

PHYSICAL CHEMISTRY

ENTHUSIAST | LEADER | ACHIEVER



STUDY MATERIAL

Solid State

ENGLISH MEDIUM

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SOLID STATE

1.0 INTRODUCTION

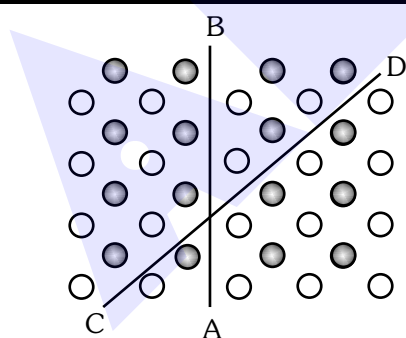
The solid are characterised by incompressibility, rigidity and mechanical strength. The molecules, atoms or ions in solids are closely packed means they are held together by strong forces and can not move randomly. Thus solids have definite volume, shape, slow diffusion, low vapour pressure and possesses the unique property of being rigid. Such solids are known as **true solids** like NaCl, KCl, Sugar, Ag, Cu etc. On the other hand the solid which loses shapes on long standing, flows under its own weight and easily distorted by even mild distortion forces are called **pseudo solids** such as glass, pitch etc.

Some solids such as NaCl, Sugar, Sulphur etc. have properties not only of rigidity and incompressibility but also of having typical geometrical forms. These solids are called as **crystalline solids**. In such solids there is definite arrangements of particles (atoms, ions or molecules) throughout the entire three dimensional network of a crystal in long-range order. This three dimensional arrangement is called **crystal lattice or space lattice**. Other solids such as glass, rubber, plastics etc. have rigidity and incompressibility to a certain extent but they do not have definite geometrical forms or do not have long range order are known as **amorphous solids**.

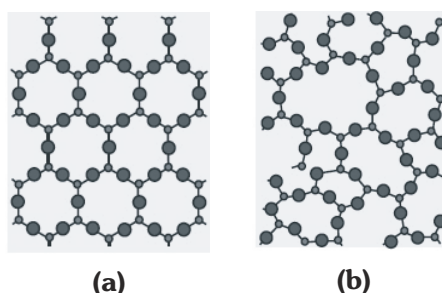
Distinction between Crystalline and Amorphous Solids

Property	Crystalline solids	Amorphous solids
Shape	Definite characteristic geometrical shape	Irregular shape
Melting point	Melt at a sharp and characteristic temperature	Gradually soften over a range of temperature
Cleavage property	When cut with a sharp edged tool, they split into two pieces and the newly generated surfaces are plain and smooth	When cut with a sharp edged tool, they cut into two pieces with irregular surfaces
Heat of fusion	They have a definite and characteristic heat of fusion	They do not have definite heat of fusion
Anisotropic nature	Anisotropic in nature (direction dependent)	Isotropic in nature (direction independent)
Nature	True solids	Pseudo solids or super cooled liquids
Arrangement of particles	Long range order	Only short range order.
Examples	NaCl, Metals, Diamond	Rubber, Plastics

GOLDEN KEY POINTS



Anisotropy in crystals is due to different arrangement of particles along different directions.



(a) and (b)
Two dimensional structure of
(a) quartz and (b) quartz glass

Table (a) : Classification of crystalline solids

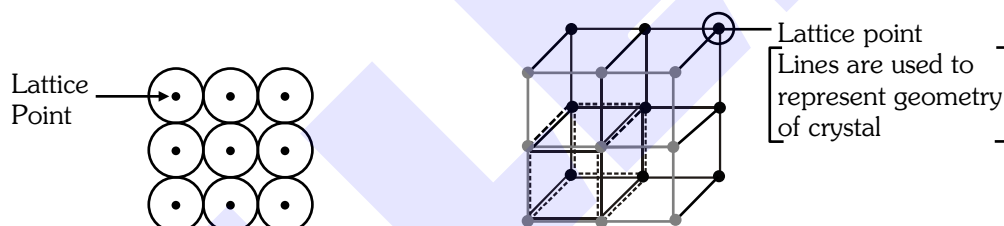
There is another category of solids known as polycrystalline solids. They appear amorphous but have microcrystalline structures. Metals often occur in polycrystalline condition. There are a large number of fine crystals randomly oriented so a sample as a whole may appear to be isotropic even though a single crystal is anisotropic.

Amorphous solids may become crystalline at some temperature. Some glass objects from ancient civilisations are found to become milky indicating crystallisation.

S. No.	Type of Solid	Constituent Particles	Bonding/ Attractive Forces	Examples	Physical Nature	Electrical Conductivity	Melting Point
1.	Molecular solids (i) Non polar	Molecules	Dispersion or London forces	Ar, CCl ₄ , H ₂ , I ₂ , CO ₂	Soft	Insulator	Very low
	(ii) Polar		Dipole-dipole interactions	HCl, SO ₂	Soft	Insulator	Low
	(iii) Hydrogen bonded		Hydrogen bonding	H ₂ O (ice)	Hard	Insulator	Low
2.	Ionic solids	Ions	Coulombic or electrostatic	NaCl, MgO, ZnS, CaF ₂	Hard but brittle	Insulators in solid state but conductors in molten and in aqueous solution	High
3.	Metallic solids	Positive metal ions in a sea of delocalised e ⁻	Metallic bonding	Fe, Cu, Ag, Mg	Hard but malleable and ductile	Conductors in solid and in molten state	Fairly high
4.	Covalent or network solids	Atoms	Covalent bonds	SiO ₂ , SiC, AlN C(diamond), C(graphite)	Hard Soft	Insulators Conductor	Very high

1.1 Space Lattice/Crystalline Lattice/3-D Lattice

- Space lattice is a regular arrangement of lattice points (atoms or ions or molecules) showing how the particles are arranged at different sites in 3D-view.



- "The three dimensional distribution of component particles in a crystal can be found by X-ray diffraction of different faces of the crystal.
- On the basis of the classification of symmetry, the crystals have been divided into seven systems. These seven systems with the characteristics of their axes (Interfacial angles and intercepts) where some examples of each are given in the following table (b).

These crystal systems differ in length of unit cell edges (a , b and c) and the angles between the unit cell edges.

In cubic and trigonal (rhombohedral) systems, the three unit edges are of equal lengths but for the rest five systems it is not so. The interfacial angles are all 90° in the cubic, tetragonal and orthorhombic systems but it is not so for the rest four systems.

1.2 Unit Cell (U.C.)

Unit cell of the crystalline substance is defined as the smallest repeating portion which shows the complete geometry of the crystalline substance like brick in wall. A unit cell is the smallest portion of the whole crystal. A unit cell is characterized by the edge lengths a , b and c along the three axes of the unit cell and the angles α , β and γ between the pair of edges bc , ca and ab respectively.

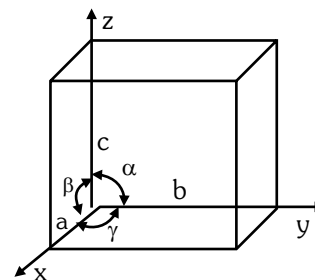
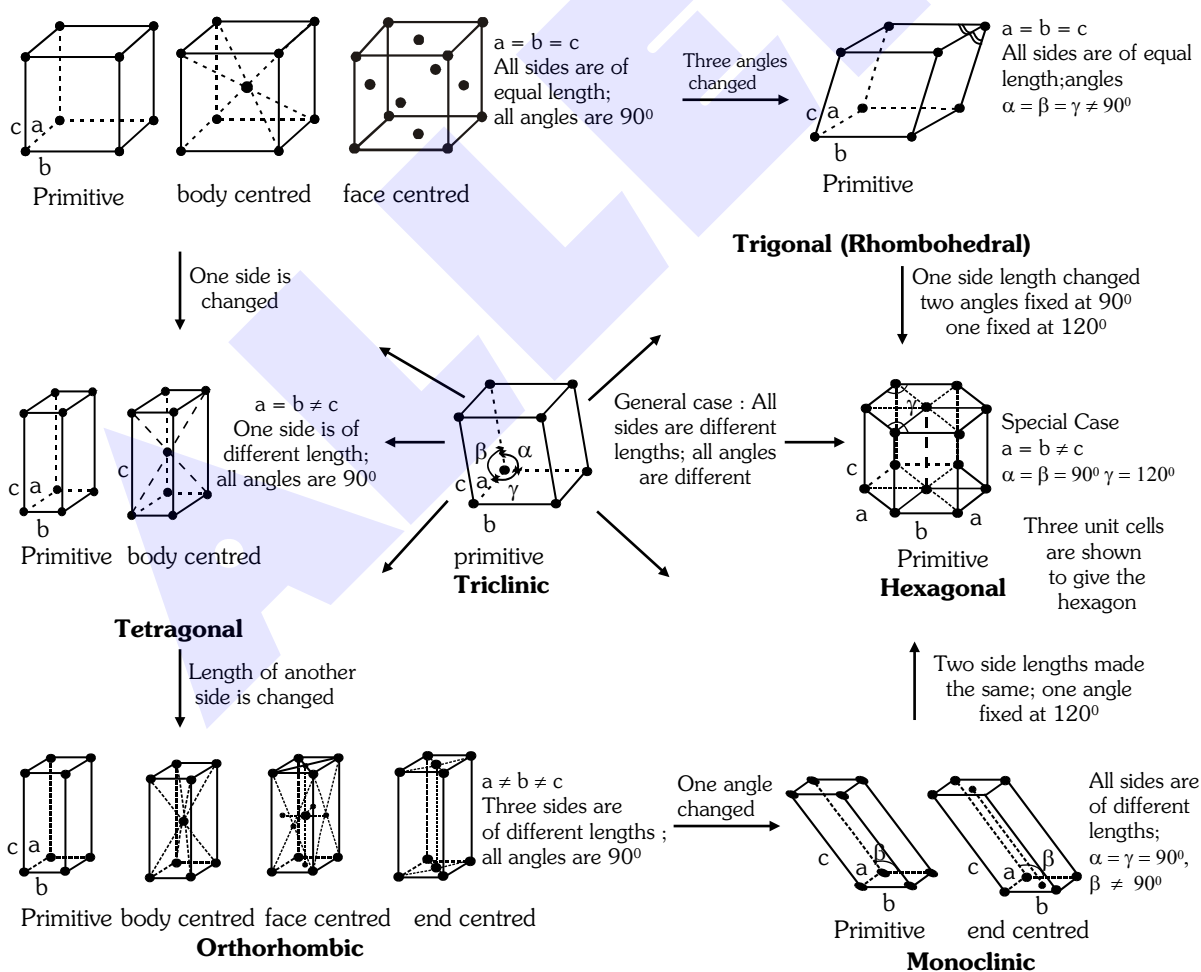


