 :

(ii) The number (n) of Schottky defects present in an ionic crystal containing N ions at temperature T is given by : $n = N \exp\left(-\frac{E}{2kT}\right)$ where E is the energy required to create these ' n ' Schottky defects and

$$k \text{ is Boltzmann constant} = R / N_0 = 1.38 \times 10^{23} \text{ JK}^{-1}$$

(ii) Similarly, if N_i is the number of interstitial sites in an ionic crystal having N ions, the number ' n ' of Frenkel defects is given by :

$$n = \left(\frac{N}{N_i}\right)^{\frac{1}{2}} \exp\left(-\frac{E}{2kT}\right) \text{ where } E \text{ is the energy required to create these 'n' Frenkel defects.}$$

(iii) It may be noted that number of Schottky & Frenkel defects increases exponentially with increase in temperature.

(iv) In NaCl, there are approximately 10^6 Schottky pairs per cm^3 at room temperature. In 1 cm^3 , there are about 10^{22} ions and therefore there is one Schottky defect per 10^{16} ions.

(c) Interstitial Defects

Atoms (or ions), which occupy normally vacant interstitial positions in a crystal, are called **interstitials**. The important factor in determining the formation of interstitials is the size of the atom (or ion), because they are accommodated into the voids.

16.2.2 Non-stoichiometric Defects

If an imperfection causes the ratio of cations and anions to become different from that indicated by the ideal chemical formula, the defect is called **non-stoichiometric**.

These defects result in either excess of the metal atoms or excess of the non-metal. These can occur as follows :

➤ Metal excess ➤ Metal deficiency ➤ Impurity defects

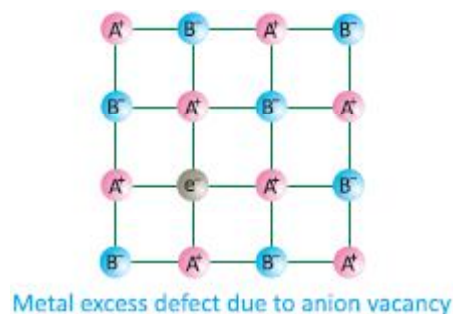
(a) Metal excess

This may occur in either of the following two ways

(i) By anion vacancies

A negative ion may be missing from its lattice site, leaving a hole, which is occupied by an electron thereby maintaining an electrical balance. The trapped electrons are called ***F-centers*** or color centers because they are responsible for imparting color to the crystal. The defect is similar to Schottky defect and is found in crystals having Schottky defects.

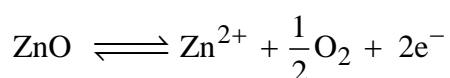
Example : NaCl when heated in Na vapor atmosphere, the excess Na atoms deposit on the surface. Now Cl^- diffuse to the surface where they combine with the Na atoms, which lose the electrons. The electrons diffuse into the vacant sites created. The electrons absorb some energy from the white light and re-emit the yellow color to NaCl crystal. Excess of Li in LiCl gives a pink color. Excess of K in KCl makes it violet.



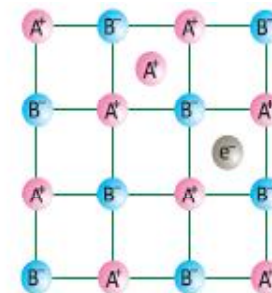
(i) By the presence of extra cations in the interstitial sites

Extra cations occupying interstitial sites with electrons present in another interstitial site to maintain electric neutrality causes metal excess. This defect is similar to Frenkel defect and is formed in crystals having Frenkel defects.

Example : If ZnO is heated, it loses oxygen and turns yellow.



The excess Zn^{2+} ions thus formed get trapped into the vacant interstitial sites and the electrons in the neighboring interstitial sites. It turns yellow when hot and white when cold.



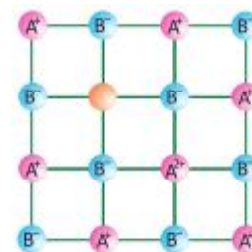
Metal excess defect
caused by extra cation in interstitial position

Note : Crystals with either type of metal excess defect act as semiconductors.

(b) Metal deficiency

This defect occurs when metals shown variable valency. It occurs due to the missing of a cation with higher charge (e.g., +2 instead of +1) in the adjacent site.

Example : Transition elements, FeO, FeS and NiO.



Metal deficiency due to missing of a cation of lower valency and presence of a cation of higher valency

16.2.3 Impurity Defects

These defects arise when foreign atoms are present at the lattice site (in place of host atoms) or at the vacant interstitial sites. The formation of former depends upon the electronic structure of the impurity while that of the latter on the size of the impurity.

(a) Introducing impurity defect in covalent solids

Group 13 elements such as Ga and Al and group 15 elements such as P and As can enter the crystal structure of group 14 element Ge or Si substitutionally.

The Group 15 elements have one excess valence electrons as compared to Group 14 elements (Si or Ge). Therefore after forming four covalent bonds, one electron remains in excess which gives rise to electrical conduction.

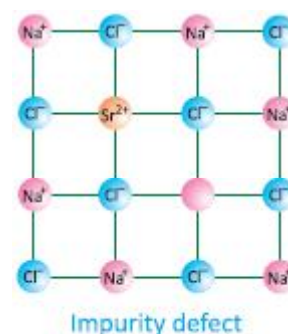
Group 13 elements have one valence electron less compared to Group 14 elements leading to electron deficient bond a hole. Such holes can move across the crystal giving rise to electrical conductivity.

