

SOLID STATE

SOLIDS

Solids are characterised by the state of matter in which particles are closely packed and held together by strong inter molecular attractive force.

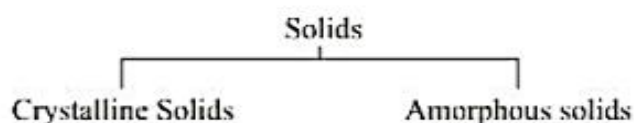
Properties of solids

- (a) In solid state the particles are not able to move randomly.
- (b) They have definite shape and volume.
- (c) Solids have high density.
- (d) Solids have high and sharp melting point which depends on the strength or value of binding energy.
- (e) They are very low compressible.
- (f) They show very slow diffusion.

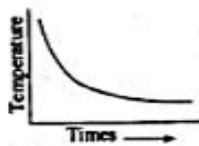
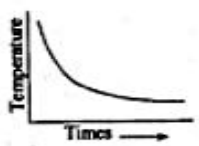


Can you guess which type of kinetic energy will be more dominant in solids, Rotational, translational or vibrational?

Types of Solids



Difference between crystalline and amorphous solids

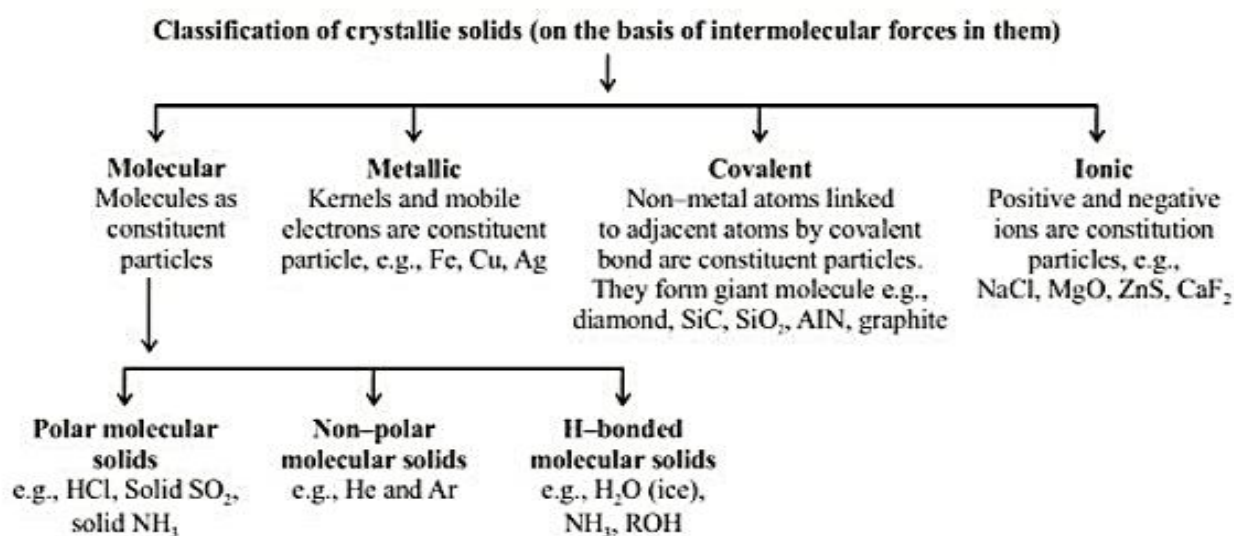
S.N.	Property	Crystalline solids	Amorphous solids
1	Shape	They have definite and regular geometrical form.	They do not have definite and regular geometrical form.
2	Melting point	They have definite melting point.	They do not have definite melting point.
3	Heat of fusion	They have a definite heat of fusion.	They do not have definite heat of fusion
4	Compressibility	They are rigid and incompressible.	These may be compressed to any appreciable extent.
5	Cutting with a Sharp edged tool	They give clean cleavage i.e. they break into two pieces with plane surfaces. 	They give irregular cleavage i.e. they break into two pieces with irregular surface. 
6	Isotropy and Anisotropy	They are anisotropic.	They are isotropic.
7	Physical state	True solids	pseudo solids and are considered as super cooled liquid.
	Examples	Quartz, Diamond	Rubber, Plastic



CLASSIFICATION OF CRYSTALS

According to attractive force which hold crystal together are generally of five types and thus crystal can be classified into four types:

Type of Solid	Intermolecular forces	Properties	Examples
Ionic	Ion-Ion forces	Brittle, hard, high Melting point Insulator in solid but conductance fused and aqueous solution	NaCl, KCl, $MgCl_2$
Molecular	Dispersion forces/Dipole-Dipole /H-bond	Soft, low melting point, Insulators	H_2O , Br_2 , CO_2 , CH_4
Covalent or network	Covalent bonds	Hard, Very high melting point	C-Diamond, SiO_2
Metallic	Metallic bonds	Variable hardness and melting point, malleable and ductile, conducting	Na, Zn, Cu, Fe



It is advisable that students should memories one or two examples of each type of crystalline solids.