Table (b) : The Seven Crystal Systems

S. No.	System	Name of Lengths	Edge Angles	Bravais Lattices	Examples
1.	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	Primitive, Face-centred, Body centred = 3	NaCl, Zinc blende, Cu
2.	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Primitive, Body centred = 2	White tin, SnO_2 , TiO_2 , CaSO_4
3.	Orthorhombic or Rhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Primitive, Face-centred, Body centred, End centred = 4	Rhombic sulphur, KNO_3 , BaSO_4 Match Box
4.	Rhombohedral or Trigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	Primitive = 1	Calcite (CaCO_3), HgS (cinnabar)
5.	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$	Primitive = 1	Graphite, ZnO , CdS
6.	Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ$, $\beta \neq 90^\circ$	Primitive, End centred = 2	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ Monoclinic sulphur
7.	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	Primitive = 1	$\text{K}_2\text{Cr}_2\text{O}_7$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, H_3BO_3
				Total = 14	



1.3 Co-ordination Number

The number of nearest neighbouring particles around a specific particle in a given crystalline substance is called as co-ordination number of that crystalline substance.

1.4 Packing Efficiency or Packing fraction (P.E.)

"Packing efficiency is defined as the ratio of volume occupied by the atoms to the total volume of the crystalline substance"

$$P.E. = \frac{\text{Volume occupied by atoms present in a crystal}}{\text{Volume of crystal}}$$

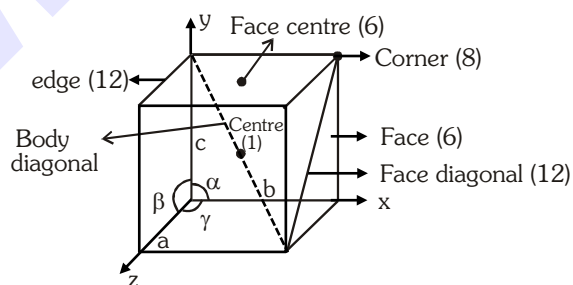
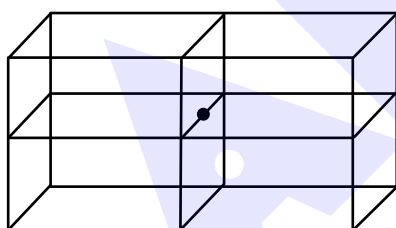
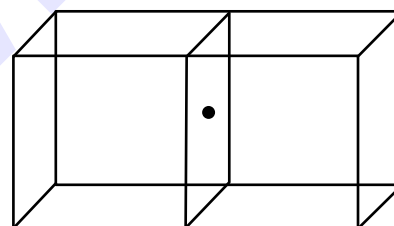
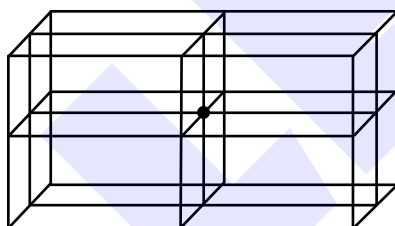
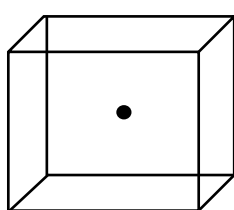
$$P.E. = \frac{\text{Volume occupied by atoms present in unit cell}}{\text{Volume of unit cell}} \quad \text{or} \quad P.E. = \frac{Z \times (4/3)\pi r^3}{V}$$

Where z = number of atoms present in unit cell / Number of formula units for ionic crystals.

GOLDEN KEY POINTS

● In a cube

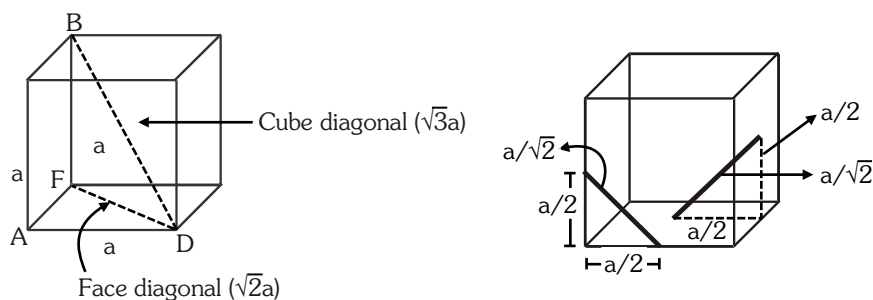
1. Number of corners = 8
2. Number of faces = 6
3. Number of edges = 12
4. Number of body centre = 1
5. Number of body diagonals = 4
6. Number of face diagonals = 12



Contribution of an atom at different lattice points of cube :

- A corner of a cube is common in 8 cubes. So $\frac{1}{8}$ th part of an atom is present at this corner of cube.
- A face of a cube is common in 2 cubes. So $\frac{1}{2}$ th part of an atom is present at the face of a cube.
- An edge of a cube is common in four cubes, so $\frac{1}{4}$ th part of the atom is present at the edge of a cube.
- A cube centre is not common in any another cube, so one complete atom is present at the cube centre.

1.5 Length of Face Diagonal and Cube Diagonal



$$\text{Distance between 2 adjacent face centres} = \frac{a}{\sqrt{2}} = \frac{a\sqrt{2}}{2}$$

$$\text{Distance between 2 adjacent edge centres} = \frac{a}{\sqrt{2}} = \frac{a\sqrt{2}}{2}$$

Consider the triangle AFD (with the help of pythagoruous theorem)

$$FD = \sqrt{AF^2 + AD^2} = \sqrt{a^2 + a^2} = \sqrt{2}a \quad (\text{length of face diagonal.})$$

Consider the triangle BFD (with the help of pythagoruous theorem)

$$BD = \sqrt{BF^2 + FD^2} = \sqrt{a^2 + (\sqrt{2}a)^2} = \sqrt{3}a \quad (\text{length of cube diagonal})$$

Illustrations

Illustration 1. Which of the following is a non-crystalline solid ?

- (1) CsCl (2) NaCl (3) CaF₂ (4) Glass

Solution. **Ans. (4)**

Illustration 2. Which of the following statements is incorrect about amorphous solids?

- (1) They are anisotropic
 (2) They are rigid and incompressible
 (3) They melt over a wide range of temperature
 (4) There is no orderly arrangement of particles

Solution **Ans. (1)**

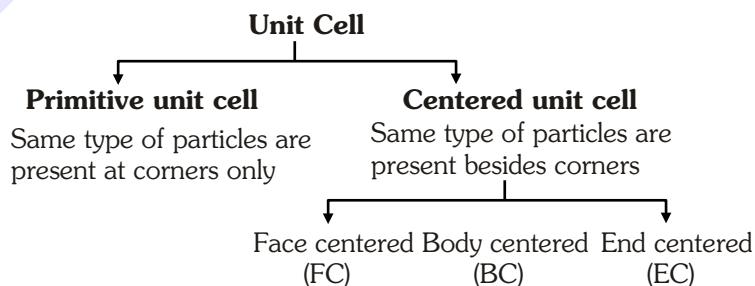
Illustration 3. **Assertion :** Crystalline solids are anisotropic.

Reason : The constituent particles are very closely packed.

- (1) A (2) B (3) C (4) D

Solution. **Ans. (2)**

1.6 (I) CLASSIFICATION OF UNIT CELL (As per Bravais)



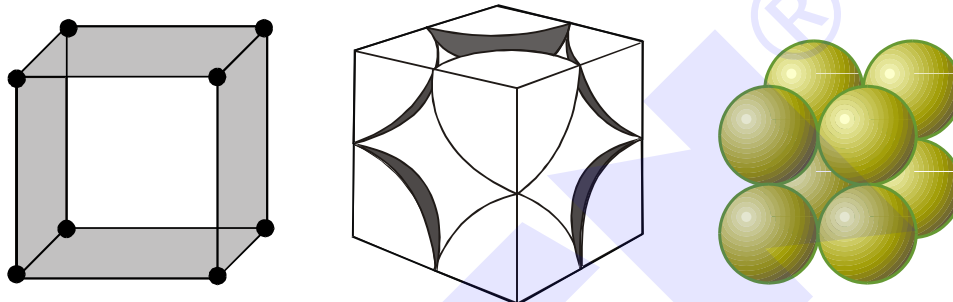
- In end centered same type of particles are present at corners and any two opposite face centres.
- End centered type of Bravais lattice is present only in orthorhombic and monoclinic type unit cell.