Group 14 elements doped with group 15 elements are called **n-type semiconductors**, where the symbol 'n' indicating negative charge which flows in them. Group 14 elements doped with group 13 elements are called **p-type semiconductors**, the symbol 'p' indicating positive hole movement.

(b) Introducing impurity defect in ionic solids

In case of ionic solids, the impurities are introduced by adding impurity of ions. If the impurity ions are in a different oxidation state from that of the host ions, vacancies are created.

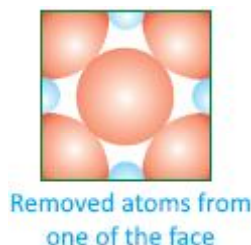
Example : If molten NaCl, containing a little of SrCl_2 as impurity, is allowed to cool, in the crystals of NaCl formed, at some lattice sites Na^+ ions are substituted of Sr^{2+} ion. For ever Sr^{2+} thus introduced, two Na^+ ions are removed to maintain electrical neutrality.

**Illustration - 20**

If all the atoms touching 1 face plane are removed in a solid A^+B^- having rock salt type structure, then the formula of the left compound and defect brought by this removal respectively is :

- | | |
|----------------------------|------------------------------|
| (A) AB , Frenkel defect | (B) A_2B , Frenkel defect |
| (C) AB , Schottky defect | (D) A_2B , Schottky defect |

SOLUTION :



Atoms at the corners and face centre are 'B' type atoms No. of B atom left = $4 - \left(\frac{1}{8} \times 4\right) - \left(\frac{1}{2} \times 1\right) = 3$

'A' atoms are present at body centre with probability (share) = 1 and at edge centres with probability (share) = $\frac{1}{4}$

Hence no. of A atoms left after removal will be $4 - \left(\frac{1}{4} \times 4\right) = 3$

Hence 3 "A type" and 3 "B type" atoms left. So, the formula is AB.

Note : As atoms are completely removed. Hence it is schottky type of defects.

Illustration - 21 *The addition of CaCl_2 Crystal to a KCl crystal*

- (A) lowers the density of the KCl crystal (B) raises the density of the KCl crystal
(C) does not affect the density of the KCl crystal (D) increases the Frenkel defects of the KCl crystal

SOLUTION :

Once Ca^{2+} lets two K^+ leave the crystal to maintain the electrical neutrality of the compound.

The Mass of two K^+ is greater than the mass of Ca^{2+} , hence density decreases.

PROPERTIES OF SOLIDS**Section - 17**

Properties of the solids depend mainly upon their structure and composition. **Three main properties are discussed below :**

17.1 Electrical properties

Electrical conductivity varies from $10^8 \text{ ohm}^{-1} \text{ cm}^{-1}$ in metals to $10^{-12} \text{ ohm}^{-1} \text{ cm}^{-1}$ in insulators. Based on their conductivity. Solids can be divided into three categories :

(a) Conductors

Solids through which electricity can flow to a large extent are called **conductors**. Depending upon the type of charge carriers, the conductors are further classified as metallic and electrolytic conductors. In metallic conductors, electrons are the charge carriers. In electrolytic conductors, ions are the charge carriers. Therefore electrolytic conductors conduct only when there are mobile ions i.e., in molten state. However in solid state they conduct electricity only to a small extent, which is due to the presence of defects (**hole, electrons etc**). e.g., NaCl, KCl.

(b) Insulators

The solids which almost do not allow the electricity to pass through them are called insulators. e.g., S, P.

(c) Semiconductors

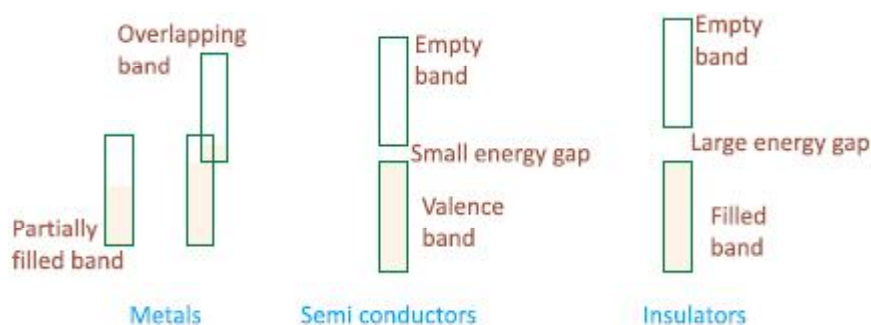
The solids whose conductivity lies between metallic conductors and insulators are called semiconductors. The electrical conductivity of semiconductors is due to the presence of impurities and defects. Their conductivity increases with increase in temperature as the defects increase with the increase in temperature.

The magnitude of the electrical conductivity strongly depends on the number of electrons available to participate in the conduction process.

In metals, the atomic orbitals form molecular orbitals, which are so close in energy to each other as to form a band. If conduction band is not completely full or it lies very close to a higher unoccupied band, then electrons can flow easily under an electric field thereby showing conductivity.

In case of semiconductors, the energy gap between valence band and the conduction band is small and hence some of the electrons may jump from valence band to conduction band and the result is some conductivity.