Type of Symmetry in Crystals

- a. **Law of symmetry** : It states that all crystals of a substance possess the same element of symmetry. Three important elements of symmetry are :
- I. Plane of symmetry II. Axis of symmetry III. Center of symmetry



b. The total number of elements of a symmetry in a cubic crystal = 23

I. Plane of symmetry = 3 (rectangular plane of symmetry)
+ 6 (diagonal plane of symmetry) = 9

II. Axis of symmetry = 3 (four-fold or a tetrad axis of symmetry)
+ 4 (three-fold or a triad axis of symmetry)
+ 6 (two-fold or diad axis of symmetry) = 13

III. Center of symmetry or inversion of symmetry = 1

\therefore Total number of elements of symmetry in a cubic crystals = $9 + 13 + 1 = 23$



Axis of six-fold or a hexed axis of symmetry : This type of symmetry is possible in hexagonal crystals and not in cubic crystals.

STUDY OF CYRSTALS

Crystal - A crystal is a homogenous portion of a solid substance made by regular pattern of structural units bonded by plane surface making definite angles with each other.

Space lattice - The arrangement of constituents like atom, ions and molecules in different sites in three dimensional space is called space lattice.

Unit cell - The smallest repeating unit in space lattice which when repeats over and over again, results in a crystal of the given substance called unit cell.

Face - The plane surface of the crystal are called faces.

Edge - An edge is formed by the intersection of two adjacent faces.

Interfacial angle - The angle between two perpendicular intersecting faces is called interfacial angles.

CRYSTAL SYSTEM

Bravais showed that there are only seven types of crystal system.

These are -

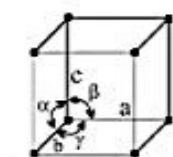
- | | |
|------------------|------------------|
| (a) Cubic | (b) Tetragonal |
| (c) Orthorhombic | (d) Rhombohedral |
| (e) Hexagonal | (f) Monoclinic |
| (g) Triclinic | |

	Crystal Systems	Bravais Lattice	Unit Cell Parameters		Example
			Intercepts	Crystal Angles	
1	Cubic	Primitive, Face Centered, Body Centered	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	NaCl, Zinc blend, Cu
2	Orthorhombic	Primitive, Face Centered, Body Centered, End Centered	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Rhombic sulphur, KNO_3 , BaSO_4
3	Tetragonal	Primitive, Body Centered	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	White tin, SnO_2 , TiO_2 , CaSO_4
4	Monoclinic	Primitive, End Centered	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$	Monoclinic sulphur, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
5	Rhombohedral or Trigonal	Primitive	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	Calcite (CaCO_3), HgS (Cinnabar)
6	Triclinic	Primitive	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	$\text{K}_2\text{Cr}_2\text{O}_7$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, H_3BO_3
7	Hexagonal	Primitive	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	Graphite, ZnO, CdS

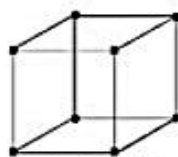


Students should memories all the cell parameters for each type of crystal systems. Remembering examples for each type is not required except for very common substances like NaCl, Graphite etc.

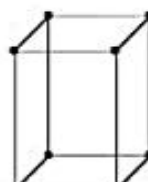
SEVEN CRYSTAL SYSTEM



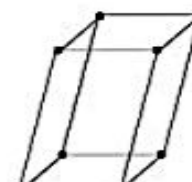
Simple Cubic
 $a = b = c$
 $\alpha = \beta = \gamma = 90^\circ$



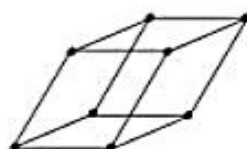
Orthorhombic
 $a \neq b \neq c$
 $\alpha = \beta = \gamma = 90^\circ$



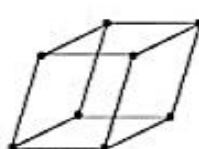
Tetragonal
 $a = b \neq c$
 $\alpha = \beta = \gamma = 90^\circ$



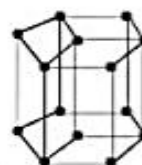
Monoclinic
 $a \neq b \neq c$
 $\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$