(II) TYPES OF CUBIC UNIT CELL

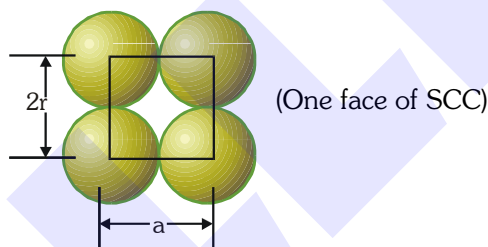
The distance between successive lattice planes of the same type is called the spacing of planes or interplanar distance between the planes. On the basis of this aspect, the lattices may be divided in following classes :

(A) SIMPLE/PRIMITIVE/BASIC CUBIC UNIT CELL

A unit cell having lattice point only at corners is called primitive or simple unit cell. i.e. in this case there is one atom at each of the eight corners of the unit cell considering an atom at one corner as the centre, it will be found that this atom is surrounded by six equidistant neighbours (atoms) and thus the co-ordination number will be six. If 'a' is the side of the unit cell, then the distance between the nearest neighbours shall be equal to 'a'.



(a) Relationship between edge length 'a' and atomic radius 'r' : $a = 2r$ i.e. $r = \frac{a}{2}$



(b) Number of atoms present in unit cell (z) : In this case one atom lies at the each corner.

Hence simple cubic unit cell contains a total of $\frac{1}{8} \times 8 = 1$ atom / unit cell.

(c) Packing efficiency (P. E.) :

$$\text{P.E.} = \frac{\text{Volume occupied by atoms present in unit cell}}{\text{Volume of unit cell}} = \frac{Z \times \frac{4}{3} \pi r^3}{V} \left[\because \text{Volume of atom} = \frac{4}{3} \pi r^3 \right]$$

$$\text{For SC : P.E.} = \frac{1 \times \frac{4}{3} \times \pi \times \left(\frac{a}{2}\right)^3}{a^3} = \frac{\pi}{6} = 0.524 \text{ or } 52.4\% \quad [\because r = \frac{a}{2} \text{ and } V = a^3, z = 1]$$

In SC, 52.4% of total volume is occupied by atoms

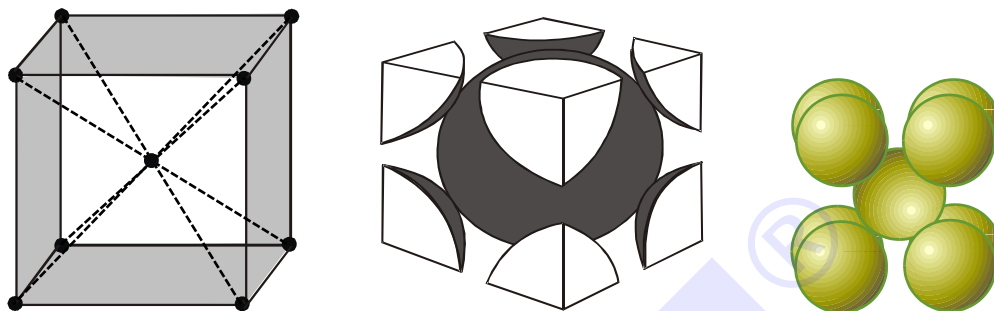
% void space = 47.6

(B) BODY CENTRED CUBIC UNIT CELL (BCC)

A unit cell having lattice point at the body centre in addition to the lattice point at every corner is called as body centered unit cell : where body diagonal particles are touching particle.

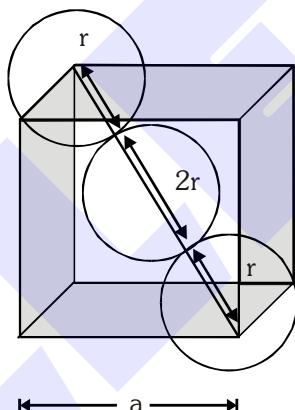
Here the central atom is surrounded by eight equidistant atoms and hence the co-ordination number is eight.

The nearest distance between two atoms will be $\frac{a\sqrt{3}}{2}$

**(a) Relationship between edge length 'a' and atomic radius 'r'**

In BCC, along cube diagonal all atoms touches each other and the length of cube diagonal is $\sqrt{3}a$.

So, $\sqrt{3}a = 4r$ i.e. $r = \frac{\sqrt{3}a}{4}$

**(b) Number of atoms present in unit cell (z) :**

$$Z = \left(\frac{1}{8} \times 8\right) + (1 \times 1) = 1 + 1 = 2 \text{ atoms/unit cell}$$

(Corner) (Body centre)

In this case one atom lies at the each corner of the cube.

Thus contribution of the 8 corners is $\left(\frac{1}{8} \times 8\right) = 1$, while that of the body centred is 1 in the unit cell.

Hence total number of atoms per unit cell is $1 + 1 = 2$ atoms

(c) Packing efficiency :

$$\text{P.E.} = \frac{Z \times \frac{4}{3} \pi r^3}{V} = \frac{2 \times \frac{4}{3} \times \pi \left(\frac{\sqrt{3}a}{4}\right)^3}{a^3} = \frac{\sqrt{3}\pi}{8} = 0.68 \quad [\because Z = 2, r = \frac{\sqrt{3}a}{4}, V = a^3]$$

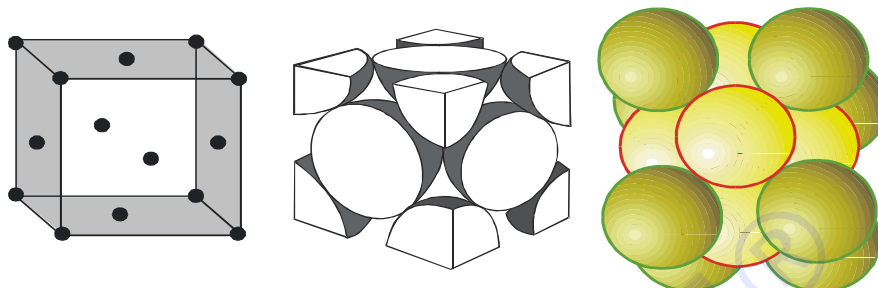
In B.C.C. , 68% of total volume is occupied by atoms.

% void space = 32

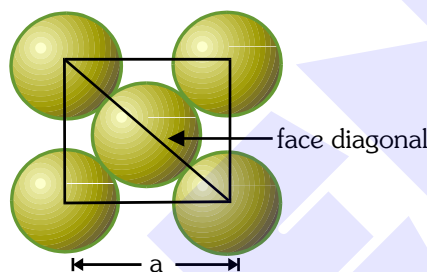
(C) FACE CENTRED CUBIC UNIT CELL (FCC)

A unit cell having lattice point at every face centre in addition to the lattice point at every corner called as face centred unit cell. i.e. in this case there are eight atoms at the eight corners of the unit cell and six atoms at the centre of six faces. The co-ordination number will be 12 and the distance between

the two nearest atoms will be $\frac{a\sqrt{2}}{2}$



(a) Relationship between edge length 'a' and atomic radius 'r' :



In FCC, along the face diagonal all atoms touches each other and the length of face diagonal is $\sqrt{2}a$.

So $4r = \sqrt{2}a$ i.e. $r = \frac{\sqrt{2}a}{4} = \frac{a}{2\sqrt{2}}$ $r = \frac{a}{2\sqrt{2}}$

(b) Number of atoms per unit cell (z) :

$$Z = \left(\frac{1}{8} \times 8\right) + \left(6 \times \frac{1}{2}\right) = 1 + 3 = 4 \text{ atoms/unit cell}$$

Corner faces

In this case one atom lies at the each corner of the cube and one atom lies at the centre of each face of the cube. It may noted that only $\frac{1}{2}$ of each face sphere lie within the unit cell and there are six such faces.

The total contribution of 8 corners is $\left(\frac{1}{8} \times 8\right) = 1$, while that of 6 face centred atoms is $\left(\frac{1}{2} \times 6\right) = 3$ in the unit cell. Hence total number of atoms per unit cell is $1 + 3 = 4$ atoms.

(c) Packing efficiency :

$$\text{P.E.} = \frac{Z \times \frac{4}{3} \pi r^3}{V} = \frac{4 \times \frac{4}{3} \pi \times \left(\frac{a}{2\sqrt{2}}\right)^3}{a^3} = \frac{\pi}{3\sqrt{2}} = 0.74 \text{ or } 74\% \quad \left[\because Z=4, r = \frac{a}{2\sqrt{2}}, V = a^3 \right]$$

i.e. In FCC, 74% of total volume is occupied by atoms.

% void space = 26

SUMMARY TABLE

Unit cell	No. of atoms per unit cell	Relation between r & a	Co-ordination Number	Volume occupied by particles (%)
Simple cube	$8 \times \frac{1}{8} = 1$	$r = \frac{a}{2}$	6	$\frac{\pi}{6} \times 100 = 52.4$
Body centred cube (BCC)	$8 \times \frac{1}{8} + 1 = 2$	$r = \frac{a\sqrt{3}}{4}$	8	$\frac{\pi\sqrt{3}}{8} \times 100 = 68$
Face centred cube (FCC)	$8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$	$r = \frac{a\sqrt{2}}{4}$	12	$\frac{\pi}{3\sqrt{2}} \times 100 = 74$

Illustrations

Illustration 4. If the radius of an atom of an element is 75 pm and the lattice is body-centred cubic, the edge length of the unit cell will be

- (1) 32.475 pm (2) 173.2 pm (3) 37.5 pm (4) 212.1 pm

Solution. **Ans. (2)**

Illustration 5. **Assertion :** A particle present at the corner of the face centred unit cell has 1/8th of its contribution of the unit cell.

Reason : In any space lattice, the corner of the unit cell is always shared by the eight unit cells.