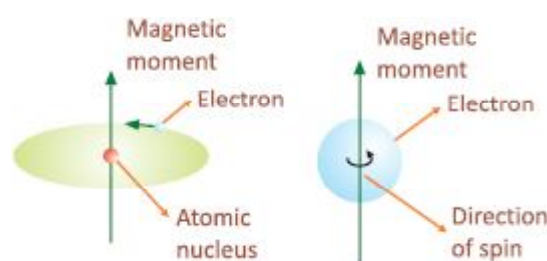
In case of insulators, the difference of energy between valence band and conduction band is so large that electron transition doesn't take place. Hence, no conductivity is shown. The in-between region is called **Forbidden zone**.



17.2 Magnetic Properties of Solids

The magnetic properties of materials are a consequence of magnetic moments associated with individual electrons. The magnetic moment of an electron is due to its orbital motion and also due to its spin around its own axis.

A moving electron may be considered to be a small current loop, generating a small magnetic field, which has a magnetic moment along the axis of rotation and the magnetic moment due to electron spin is directed along the spin axis.



The fundamental magnetic moment is the Bohr Magneton (μ_B), which is equal to $9.27 \times 10^{-24} \text{ Am}^2$.

For each electron in an atom, the spin magnetic moment is $\pm \mu_B$ (depending on the two possibilities of the spin). The contribution of the orbital magnetic movement is equal to $m_l \mu_B$ where m_l is the magnetic quantum number of the electron. Materials can be classified depending on their response to external magnetic field.

- (a) **Diamagnetic Materials :** Substances which are weakly repelled by external magnetic fields. This property is shown only by those substances which contain fully-filled orbitals i.e., no unpaired electrons are present e.g, TiO_2 , NaCl .

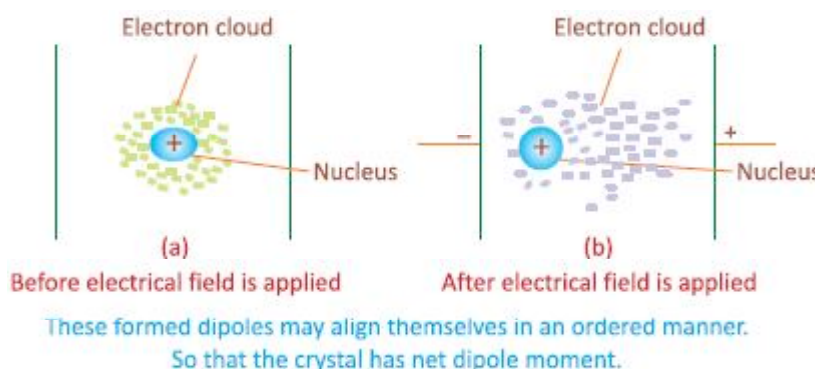
- (b) **Paramagnetic Materials** : Substances which are attracted by the magnetic field but lose their magnetism in the absence of the magnetic field. This property is shown by those substances whose atoms, ions or molecules contain unpaired electrons eg., O_2 , Cu^{2+}
- * (c) **Ferromagnetic Materials** : Substance which show permanent magnetism even when the magnetic field is removed e.g., Fe, Ni. The spontaneous alignment of magnetic moments due to unpaired electrons in the same direction gives rise to ferromagnetism.
- * (d) **Anti-Ferromagnetic Substances** : Anti-ferromagnetic substances are expected to possess paramagnetism or ferromagnetism on the basis of unpaired electrons present in them but actually they possess zero net magnetic moment. This is because the alignment of dipole is in a compensatory way so as to give a net zero dipole moment, then we get anti-ferromagnetic substances e.g., MnO
- * (e) **Ferrimagnetic Substances** : Ferrimagnetic substance are expected to possess large magnetism on the basis of the number of unpaired electrons present in them, but actually have small net magnetic moment. This is because the moments are aligned in parallel and anti-parallel directions in unequal number resulting in a net dipole moment. e.g., Fe_3O_4



Note : Ferromagnetic, Antiferromagnetic and Ferrimagnetic solids transform to the paramagnetic state at some temperature due to randomisation of spins. Ferrimagnetic Fe_3O_4 become paramagnetic at 850 K. It is also observed that Ferromagnetic substances have a characteristic temperature above which no ferromagnetism is observed. This is known as Curie temperature.

* 17.3 Dielectric Properties of Solids

Insulators do not conduct electricity because the electrons present in them are held tightly to the individual atoms or ions and are not free to move. However when electric field is applied, polarization takes place because the nucleus is attracted towards cathode and electron cloud towards anode.



Such polar crystals show the following electrical properties.

(a) **Piezoelectricity :**

When these crystals are subjected to mechanical stress, electricity is produced due to displacement of ions. The electricity thus produced is called **piezoelectricity** and the crystals are called **piezoelectric crystals**. But if an electric field is applied to these crystal, there will be atomic displacement causing mechanical strain.

(b) Pyroelectricity :

Some polar crystals when heated produce a small current or pyroelectricity.

(c) Ferroelectricity :

In some piezoelectric crystals the dipoles are permanently lined up even in the absence of an electric field. However, on applying electric field the direction of polarization changes. e.g., BaTiO_3 , Sodium potassium tartrate (**Rochelle Salt**).

Note :

All ferroelectric solids are piezoelectric but the reverse is not true.