Rhombohedral
 $a = b = c$
 $\alpha = \beta = \gamma \neq 90^\circ$



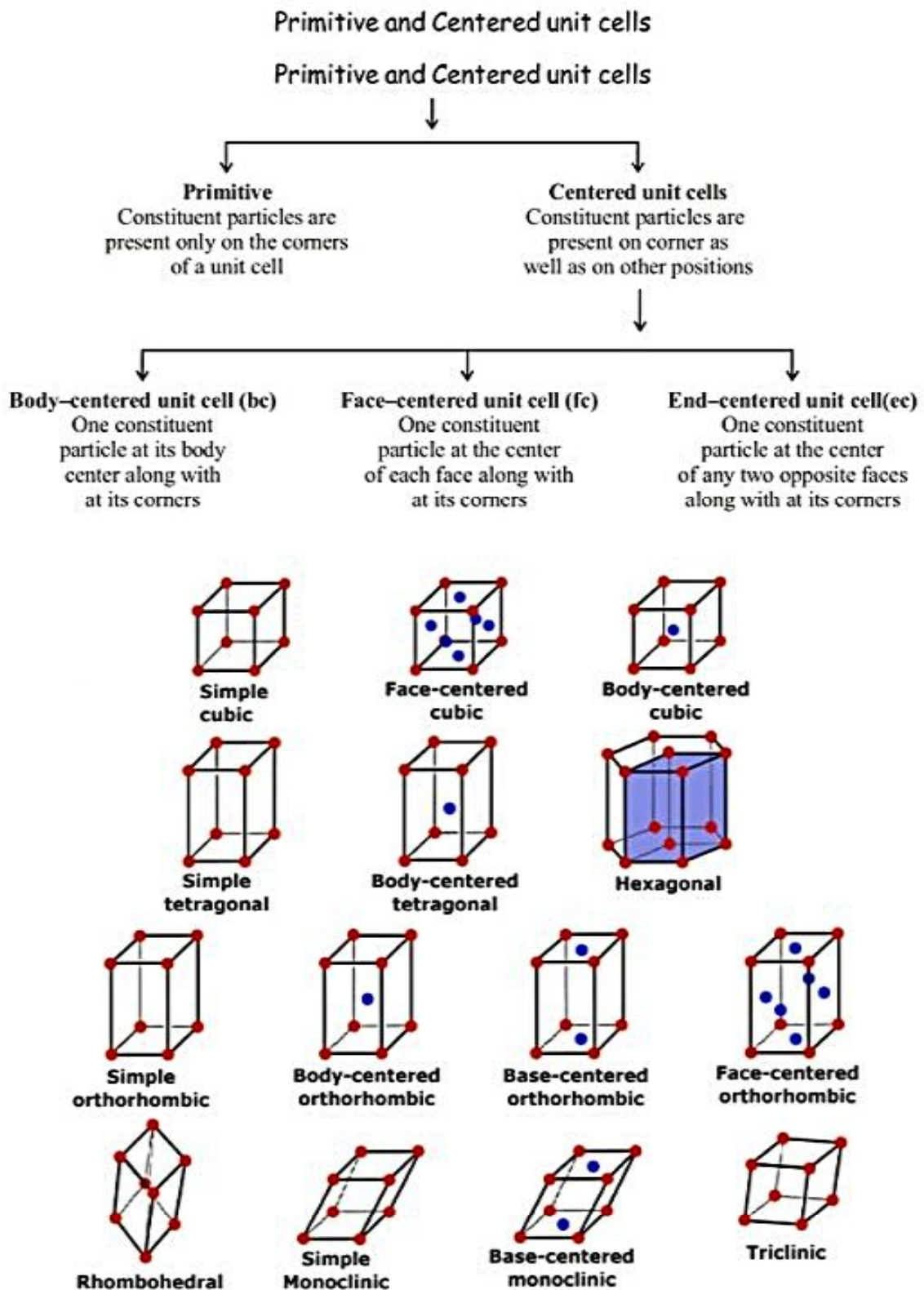
Triclinic
 $a \neq b \neq c$
 $\alpha \neq \beta \neq \gamma \neq 90^\circ$



Hexagonal Primitive
 $a = b \neq c$
 $\alpha = \beta = 90^\circ, \gamma = 120^\circ$



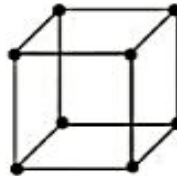
Although there are only 7 crystal systems or shapes, there are 14 different crystal lattices, called Bravais Lattices. (3 different cubic types, 2 different tetragonal types, 4 different orthorhombic types, 2 different monoclinic types, 1 rhombohedral, 1 hexagonal, 1 triclinic).



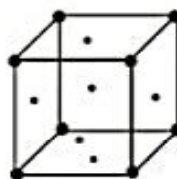
TYPES OF UNIT CELLS

There are four types of unit cells (among the cubic system).

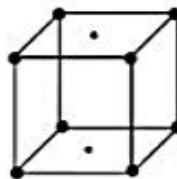
- (a) Simple or primitive. Particles are only at the corners of the unit cell.



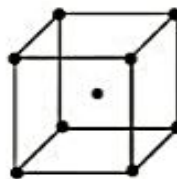
- (b) Face-centered cubic unit cell. In addition to corners, particles are present at the centre of each face of the unit cell.