- (1) A (2) B (3) C (4) D

Solution. **Ans (3)**

Illustration 6. In a face centred cubic arrangement of A and B atoms where A are present at the corner and B at the face centres, A atoms are missing from 4 corners in each unit cell ? What is the simplest formula of the compound?

Solution. No. of A atoms = $4 \times \frac{1}{8} = \frac{1}{2}$, No. of B atoms = $6 \times \frac{1}{2} = 3$ Formula = $A_{1/2}B_3 = AB_6$

1.7 DENSITY OF THE CRYSTAL (d or ρ)

If the length of edge of the unit cell is known we can calculate the density of the crystal as follow :

Let length of edge of the unit cell be 'a' cm.

$$\therefore \text{Volume of the cubic unit cell} = V \text{ cm}^3 = a^3 \text{ cm}^3$$

$$\text{Density of the unit cell} = \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}}$$

Let mass of N particles present in a lattice = m g

$$\text{mass of 1 particles present in a lattice} = \frac{m}{N} \text{ g}$$

$$\text{mass of Z particles present in lattice} = \frac{Z \times m}{N} \text{ g}$$

$$d = \frac{Z \times m}{N \times a^3}$$

where Z = number of particles or number of formula units (for ionic crystals)

m = mass of lattice in g

d = density (g/cm^3)

a = edge length in cm

if m = M (molar mass)

then $N = N_A$

$$d = \frac{Z \times M}{N_A \times a^3}$$

GOLDEN KEY POINTS

- If number of particles in a lattice = N
 number of SC unit cell = N
 number of bcc unit cell = $\frac{N}{2}$
 number of fcc unit cell = $\frac{N}{4}$
- For calculation use $N_A = 6 \times 10^{23}$
- $1 \text{ pm} = 10^{-12} \text{ m} = 10^{-10} \text{ cm}$
- $1 \text{ \AA} = 10^{-10} \text{ m} = 10^{-8} \text{ cm}$

BEGINNER'S BOX-1

1. Aluminium (Molecular weight = 27) crystallises in a cubic unit cell with edge length $a = 100 \text{ pm}$, with density, $d = 180 \text{ g/cm}^3$, then type of unit cell is
 (1) SC (2) BCC (3) FCC (4) HCP
2. An element has BCC unit cell with edge length 10 \AA . If density of element is 0.2 g/cm^3 , then its molar mass is :-
 (1) 240 (2) 60 (3) 35 (4) 280
3. In a tetragonal crystal :-
 (1) $a = b = c, \alpha = \beta = \gamma = 90^\circ \neq \gamma$ (2) $\alpha = \beta = \gamma = 90^\circ, a = b \neq c$
 (3) $\alpha = \beta = \gamma = 90^\circ, a \neq b \neq c$ (4) $\alpha = \beta = 90^\circ, \gamma = 120^\circ, a = b \neq c$
4. Edge length of a cube is 400 pm , its body diagonal would be :-
 (1) 500 pm (2) 600 pm (3) 566 pm (4) 693 pm
5. A metal crystallises into two cubic lattices fcc and bcc whose unit cell edge lengths are 3.5 and 3.0 \AA respectively, the ratio of densities of fcc and bcc is :-
 (1) 1.26 (2) 1.75 (3) 2.10 (4) 1.90

1.8 CLOSE PACKING OF IDENTICAL SOLID SPHERES

The solids which have non-directional bonding, their structures are determined on the basis of geometrical consideration. For such solids, it is found that the lowest energy structure is that in which each particle is surrounded by the greatest possible number of neighbours. In order to understand the structure of such solids, let us consider the particles as hard sphere of equal size in three directions. Although there are many ways to arrange the hard spheres but the one in which maximum available space is occupied will be economical which is known as closed packing now we describe the different arrangements of spherical particles of equal size.

When the spheres are packed in a plane it gives two types of packing.

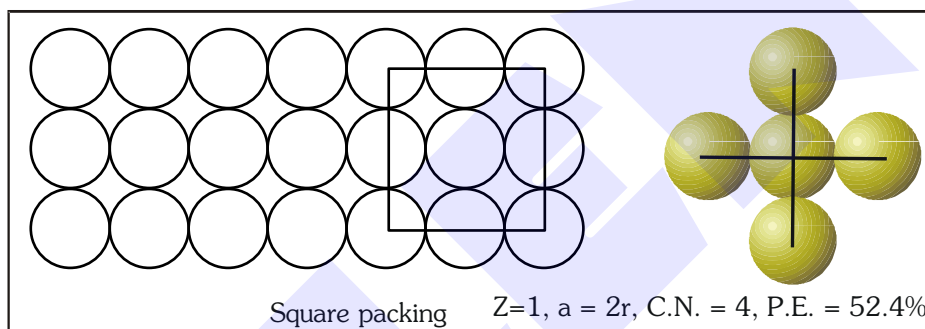
Types of Packing :-
(A) Single line arrangement
(1) Close packing of atoms in one dimension


coordination number = 2

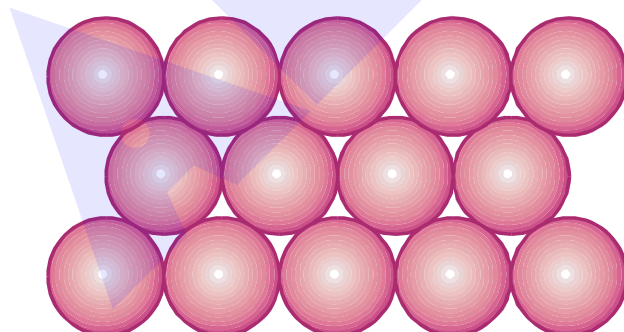
(B) Single layer arrangement

(2) Close packing of atoms in two dimensions :- When the spheres are placed in a plane, it gives two type of packing.

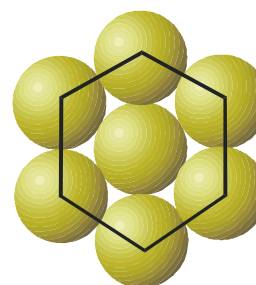
(a) Square close packing :- The centres of the spheres lie one below another. This type of arrangement is called square packing. In such packing one sphere touches four other spheres. In this case 52.4% of the volume is occupied. The remaining 47.6% of the volume is empty and is called void volume.



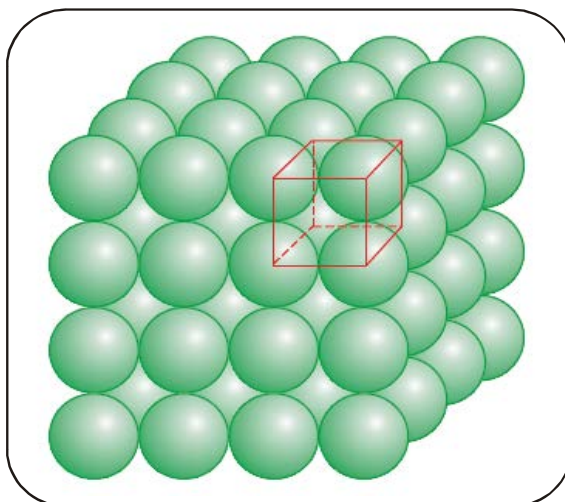
(b) Hexagonal close packing :- Another type of arrangement of atoms is shown below. This type of packing is called hexagonal packing. In such packing one sphere touches six other spheres. In this case 60.4% of the volume is occupied. The remaining 39.6% of the volume is empty and is called void volume. Therefore this type of packing is more compact than the square packing.



Hexagonal packing


 $Z=3, \text{C.N.}=6, \text{P.E.}=60.4\%$
(C) Multi layer arrangement :-
(3) Close packing of atoms in three dimensions

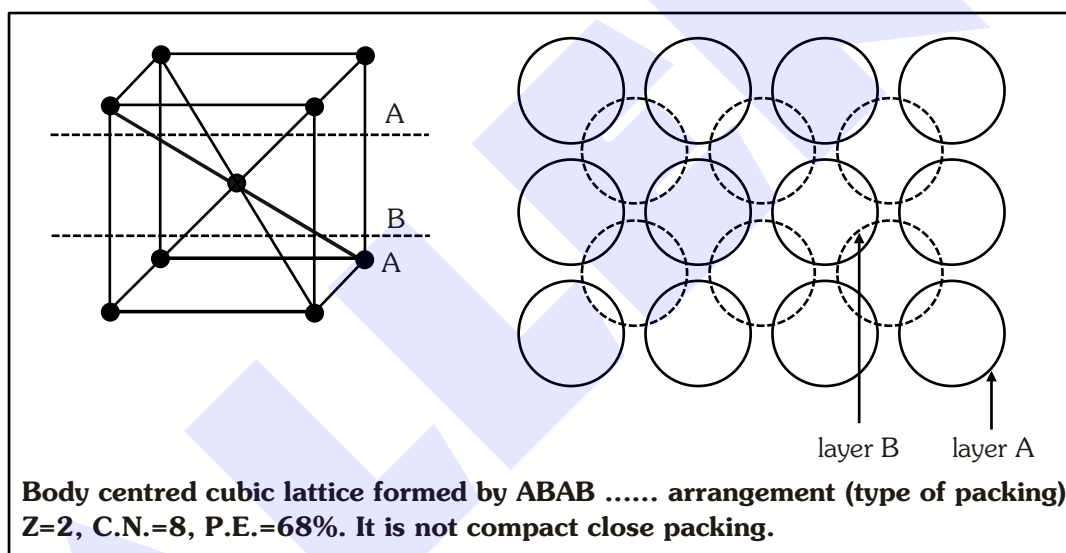
(a) Simple cubic close packing (Three dimensional close packing from two dimensional closed packed layers) When first square arrangement of layer A is exactly placed above occupies 2nd square arrangement of layer A and so on. So this type of arrangement is known as **AAA..... arrangement** and its unit cell is simple cubic unit cell.