(d) Anti-Ferroelectricity :

If there is no net dipole moment it is said to be an antiferroelectric crystal. This is because the dipoles are alternately arranged. e.g., Lead zirconate (PbZrO_3).

(e) Superconductivity :

When the electrical resistance of materials becomes almost zero, the material becomes superconductor. The temperature at which the material shows superconductivity is called **transition temperature**. e.g., $\text{YBa}_2\text{Cu}_3\text{O}_7$ at 90K.

EFFECT OF TEMPERATURE AND PRESSURE ON THE CRYSTAL STRUCTURE Section - 18

A number of metals have more than one crystal form. Iron, for example, is BCC at room temperature and changes over to the FCC form at 910°C . At 1410°C , iron again changes over to the BCC form. In general, at higher temperatures, the BCC crystal structure is to be expected as it allows larger vibrational amplitudes for atoms, thereby increasing the entropy and lowering the free energy of the crystal. This is believed to be the reason for a number of alkali metals adopting the BCC form at room temperature.

At ordinary temperature and pressures, chlorides, bromides and iodides of lithium, sodium and rubidium and some halides of silver possess the NaCl structure with 6:6 co-ordination. On application of high pressure, they transform to the CsCl structure with 8:8 co-ordination. On the other hand, CsCl on heating transforms to the NaCl structure with 6:6 co-ordination.

IN-CHAPTER EXERCISE-D

- Calcium crystallizes in a Face Centred Cubic unit with $a = 0.556 \text{ nm}$. Calculate the density if
 - it contains 0.1% Frenkel defects.
 - it contains 0.1% Schottky defects.
- Sapphire is aluminium oxide. It crystallises with aluminium ions in two-thirds of octahedral holes in a closest packed array of oxide ions. What is the formula of aluminium oxide ?

NOW ATTEMPT IN-CHAPTER EXERCISE-D FOR REMAINING QUESTIONS

SUBJECTIVE SOLVED EXAMPLES

Example - 1

Spinel is an important class of oxides consisting of two types of metal ions with the oxide ions arranged in CCP pattern. The normal spinel has 1/8 of the tetrahedral holes occupied by one type of metal ion and 1/2 of the octahedral holes occupied by another type of metal ion. Such a spinel is formed by Zn^{2+} , Al^{3+} and O^{2-} with Zn^{2+} in the tetrahedral holes. If CCP arrangement of oxide ions remains undistorted in the presence of all the cations, find the formula of spinel and fraction of the packing fraction of crystal :

SOLUTION :

No. of O^{2-} ions = 4

Now Zn^{2+} is present in one of the tetrahedral voids and two Al^{3+} are present in two out of four octahedral voids for the electrical neutrality of the crystal.

So, the formula of spinel is : ZnAl_2O_4

$$\text{P.E.} = \frac{2 \times \frac{4}{3} \pi r_{\text{Al}^{3+}}^3 + 1 \times \frac{4}{3} \pi r_{\text{Zn}^{2+}}^3 + 4 \times \frac{4}{3} \pi r_{\text{O}^{2-}}^3}{a^3}$$

where $\frac{r_{\text{Al}^{3+}}}{r_{\text{O}^{2-}}} = 0.414$, $\frac{r_{\text{Zn}^{2+}}}{r_{\text{O}^{2-}}} = 0.225$ and

$$\sqrt{2}a = 4r_{\text{O}^{2-}}$$

[Limiting case as structure is not distorted]

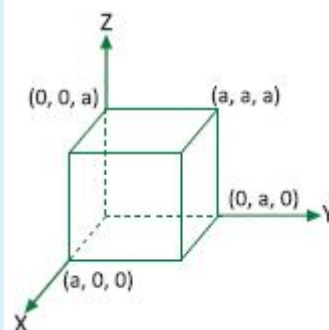
Hence P.E. = 77%

Example - 2

Assume an FCC unit cell cube (edge length a) with one of its corners

at the origin of cartesian coordinates. Find :

- the coordinates of tetrahedral and octahedral voids nearest and farthest to the origin.*
- find the distance between two successive tetrahedral voids.*
- the distance between two successive octahedral voids.*

**SOLUTION :**

- (i) co-ordinates of tetrahedral void nearest to origin

$$\equiv \left(\frac{a}{4}, \frac{a}{4}, \frac{a}{4} \right)$$

co-ordinates of tetrahedral void farthest to origin

$$\equiv \left(\frac{3a}{4}, \frac{3a}{4}, \frac{3a}{4} \right)$$

co-ordinates of octahedral void nearest to origin

$$\equiv \left(0, \frac{a}{2}, 0 \right); \left(\frac{a}{2}, 0, 0 \right); \left(0, 0, \frac{a}{2} \right)$$

co-ordinates of octahedral void farthest to origin

$$\equiv \left(\frac{a}{2}, a, a \right); \left(a, \frac{a}{2}, a \right); \left(a, a, \frac{a}{2} \right)$$

- (ii) Distance between two successive tetrahedral voids

\equiv Distance between $P\left(\frac{a}{4}, \frac{a}{4}, \frac{a}{4}\right)$ and

$$Q\left(\frac{3a}{4}, \frac{a}{4}, \frac{a}{4}\right) \text{ i.e. } \frac{a}{2}$$

- (iii) Distance between two successive octahedral voids = Distance between body centre and any

edge centre of the FCC unit cell i.e. $\frac{a}{\sqrt{2}}$

Example - 3 The number of Schottky defects (n) present in an ionic crystal containing N ions at temperature T is given by $n = Ne^{-E/2KT}$, where E is the energy required to create ' n ' Schottky defects and K is Boltzmann constant. If the mole fraction of Schottky defect in NaCl crystal at 2900 K is X (Given : ΔH of Schottky defect = 2 eV and $K = 1.38 \times 10^{-23} \text{ JK}^{-1}$, $e = 1.608 \times 10^{-19}$), then calculate $-\ln(X)$.