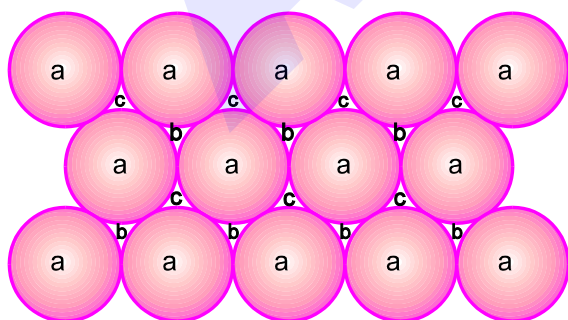
Simple cubic lattice formed by A A A ... arrangement (type of packing)

$Z = 1$, C.N.=6, P.E.=52.4%. It is not compact close packing.

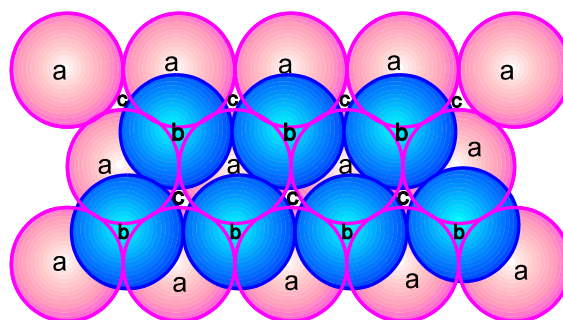
(b) Body centred cubic close packing :-



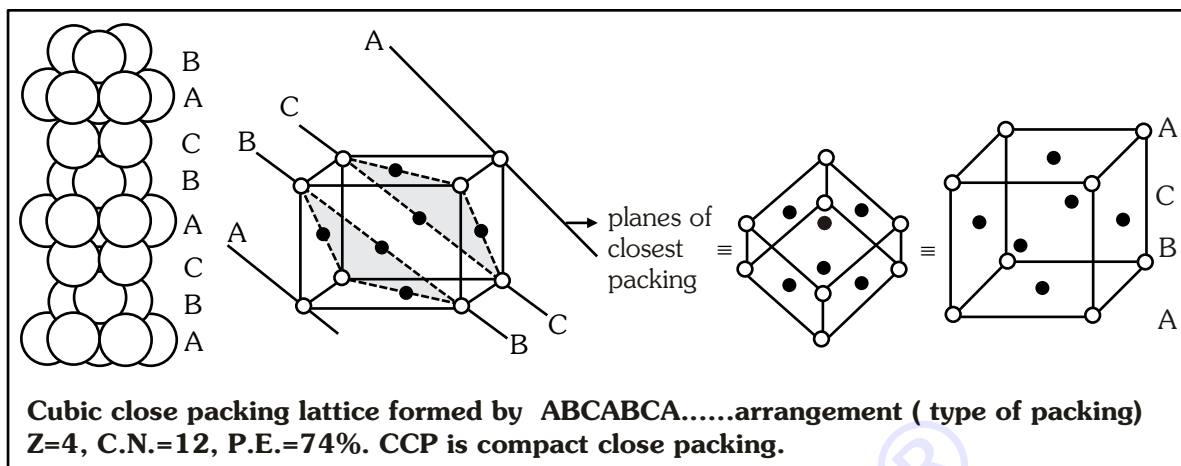
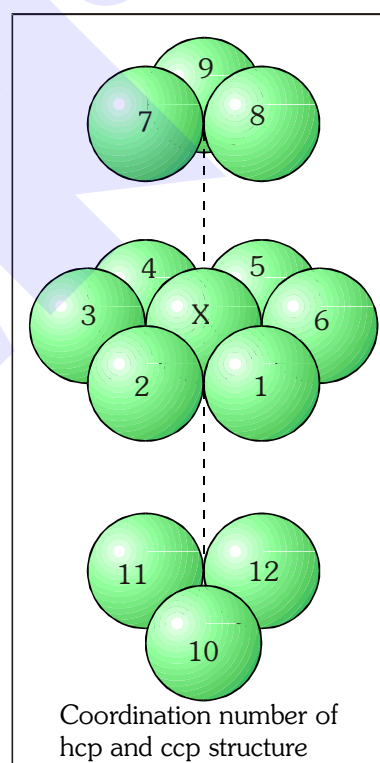
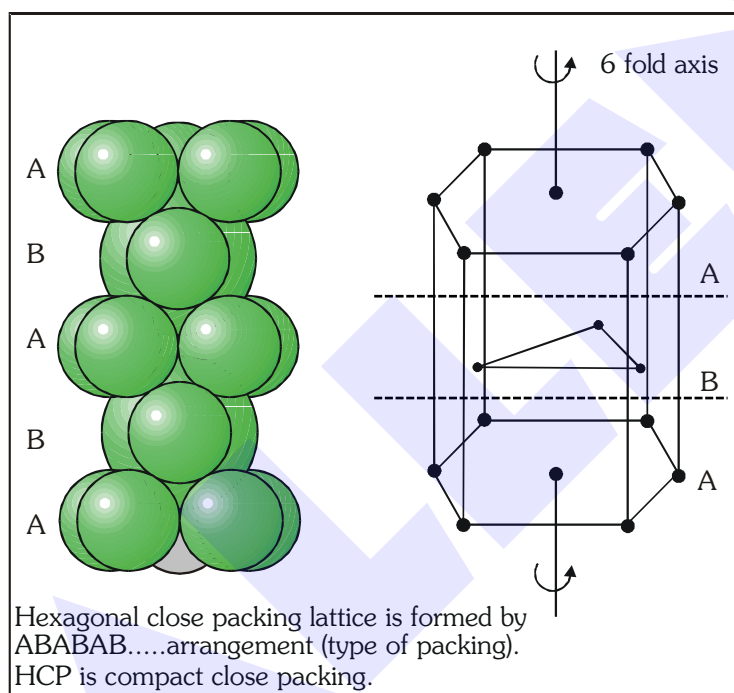
(c) Cubic close packing and hexagonal close packing :- (Three dimensional close packing from two dimensional hexagonal close packed layers)



Layer A \rightarrow [b, c] type voids



Layer B \rightarrow [c, a] type voids

Cubic close packing

Hexagonal close packing :-


$$\text{Number of particles in hexagonal unit cell (z)} = 12 \times \frac{1}{6} + 2 \times \frac{1}{2} + 3 \times 1 = 6$$

C.N. = 12, P.E. = 74%, type of packing ABAB.....

GOLDEN KEY POINTS

- Some examples of metals with their lattice types and coordination number are given in the following table.

Li	Be		□ Body Centre Cubic (bcc)									
Na	Mg	Al	■	Face Cental Cubic								
			⬡	Hexagonal Closed Packed (hcp)								
K	Ca	Cs	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au		

MULTILAYER CLOSE PACKING

Contents	SCC	BCC	CCP/FCC	HCP
Type of packing	AAAA... packing	ABAB..... packing	ABCABC close packing	ABAB close packing
No. of atoms	1	2	4	6
Co-ordination no.	6	8	12	12
Packing efficiency	52.4%	68%	74%	74%
Examples	Po	IA, Ba V & Cr group Fe, Mn	Ca, Sr, Al Co group, Ni group, Copper group, all inert gases except He	Remaining d-block elements Be & Mg

- In close packing, number of particles = N, number of OHV = N, Number of THV = 2N

Illustrations

Illustration 7. The arrangement of the first two layers, one above the other, in HCP and CCP arrangements is

- (1) Exactly same in both cases
- (2) Partly same and partly different
- (3) Different from each other
- (4) Nothing definite

Solution. **Ans. (1)**

Illustration 8. "There is no difference in the arrangement of atoms in CCP and HCP structure" Do you agree with this statement ? Explain why.

Solution. Statement is incorrect

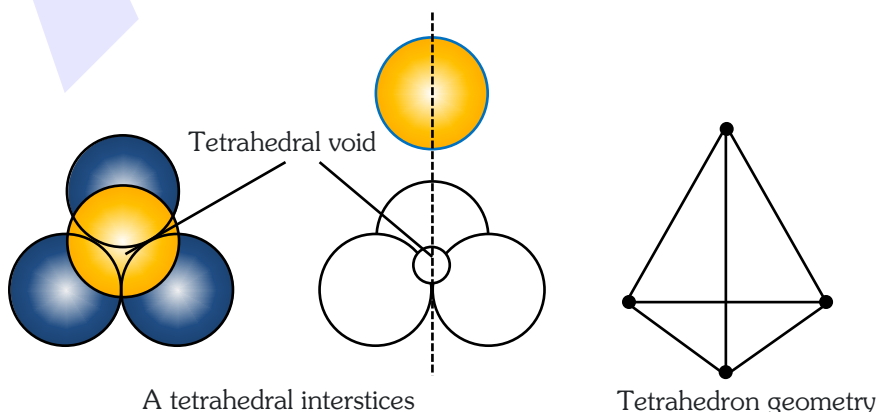
CCP ABC ABC ABC
HCP AB AB AB

1.9 INTERSTICES OR VOIDS OR HOLES IN CRYSTALS

It has been shown that the particles are closely packed in the crystals even though there is some empty space left in between the spheres. This is known as interstices (or interstitial site or hole or empty space or voids). In three dimensional close packing (CCP & HCP) the interstices are of two types : (i) tetrahedral interstices and (ii) octahedral interstices.