SOLUTION :

The number of schottky defects (n) is given as

$$n = Ne^{-E/2KT} \quad \dots (i)$$

$$\text{No. of moles of ions} = \frac{N}{N_A}$$

$$\Rightarrow \text{No. of moles of schottky defects} = \frac{n}{N_A}$$

Mole fraction of defect is given as :

$$X = \frac{\frac{n}{N_A}}{\frac{n}{N_A} + \frac{N}{N_A}} = \frac{\frac{n}{N}}{\frac{n}{N} + 1} \quad X = \frac{e^{-E/2KT}}{e^{-E/2KT} + 1}$$

[Using (i)]

Substitute the value of $E = 2 \times 1.608 \times 10^{-19} \text{ J}$
to get : $-\ln X \sim 4$

Example - 4 Sulphide of cobalt metal has a cubic structure with four formula units per unit cell. If density is 4.269 g/cc and edge length of unit cell is 6.93 \AA , determine mass of sulphur required to produce 1.5 kg of this compound.

(Molecular weight of Co = 58.94 and S = 32 amu)

SOLUTION :

$$4.269 \times 10^3 = \frac{(4) \times M \times 1.67 \times 10^{-27} \text{ kg}}{(6.93 \times 10^{-10})^3}$$

$$\text{Molecular weight (M)} = 212.69$$

Let compound be Co_xS_y

$$\Rightarrow 58.94x + 32y = 212.69$$

The possible compound is Co_2S_3

[i.e. $\text{CoS} + \text{CoS}_2$]



$$\frac{1.5}{213.89} \times 10^3 \text{ moles} \quad 3 \times \frac{1.5}{213.89} \times 10^3 \text{ moles}$$

Hence mass of sulphur required = 0.673 kg

Example - 5 *FeO crystallizes in NaCl type of crystal lattice. The crystals however are always non-stoichiometric and deficient in iron. Some cationic sites are vacant and some contain Fe^{3+} ions but the combination is such that structure is electrically neutral. The formula approximates to $\text{Fe}_{0.95}\text{O}$.*

- (i) What is the ratio of Fe^{2+} to Fe^{3+} ion in the solid ? (ii) What percentage of cation sites is vacant ?

SOLUTION :

- (i) The compound is $\text{Fe}_{0.95}\text{O} \equiv \text{Fe}_{95}\text{O}_{100}$

Let compound has $x\%$ of Fe^{2+} and $(95 - x)\%$ of Fe^{3+} such that

$$2x + 3(95 - x) - 2 \times 100 = 0 \Rightarrow x = 85$$

[Structure is neutral]

Hence,
$$\frac{\text{Fe}^{2+}}{\text{Fe}^{3+}} = \frac{85}{10} = \frac{17}{2}$$

- (ii) No. of Vacant sites = $100 - 95 = 5\%$

Example - 6 *What fraction of the Ca atoms lies on the surface of a cubic crystal that is 1.0cm in length, if the radius of Ca atoms is 96pm and it crystallizes in Body Centered Cubic arrangement.*

SOLUTION :

As Ca atoms crystallizes in body centred cubic, we have :

$$\sqrt{3}a = 4R \Rightarrow a = \frac{4 \times 96}{\sqrt{3}} \text{ pm}$$

$$\Rightarrow a = 221.7 \text{ pm}$$

Volume of unit cell

$$= a^3 = (221.7 \times 10^{-12})^3 \text{ m}^3 = 10.9 \times 10^{-30} \text{ m}^3$$

$$\text{Volume of crystal} = (10^{-2})^3 = 10^{-6} \text{ m}^3$$

$$\text{No. of unit cells} = \frac{10^{-6}}{10.9 \times 10^{-30}} = 9.17 \times 10^{22}$$

$$\Rightarrow \text{No. of atoms} = 2 \times 9.17 \times 10^{22}$$

[\therefore two atoms per unit cell]

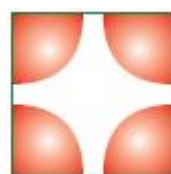
$$\text{Surface area of one face of crystal} = 10^{-4} \text{ m}^2$$

$$\text{Surface area of one face of unit cell} = a^2$$

No. of square faces visible at one face of crystal

$$= \frac{10^{-4}}{(2.217 \times 10^{-10})^2} = 2.03 \times 10^{15}$$

$$\text{No. of atoms} = 1 \times 2.03 \times 10^{15}$$



\therefore one atom per face of unit cell

$$\left(\frac{1}{4} \times 4 = 1 \right)$$

$$\text{Ratio} = \frac{2.03 \times 10^{15}}{2 \times 9.17 \times 10^{22}} = 1.11 \times 10^{-8}$$

Example - 7 Ar crystallizes in Face Centered Cubic arrangements and density of solid and liquid Ar is 1.59 g/cc and 1.42 g/cc respectively. Find the percentage of empty space in liquid Ar.