(A) Tetrahedral Interstices

We have seen that in hexagonal close packing (HCP) and cubic close packing (CCP) each sphere of second layer touches with three spheres of first layer. Thus they leave a small space in between which is known as **tetrahedral site or interstices** or the vacant space between 4 touching spheres is called as tetrahedral void. Since a sphere touches three spheres in the below layer and three spheres in the above layer hence there are two tetrahedral sites associated with one sphere.



It may be noted that a tetrahedral site does not mean that the site is tetrahedral in geometry but it means that this site is surrounded by four spheres and by joining the centres of these four spheres forms a regular tetrahedron.

In FCC, one corner and its three face centres form a tetrahedral void

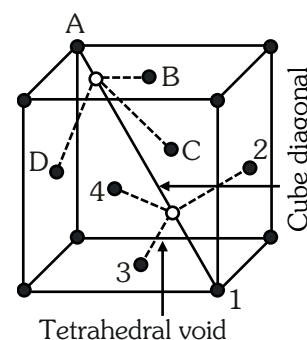
In FCC, two tetrahedral voids are obtained along one cube diagonal.

So in FCC, 8 tetrahedral voids are present.

In FCC, total number of atoms = 4

In FCC, total number of tetrahedral voids = 8

So, we can say that, in 3D close packing 2 tetrahedral voids are attached with one atom.

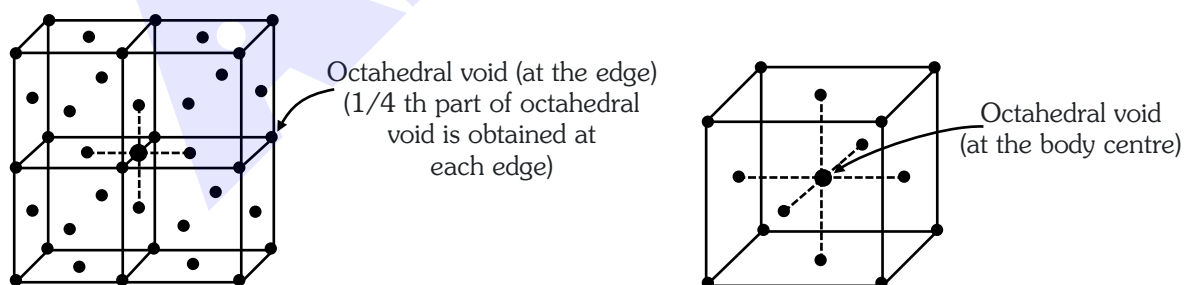
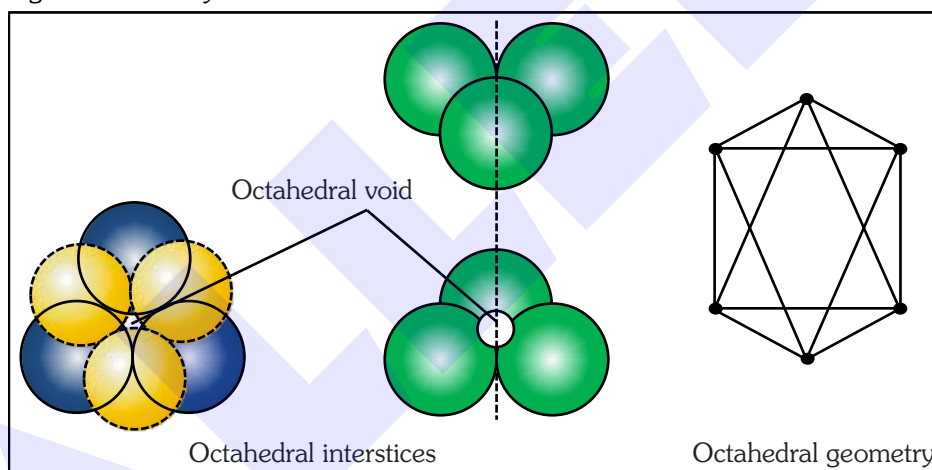


(B) Octahedral Interstices

Hexagonal close packing (hcp) and cubic close packing (ccp) also form another type of interstices which is called octahedral site. The vacant space between 6 touching spheres is called as octahedral void.

In the figure, two layers of close packed spheres are shown. The spheres of first layer are shown by full circles while that of second layer by dotted circles. Two triangles are drawn by joining the centres of three touching spheres of both the layers :

In fcc, 6 face centres form an octahedral void. On superimposing these triangles on one another one octahedral site is created. It may be noted that an octahedral site does not mean that the hole is octahedral in shape but it means that this site is surrounded by six nearest neighbour lattice points arranged octahedrally.



$$\text{In FCC, total number of octahedral voids} = (1 \times 1) + \left(12 \times \frac{1}{4}\right) = 1 + 3 = 4$$

(Cube centre) (edge centre)

In FCC, number of atoms = 4 and number of octahedral voids = 4 : number of tetrahedral voids = 8

So we can say that, in 3D close packing one octahedral void is attached with one atom.

Illustrations

Illustration 9. The number of octahedral sites in a cubical close packed array of N spheres is

- (1) $N/2$ (2) $2N$ (3) N (4) $4N$

Solution. **Ans. (3)**

Illustration 10. If A atoms are in ccp, B atoms are present at every Octahedral void, C atoms are present at 25% of tetrahedral void, find out the possible molecular formula of the compound ?

Solution. Atom A is in ccp = 4 atoms of A

Atom B is present at every octahedral void = 4 atoms of B

Atom C is present at 25% of tetrahedral void = $8 \times \frac{25}{100} = 2$ atoms of C

So, the possible molecular formula is $A_4 B_4 C_2 = A_2 B_2 C$.

1.10 STUDY OF IONIC CRYSTALS

Limiting Radius Ratio

An ionic crystal contains a large number of cations and anions. Generally cations are smaller in size than that of anions. The cations are surrounded by anions and they touch each other. These ions are arranged in space in such a way to produce maximum stability.

So the limiting radius ratio tells about :

- (i) Stability of ionic crystal
- (ii) Coordination number
- (iii) Geometry of voids

(a) Triangular : All anions touches each other and co-ordination number is 3

$$\cos \theta = \frac{R}{R+r}$$

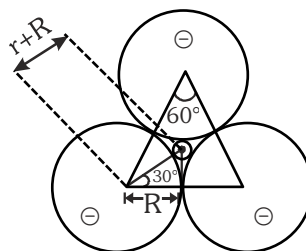
$$\cos 30^\circ = \frac{R}{r+R}$$

$$\sqrt{3}R + \sqrt{3}r = 2R$$

$$\sqrt{3}r = (2 - \sqrt{3})R$$

$$\frac{r}{R} = \frac{2 - \sqrt{3}}{\sqrt{3}} = \frac{2 - 1.73}{1.73} = \frac{0.27}{1.73} = 0.155$$

$$\text{L.R.R.} = 0.155 = \frac{r}{R} < 1$$



(b) Tetrahedral void : All anions touches each other and co-ordination number of cation is 4.

$$\text{Face diagonal AC} = \sqrt{2}a = 2R$$

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

Triangle ACD -

$$AD^2 = AC^2 + CD^2$$

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

$$AD = \sqrt{3}a$$

According to cube diagonal AD

$$\therefore \frac{\sqrt{3}a}{2} = r + R$$

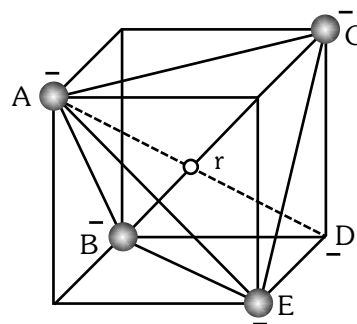
$$\therefore \sqrt{3}a = 2r + 2R = AD$$

Put the value of $a = \sqrt{2}R$

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

$$\frac{\sqrt{3} \times \sqrt{2}R}{2R} = \frac{2r + 2R}{2R} \quad \text{or} \quad \frac{\sqrt{3}}{\sqrt{2}} = \frac{r}{R} + 1$$

$$\frac{r}{R} = \frac{\sqrt{3}}{\sqrt{2}} - 1 = \frac{\sqrt{3} - \sqrt{2}}{\sqrt{2}} = \frac{1.73 - 1.414}{1.414} = 0.225$$



(c) Octahedral void : All the anions are touch each other and co-ordination number is 6.

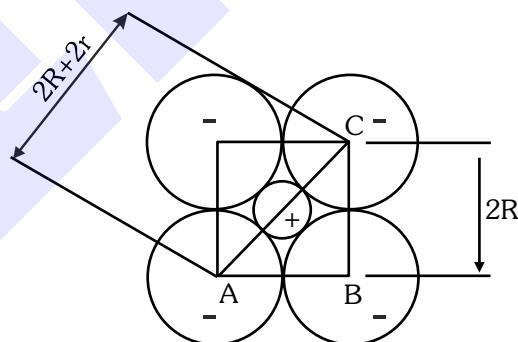
$$\begin{aligned} \text{In } \triangle ABC \quad AC^2 &= AB^2 + BC^2 \\ (2R + 2r)^2 &= (2R)^2 + (2R)^2 \end{aligned}$$

$$(2R + 2r) = \sqrt{8R^2}$$

$$2R + 2r = 2\sqrt{2}R$$

$$2R(\sqrt{2} - 1) = 2r$$

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



(d) Cubic void : All the anions are touch each other and co-ordination number is 8.