SOLUTION :

Density of solid Argon = 1.59 g/cc,

density of liquid Argon = 1.42 g/cc

Let the solid argon crystal be 100 gm

$$\text{Volume of argon crystal (solid)} = \frac{100}{1.59} \text{ cc}$$

$$\text{Volume of solid argon in crystal} = \frac{74}{100} \times \frac{100}{1.59} \text{ cc}$$

Volume of liquid argon in crystal is given as :

$$\frac{x}{100} \times \frac{100}{1.42} = \frac{74}{100} \times \frac{100}{1.59} \Rightarrow x = 66.08 \%$$

$$\text{Empty space} = 33.92 \%$$

Note: You could also have simply solved using $\frac{\text{P.E.}}{\text{density}} = \text{constant}$

Example - 8 Cadmium oxide crystallizes in NaCl type of crystal lattice. The compound is however usually non-stoichiometric with approximate formula $\text{CdO}_{0.95}$. The defect arises as some cationic positions are occupied by neutral Cd atoms instead of Cd^{2+} ions and equivalent numbers of anionic sites are vacant. (Molecular weight of Cd = 112.41 amu)

- (i) What percentage of anionic sites is vacant ?
- (ii) What is the density of non-stoichiometric solid : ($a = 470 \text{ pm.}$) ?
- (iii) If the edge length of the unit cell is 470 pm, what would be the density of the perfect solid ?

SOLUTION :

$$(i) \quad \% \text{ of anionic sites vacant} = 5 \%$$

$$(ii) \quad \text{No. of oxide ions} = \frac{95}{100} \times 4 \quad \text{Density} = \frac{4 \times [112.41 + 0.95 \times 16] \times 1.67 \times 10^{-27}}{(4.7 \times 10^{-10})^3} \text{ kg / m}^3 = 8.21 \text{ g / cc}$$

$$(iii) \quad \text{Density} = \frac{(4) \times (128.41) \times 1.67 \times 10^{-27}}{(4.7 \times 10^{-10})^3} \text{ kg / m}^3 = 8.26 \text{ g / cc}$$

Example - 9 When heated above 916°C , iron changes its crystal structure from Body Centred Cubic to Cubic Closed Packed structure. Assuming that the metallic radius of the atom does not change, calculate the ratio of density of the Body Centered Cubic crystal to that of the Cubic Closed Packing crystal.

SOLUTION :

$$\text{Density of iron in BCC} = \frac{2 \times M \times 1.67 \times 10^{-27}}{\text{Volume of unit cell}} \text{ kg} \quad \text{Also, } \sqrt{3}a = 4r$$

$$\Rightarrow d_{\text{BCC}} = \frac{2 \times M \times 1.67 \times 10^{-27}}{(4r/\sqrt{3})^3}$$

Density of iron in FCC

$$= \frac{4 \times (\text{Molecular weight}) \times 1.67 \times 10^{-27}}{\text{Volume of unit cell}} \text{ kg} \quad \Rightarrow \quad d_{\text{FCC}} = \frac{4 \times M \times 1.67 \times 10^{-27}}{\left(\frac{4r}{\sqrt{2}}\right)^3}$$

$$\text{Also, } \sqrt{2}a = 4r$$

$$\frac{d_{\text{BCC}}}{d_{\text{FCC}}} = \frac{2 \times 3\sqrt{3}}{4 \times 2\sqrt{2}} = 0.9185$$

Note: You could also have simply solved using $\frac{\text{P.E.}}{\text{density}} = \text{constant}$

Example - 10 The unit cell length of NaCl is observed to be 0.5627nm by X-ray diffraction studies. The measured density of NaCl is 2.164 g/cc . Correlate the difference of observed and calculated density and calculate the percentage of missing Na^+ and Cl^- ions. (Molecular weight of NaCl compound = 58.5 amu)

SOLUTION :

$$d_{\text{calc.}} = \frac{4 \times 58.5 \times 1.67 \times 10^{-27}}{(5.627 \times 10^{-10})^3}$$

$$\text{kg / m}^3 = 2.193\text{ g / cc}$$

$d_{\text{obs}} < d_{\text{calc}}$ implies some of the sites are vacant

$$d_{\text{obs}} = \frac{x \times 58.5 \times 1.67 \times 10^{-27}}{(5.67 \times 10^{-10})^3} \text{ kg/m}^3$$

$$d_{\text{obs}} = x \frac{d_{\text{cal}}}{4}$$

$$\Rightarrow \frac{2.164}{2.193} \times 4 = x \Rightarrow x = 3.947$$

$$\text{Hence, missing sites} = 4 - 3.947 = 0.053$$

$$\% \text{ of missing sites} = \frac{0.053}{4} \times 100 = 1.325\%$$

Example - 11 In an atomic Face Centered Cubic, all the lattice positions are occupied by A and the body centred octahedral hole is appropriately occupied by B, without disturbing the Face Centered Cubic of A. Calculate packing fraction of this solid.