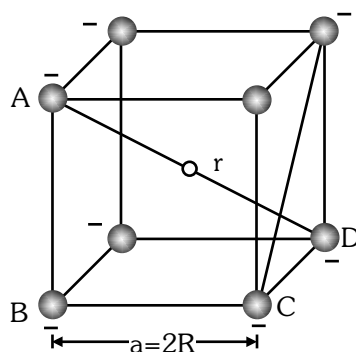
According to cube diagonal

$$AD = \sqrt{3}a = 2r + 2R \quad (a = 2R = BC)$$

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

Dividing by 2r on both sides.

$$\sqrt{3} = \frac{r}{R} + 1 \Rightarrow \frac{r}{R} = \sqrt{3} - 1 = 1.732 - 1 = 0.732$$



GOLDEN KEY POINTS

- The preferred direction of the structure with increase in the radius ratio is as follows :

Plane triangular $\xrightarrow{0.225}$ Tetrahedral $\xrightarrow{0.414}$ octahedral $\xrightarrow{0.732}$ Cubic

- LIMITING RADIUS RATIO FOR VARIOUS TYPES OF VOIDS**

Limiting radius ratio = r/R	Coordination Number	Structural Arrangement (Type of voids)	Example
$0.155 \leq r/R < 0.225$	3	Plane Trigonal	Boron Oxide(B_2O_3)
$0.225 \leq r/R < 0.414$	4	Tetrahedral	ZnS, SiO_2
$0.414 \leq r/R < 0.732$	6	Octahedral	NaCl, MgO
$0.732 \leq r/R < 1.000$	8	Cubical	CsCl

Illustrations

Illustration11. Each unit cell of NaCl consists of 14 Cl^- ions and

- (1) 13 Na^+ (2) 14 Na^+
(3) 6 Na^+ (4) All are wrong

Solution. **Ans. (1)**

Illustration12. A solid A^+B^- has NaCl type close packed structure. If the anion has a radius of 250 pm, what should be the ideal radius for the cation ? Can a cation C^+ having a radius of 180 pm be slipped into the tetrahedral site of the crystal A^+B^- ? Give reason for your answer.

Solution In Na^+Cl^- crystal each Na^+ ion is surrounded by 6 Cl^- ions and vice versa. Thus Na^+ ion is placed in octahedral hole.

The limiting radius ratio for octahedral site = 0.414 or $\frac{A^+}{B^-} = \frac{r}{R} = 0.414$

Given that radius of anion (B^-) $R = 250$ pm

i.e. radius of cation (A^+) $r = 0.414 R = 0.414 \times 250$ pm = 103.5 pm

Thus ideal radius for cation (A^+) is $r = 103.5$ pm.

We know that (r/R) for tetrahedral hole is 0.225.

$\therefore \frac{r}{R} = 0.225$: So $r = 56.25$ pm

Thus ideal radius for cation is 56.25 pm for tetrahedral hole. But the radius of C^+ is 180 pm. It is much larger than ideal radius i.e. 56.25 pm. Therefore we can not slipped cation C^+ into the tetrahedral site.

1.11 SOME IONIC CRYSTALS

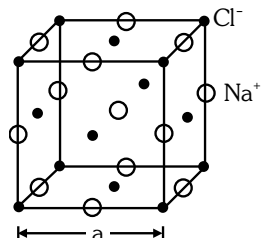
S. No.	Type of Ionic Crystal	Geometry	Co-ordination Number	No. of formula's per U.C.	Examples
1.	NaCl (1 : 1) (Rock Salt Type)	$\text{Na}^+ \rightarrow \text{At every OHV}$ C.C.P. \angle $\text{Cl}^- \rightarrow \text{Every element of C.C.P.}$	6:6	$4\text{Na}^+ + 4\text{Cl}^-$ 4NaCl (4)	Halides of (Li, Na, K, Rb) Oxides and sulphides of alkaline, earth metals (Except BeS) AgCl, AgBr, NH_4X
2.	CsCl Type (1 : 1)	$\text{Cs}^+ \rightarrow \text{At body centre of}$ B.C.C. \angle type $\text{Cl}^- \rightarrow \text{At every corner}$	8:8	$1\text{Cs}^+ + 1\text{Cl}^-$ 1CsCl (1)	Halides of 'Cs' TlCl, TlBr, CsS
3.	ZnS Type (1 : 1) (Zinc Blende Type) (Sphalerite)	$\text{Zn}^{+2} \rightarrow \text{At 50\% of T.H.V. or}$ C.C.P. \angle type at alternate tetrahedral void $\text{S}^{2-} \rightarrow \text{Every element of C.C.P.}$	4:4	$4\text{Zn}^{+2} + 4\text{S}^{2-}$ 4ZnS (4)	BeS, BeO, CaO, AgI, CuCl, CuBr, CuI
4.	CaF_2 Type (1 : 2) Fluorite Type	$\text{Ca}^{+2} \rightarrow \text{Every element of C.C.P.}$ C.C.P. \angle type $\text{F}^- \rightarrow \text{At every T.H.V.}$	$4\text{Ca}^{+2}, 8\text{F}^-$ $8 : 4$	$4\text{Ca}^{+2} + 8\text{F}^-$ 4CaF_2 (4)	BaCl ₂ , BaF SrCl ₂ , SrF ₂ CaCl ₂ , CaF ₂
5.	Na_2O Type (2 : 1) (Antifluorite)	$\text{Na}^+ \rightarrow \text{At every T.H.V.}$ C.C.P. \angle type $\text{O}^{2-} \rightarrow \text{Every element of C.C.P.}$	$8\text{Na}^+, 4\text{O}^{2-}$ $4 : 8$	$8\text{Na}^+ + 4\text{O}^{2-}$ $4\text{Na}_2\text{O}$ (4)	Li ₂ O, Li ₂ S Na ₂ O, Na ₂ S K ₂ O, K ₂ S
6.	ZnS Type (1 : 1) (Wurtzite) another geometry of ZnS	$\text{Zn}^{+2} \rightarrow 50\% \text{ of T.H.V. or}$ H.C.P. \angle type (at alternate T.H.V.) $\text{S}^{2-} \rightarrow \text{Every element of H.C.P.}$	4 : 4	$6\text{Zn}^{+2} + 6\text{S}^{2-}$ 6ZnS (6)	Same as sphalerite

● **NaCl TYPE**

For NaCl :

Distance between two nearest ions ($r^+ + r^-$) :-

$$2r^+ + 2r^- = a \quad \text{i.e.} \quad r^+ + r^- = \frac{a}{2}$$

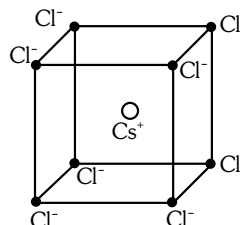


CsCl TYPE

For CsCl :

Distance between two nearest ions ($r^+ + r^-$) :-

$$2r^+ + 2r^- = \sqrt{3}a \quad \text{i.e.} \quad r^+ + r^- = \frac{\sqrt{3}}{2}a$$

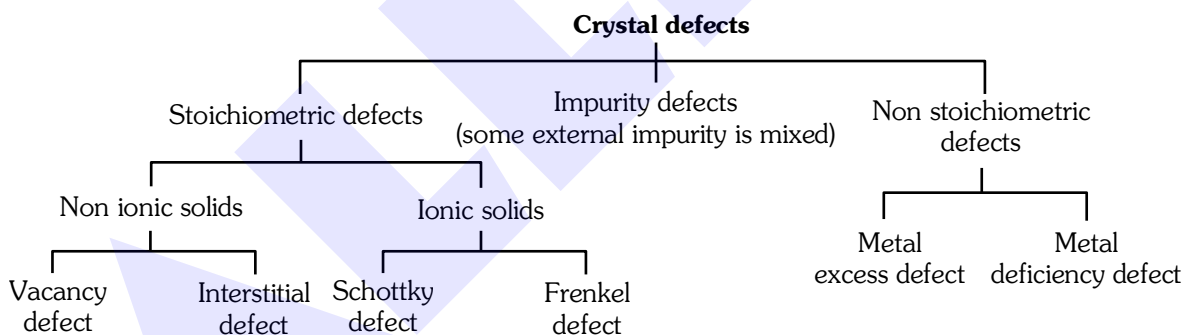


In both structures cation and anion can exchange their position.

1.12 DEFECTS OR IMPERFECTIONS IN SOLIDS

Ideal crystal : The crystal in which all the lattice points are occupied by the component particles or groups of particles is called an ideal crystal. Ideal crystals are grown up at absolute kelvin temperature (zero K).

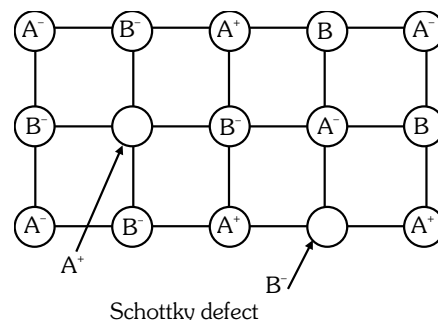
Solid state is characterised by vibratory motion about the mean position of constituent particles. At absolute zero, all the types of motions cease, and therefore crystals tend to have a perfectly ordered arrangement. As the temperature increases, molecular motions (vibratory amplitudes) increase and therefore the ions may lose their usual sites and either get missed or occupy interstitial positions in the crystal, i.e., deviations from ordered arrangement take place. Any deviation from the perfectly ordered arrangement gives rise to a defect or imperfection in the crystal. Defect in crystals are produced either due to thermal effects or by adding certain impurities in the pure crystals (doping). Defects in crystals are of mainly two types. (1) **Point defects** are irregularities or deviations from ideal arrangement around a point or an atom in a crystalline substance. (2) **Line defects** are irregularities or deviations from ideal arrangement in entire rows of lattice points. We discuss mainly about point defects.



(A) Stoichiometric Defects

These are point defects that do not disturb stoichiometry of solid. Also called as intrinsic or thermodynamic defects.