SOLUTION :

No. of A atoms = 4, No. of B atoms = 1

$$\text{Packing fraction} = \frac{4 \times \frac{4}{3} \pi r_A^3 + 1 \times \frac{4}{3} \pi r_B^3}{a^3}$$

$$\sqrt{2}a = 4r_A \text{ and } 2(r_A + r_B) = a$$

$$r_A + r_B = \sqrt{2} r_A \Rightarrow \frac{r_B}{r_A} = (\sqrt{2} - 1)$$

$$\text{Hence packing fraction} = \frac{4}{3} \pi \frac{[4r_A^3 + (\sqrt{2} - 1)^3 r_A^3]}{(2\sqrt{2} r_A)^3}$$

$$\frac{\pi}{12\sqrt{2}} [4 + (\sqrt{2} - 1)^3] = 0.75$$

Example - 12 A metallic element has simple cubic arrangement where edge length = 288 pm, density = 7.5 g cm⁻³. Find the number of atoms in 100g of the metal.

SOLUTION :

$$d = \frac{(\text{Number of atoms}) \times (\text{Molecular weight}) \times 1.67 \times 10^{-27} \text{ kg}}{\text{Volume of unit cell}}$$

$$7.5 \times 10^{-3} \text{ kg/cm}^3 = \frac{(1) \times M \times 1.67 \times 10^{-27} \text{ kg}}{(2.88 \times 10^{-8})^3 \text{ cm}^3} \Rightarrow M = 107.28$$

$$\text{No. of atoms} = \frac{g}{M} \times 6.023 \times 10^{23} = \frac{100}{107.8} \times 6.023 \times 10^{23} = 5.6 \times 10^{23}$$

Example - 13 Find the concentration of cation vacancies in a lattice of NaCl which has been doped with 10⁻³ mole % of SrCl₂.

SOLUTION :

10⁻³ mole % of Sr Cl₂ \equiv 10⁻³ moles of Sr Cl₂ in 100 moles of NaCl \equiv 10⁻⁵ moles are present in 1 mole of NaCl Hence 10⁻⁵ moles of Sr²⁺ are present

Note that for Sr²⁺ to occupy the place of Na⁺ in the crystal, it has to remove two Na⁺ leaving one hole

[to balance the charge].



$$\text{No. of atoms} = (\text{No. of moles}) \times 6.023 \times 10^{23}$$

$$\text{No. of atoms in } 10^{-5} \text{ Sr}^{2+}$$

$$= 10^{-5} \times (6.023 \times 10^{23}) = 6.023 \times 10^{18}$$

$$\text{So, no. of cation vacancies} = \text{no. of Sr}^{2+} \text{ present.}$$

Example - 14 The molar volume of KCl and NaCl are 37.46 mL and 27.94 mL respectively. Find the ratio of the unit cube edges of the two crystals. (Assume both have same packing efficiency)

SOLUTION :

$$\begin{aligned} \text{volume of } 6.023 \times 10^{23} \text{ formula units of KCl} \\ = 37.46 \text{ ml} \end{aligned}$$

$$\text{volume of 4 formula units of}$$

$$\text{KCl} = \frac{37.46}{N_A} \times 4 \text{ ml}$$

$$\text{volume occupied by KCl formula units}$$

$$= \frac{x}{100} \times \text{volume of unit cell}$$

$$\Rightarrow \text{volume of unit cell of KCl crystal}$$

$$= \frac{100}{x} \times \frac{37.46}{N_A} \times 4 \text{ mL}$$

$$\text{Similarly volume of unit cell of NaCl crystal}$$

$$= \frac{100}{x} \times \frac{27.94}{N_A} \times 4 \text{ mL}$$

$$\frac{\text{volume of unit cell}_{\text{KCl}}}{\text{volume of unit cell}_{\text{NaCl}}} = \frac{a_{\text{KCl}}^3}{a_{\text{NaCl}}^3} = \frac{37.46}{27.94}$$

$$\Rightarrow \frac{a_{\text{KCl}}}{a_{\text{NaCl}}} = \left(\frac{37.46}{27.94} \right)^{1/3} = 1.113$$

Example - 15 Calculate the void space in closest packing of n spheres of radius 1 unit, n spheres of radius 0.414 units and $2n$ spheres of radius 0.225 units.

SOLUTION :

$$\text{It resembles face centered cubic situation : } \sqrt{2} a = 4 \times 1 \Rightarrow a = 2\sqrt{2}$$

$$\text{Also, No. of unit cells} = \frac{n}{4}$$

$$\text{Volume of atoms} = \frac{n}{4} \left[4 \times \frac{4}{3} \pi (1)^3 + 4 \times \frac{4}{3} \pi (0.414)^3 + 4 \times 2 \times \frac{4}{3} \pi (0.225)^3 \right] = 4.58n$$

$$\text{Volume of crystal} = \left(\frac{n}{4} \right) \times a^3 = 4\sqrt{2}n$$

$$\therefore \text{Percentage of space occupied} = \frac{4.58n}{4\sqrt{2}n} \times 100 = 81\%$$

$$\text{Hence, void space} = 19\%$$

ANSWERS TO IN-CHAPTER EXERCISE

- B** 1. Al_2O_3
- D** 1. 1.554 g/cc, 1.55 g/cc

SOLUTIONS TO IN-CHAPTER EXERCISE - B

1. Two third of octahedral voids are occupied by aluminium implies aluminium proportion $= \frac{2}{3} \times 4$ and no. of oxide ions = 4.
So, the formula is $\text{Al}_{8/3}\text{O}_4 \equiv \text{Al}_2\text{O}_3$

SOLUTIONS TO IN-CHAPTER EXERCISE - D

1. (a) Frenkel defects do not change the density of the crystal.