- (a) **Vacancy defect :** Some lattice sites are vacant. As a result density of solid decreases. This defect can also develop when a substance is heated.
- (b) **Interstitial defect :** When constituent particles (atoms or molecules) occupy interstitial site. As a result density of substance increases. Ionic solids show these defects as Schottky & Frenkel defects.
- (c) **Schottky defect :** This type of defect is produced when equal number of cations and anions are missing from their respective positions leaving behind a pair of holes. The crystal as a whole remains neutral because the number of missing positive ions (cations) and negative ions (anions) is the same

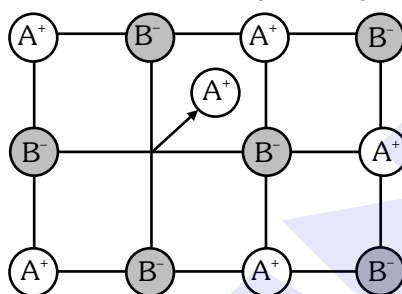


- It is kind of vacancy defect.
- Schottky defect appears generally in ionic compounds in which radius ratio $[r^+/r^-]$ is not far below unity. For this defect, the cations and anion should not differ much in size.
- For schottky defect, co-ordination numbers of the ions should be high, Examples of ionic solids showing this defect are NaCl, CsCl, KCl, AgBr etc.

Consequences of schottky defect :

- Density of the crystal decreases
- The crystal begins to conduct electricity to small extent by ionic mechanism.
- The presence of too many 'voids' lowers lattice energy or the stability of the crystal.

- (d) **Frenkel defect :** This type of defect is created when an ion leaves its appropriate site in the lattice and occupies an interstitial site. A hole or vacancy is thus produced in the lattice.



Frenkel defect

The electroneutrality of the crystal is maintained since the number of positive and negative ions is the same. Since positive ions are small, in size, they usually leave their positions in the lattice and occupy interstitial positions. It is also called dislocation defect.

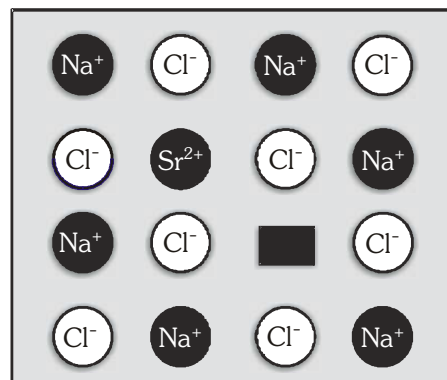
Frenkel defect is exhibited in ionic compounds in which the radius ratio $[r^+/r^-]$ is low. The cations and anions differ much in their sizes and the ions have low co-ordination numbers. Examples are ZnS, AgBr, AgI, AgCl.

Consequences of Frenkel defect :

- It is a kind of dislocation defect.
- The closeness of like charges tends to increase the dielectric constant of the crystal.
- The crystal showing a frenkel defect conducts electricity to a small extent by ionic mechanism.
- The density of the crystal remains the same.

(B) Impurity Defect

If molten NaCl containing a little amount of SrCl_2 is crystallised, some of the sites of Na^+ ions are occupied by Sr^{2+} . Each Sr^{2+} replaces two Na^+ ions. It occupies the site of one ion and the other site remains vacant. The cationic vacancies thus produced are equal in number to that of Sr^{2+} ions. Another similar example is the solid solution of CdCl_2 and AgCl.


 Induction of cation vacancy in NaCl by substitution of Na^+ by Sr^{2+}
(C) Non-stoichiometric Defects

These types of defects are observed in the compounds of transitional elements. These defects arise either due to the presence of excess metal ions or excess non-metal ions.

(a) **Metal excess defect due to anion vacancies** : A compound may have excess metal ion if an anion (negative ion) is absent from its appropriate lattice site creating a 'void' which is occupied by an electron. Ionic crystal which are likely to possess Schottky defect, may also develop this type of metal excess defect. When alkali metal halides are heated in an atmosphere of vapours of the alkali metal, anion vacancies are created. The anions (halide ions) diffuse to the surface of the crystal from their appropriate lattice sites to combine with the newly generated metal cations. The e^- lost by the metal atom diffuse through the crystal are known as F-centres. The main consequence of metal excess defect is the development of colour in the crystal. For example, when NaCl crystal is heated in an atmosphere of Na vapours, it becomes yellow.

Similarly, KCl crystal when heated in an atmosphere of potassium vapours, it appears violet.

(b) **Metal excess defect due to interstitial cations** : This type of defect is shown by crystals which are likely to exhibit Frenkel defect. An excess positive ion is located in the interstitial site. To maintain electrical neutrality, an electron is present in the interstitial site. An example showing this type of defect is ZnO. When ZnO is heated, it loses oxygen $\text{ZnO} \xrightarrow{\text{On heating}} \text{Zn}^{+2} + \frac{1}{2} \text{O}_2 \text{ gas}$. The excess Zn^{++} ions are accommodated in the interstitial sites, the electrons are enclosed in the neighbouring interstitials. The yellow colour of ZnO when hot is due to these trapped electrons. These electrons also explain electrical conductivity of the ZnO crystal.

(c) **Metal Deficiency Defect**

There are many solids which are difficult to prepare in the stoichiometric composition and contain less amount of the metal as compared to the stoichiometric proportion. A typical example of this type is FeO which is mostly found with a composition of $\text{Fe}_{0.95}\text{O}$. It may actually range from $\text{Fe}_{0.93}\text{O}$ to $\text{Fe}_{0.96}\text{O}$. In crystals of FeO some Fe^{2+} cations are missing and the loss of positive charge is made up by the presence of required number of Fe^{3+} ions.

GOLDEN KEY POINTS

- On increasing temperature coordination number decreases.
- On increasing pressure; coordination number increases.
- If in a crystal complete lattice of ion along a line are disappeared, such defect is called line defect.
- Schottky defects and Frenkel defects are point defects.
- **Structure of diamond** : Solids which follow the structure of diamonds known as diamond cubic. Diamond has CCP structure where carbon atoms are present at corners and face centre with four more atoms present at alternate tetrahedral voids or 50% THV so number of effective atoms

$$Z = \left(8 \times \frac{1}{8} + 6 \times \frac{1}{2} \right) + (4 \times 2) \times \frac{1}{2} = 8.$$

The carbon atoms present in THV touch their four surrounding atoms so coordination number is equal to four.

$$2r = \frac{\sqrt{3}}{4} a ; a = \frac{8r}{\sqrt{3}} ; \text{PE} = \frac{8 \times \frac{4\pi}{3} r^3}{\left(\frac{8r}{\sqrt{3}} \right)^3} = 0.34 ; \text{So \% PE} = 34$$

Illustrations

Illustration 13. In the Schottky defect

- (1) cations are missing from the lattice sites and occupy the interstitial sites
- (2) equal number of cations and anions are missing
- (3) anions are missing and electrons are present in their place
- (4) equal number of extra cations and electrons are present in the interstitial sites

Solution

Ans. (2)

Illustration 14. Schottky defect lowers the density of ionic crystals while Frenkel defect does not. Discuss.

Solution.

In Schottky defect, certain cations and anions are missing from the crystal lattice. Therefore, the density of the crystal decreases. However, in Frenkel defect the ions do not leave the lattice but they simply change their positions from lattice points to the interstitial spaces. As a result, the density of the crystal remains unchanged.

BEGINNER'S BOX-2

1. The edge length of face centred cubic unit cell having rock salt structure is 508 pm. If the radius of the cation is 110 pm, the radius of the anion is—
 (1) 144 pm (2) 288 pm (3) 618 pm (4) 398 pm
2. In a solid 'AB' having the NaCl structure, 'A' atoms are arranged in CCP and B atoms are in OHV. If all the face-centred atoms along one of the axes are removed, then the resultant stoichiometry of the solid is—
 (1) AB_2 (2) A_2B (3) A_4B_3 (4) A_3B_4
3. How many unit cells are present in a cube shaped ideal crystal of NaCl of mass 1.00 g ?
 [Atomic mass : Na = 23, Cl = 35.5]
 (1) 5.14×10^{21} (2) 1.28×10^{21} (3) 1.71×10^{21} (4) 2.57×10^{21}
4. A solid AB has the NaCl structure. If radius of the cation A^+ is 120 pm, the maximum value of the radius of the anion B^- is
 (1) 290 pm (2) 350 pm (3) 250 pm (4) 400 pm
5. If the distance between Na^+ and Cl^- ions in sodium chloride crystal is x pm, then length of the edge of the unit cell is
 (1) 2x pm (2) 4x pm (3) x/2 pm (4) x/4 pm
6. HCP crystal is made of A ions and B ions are arranged in $2/3^{rd}$ of octahedral voids. The simplest formula of compound is
 (1) A_4B_6 (2) A_6B_4 (3) A_2B_3 (4) A_3B_2
7. A FCC crystal of O^{2-} (oxide) ions has M^{n+} ions in 50% of octahedral voids, then the value of n is
 (1) 2 (2) 3 (3) 4 (4) 1
8. If the edge length of a KCl unit cell is 488 pm, what is the length of KCl bond if it crystallises in the FCC structure ?
 (1) 122 pm (2) 244 pm (3) 488 pm (4) 974 pm
9. In a solid lattice, the cation has left a lattice site and is located at interstitial position, the lattice defect is
 (1) interstitial defect (2) vacancy defect (3) Frenkel defect (4) Schottky defect

ANSWER'S KEY

BEGINNER'S BOX-1	Que.	1	2	3	4	5				
	Ans.	3	2	2	4	1				

BEGINNER'S BOX-2	Que.	1	2	3	4	5	6	7	8	9	
	Ans.	1	4	4	1	1	4	3	2	3	