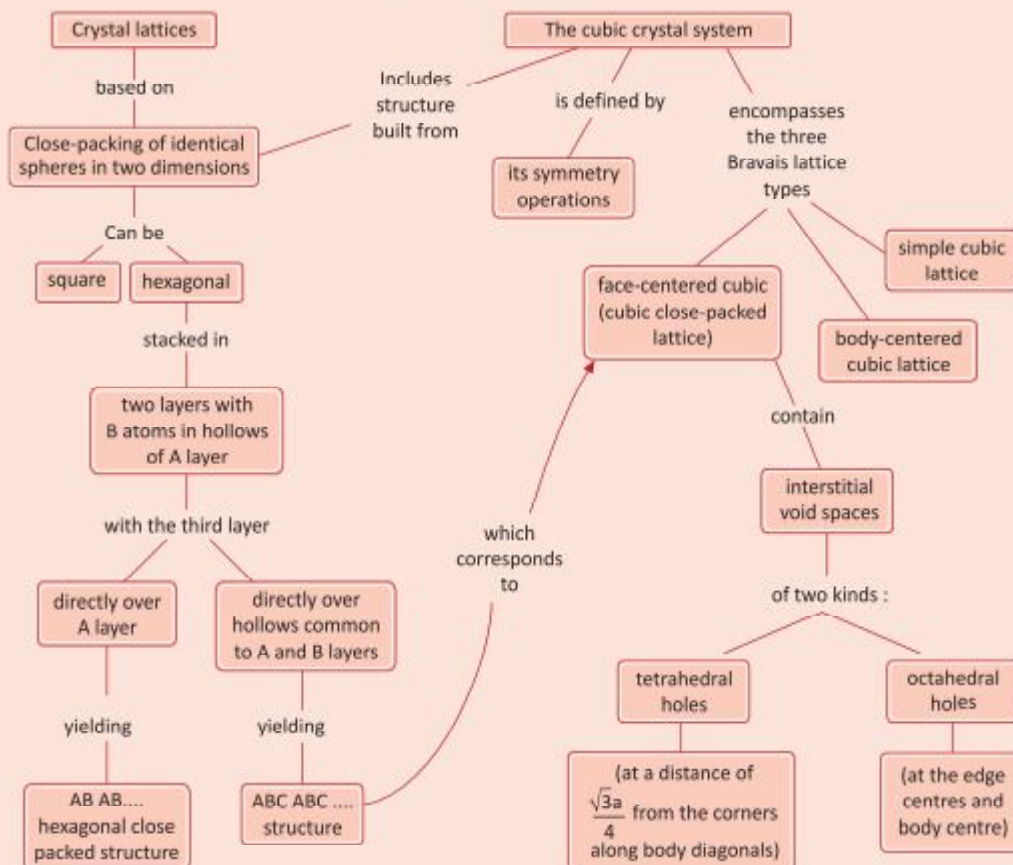
$$\text{Density} = \frac{4 \times 40 \times 1.67 \times 10^{-27} \text{ kg}}{(5.56 \times 10^{-10})^3 \text{ m}^3} = 1.554 \text{ g/cc}$$

- (b) Density

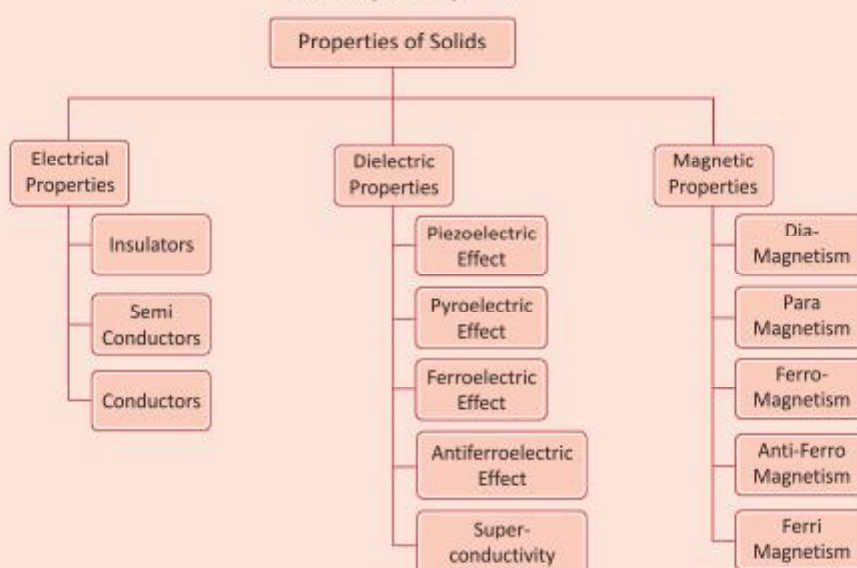
$$= \frac{\left(4 - \frac{0.1}{100} \times 4\right) \times 40 \times 1.67 \times 10^{-27} \text{ kg}}{\left(5.56 \times 10^{-10}\right)^3 \text{ m}^3} = 1.55 \text{ g/cc}$$

Concepts Map

Concept Map - 1



Concept Map - 2



My Chapter Notes