- (c) End-face-centered cubic unit cell. A particle is present at each corner plus particles are present on the end faces of the unit cell.



- (d) Body-centered cubic unit cell. In addition to the particles at the corners, there is one particle in the body-centre of the unit cell.



Coordination Number

If atoms are represented by spheres, the number of spheres which are touching a particular sphere is called *coordination number* of that sphere. In ionic crystals, the coordination number may be defined as the number of the oppositely charged ions surrounding a particular ion.

The number of particles per Unit Cell

- (a) An atom at the corner is shared by 8 unit cells. Therefore, its contribution is $= 1/8$.
 (b) An atom at the face is shared by 2 unit cells. Therefore, its contribution is $= 1/2$.
 (c) An atom present in the body is unshared. Therefore, its contribution is 1.
 (d) An atom present on the edge is shared by four unit cells. Therefore, its contribution is $= 1/4$.

Thus, in

- (e) a primitive or simple cubic unit cell, the total number of particles is $1/8 \times 8 = 1$.
 (f) a face-centred cubic unit cell, the total number of particles is $1/8 \times 8 + 1/2 \times 6 = 4$.
 (g) a body-centred cubic unit cell, the total number of particles is $1/8 \times 8 + 1 = 2$.

The number of atoms per unit cell are in the same ratio as the stoichiometry of the compound or the ratio of the number of particles A and B present per unit cell gives the formula of the compound formed between A and B

Illustration

1. A compound formed by elements X and Y crystallises in the cubic structure, where Y atoms are at the corners of the cube and X atoms are at the alternate faces. What is the formula of the compound?

Sol. Y atoms are at the corners of the cubic unit cell and contribution of each is = $1/8$. So, the total number of Y atoms per unit cell = $8 \times 1/8 = 1$. X atoms are on alternate faces and contribution of each = $1/2$. So, the number of X atoms per unit cell is $2 \times 1/2 = 1$. Hence, the formula is XY.

2. Calculate the number of atoms in a cubic unit cell having one atom on each corner and two atoms on each body diagonal.

Sol. Atoms at the corner contribute $1/8$ and so the total number of corner atoms per unit cell is equal to one. Now, there would be four body diagonals in a cube and each diagonal has 2 atoms not shared by any other unit cell. So, there are total 8 atoms within the body of the unit cell and the total number of atoms per unit cell would be nine.

Exercise

1. In a solid 'AB' having NaCl structure atoms, occupy the corners of the unit cell. If all the face centred atoms along one of the axis are removed, then the resultant stoichiometry of the solid is-

(A) AB_2 (B) A_2B (C) A_4B_3 (D) A_3B_4

Ans. (C)

Packing of Constituent Particles in Crystals

The structure of crystalline solids is determined by the packing of their constituents. During formation, the constituent particles get closely packed together. The available space is most economically used and a state of maximum possible density is reached. The various modes of packing are considered by assuming the particles to be spherical. The arrangement should be such that the spheres should occupy maximum available space.

The packing of spheres takes place as follows:

1. When the spheres are placed in a horizontal row touching each other in such a way that the rows have a horizontal as well as vertical alignment, the spheres are found to form a square. This is called square close packing (Figure 1(a))



Figure I(a)

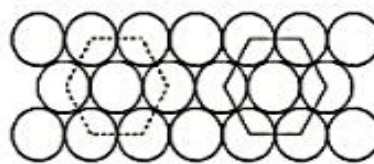


Figure I(b)

2. When the spheres are packed in such a way that the spheres in every second row are placed in the depressions between the spheres of the first row and in the third row the spheres are vertically aligned with spheres in the first row, a hexagonal close packing is obtained, since the packing of this type gives a hexagonal pattern. (Figure I (b)).

A comparison of the two ways of packing of spheres shows that in arrangement (i) the spheres are less closely packed than in arrangement (ii). It has been calculated that in arrangement (i) only 78.54% of the available space is occupied by the spheres. In the second arrangement, 90.7% of the space is occupied. Thus, arrangement (ii) is more economical and, therefore, it represents a close packing of spheres. It can be seen that in arrangement (i) each sphere is in contact with four other spheres.

On the other hand, in arrangement (ii), each sphere is in contact with six other similar spheres.

Thus, arrangement (ii) represents an efficient closest packing of spheres in a layer. We can now build other layers over the first layer to extend the packing in three dimensions. Let us mark the spheres in the first layer as A. It is clear from the following figure II(a) and figure II(b) that there are two types of voids (hollows) in the first layer. These are marked as *a* and *b*.

Now, if a second layer is placed with spheres vertically aligned with those in the first layer, its voids will come above the voids in the first layer and this would again be an inefficient way of filling the space. Obviously, for the second layer, the spheres are to be placed in either of the voids.

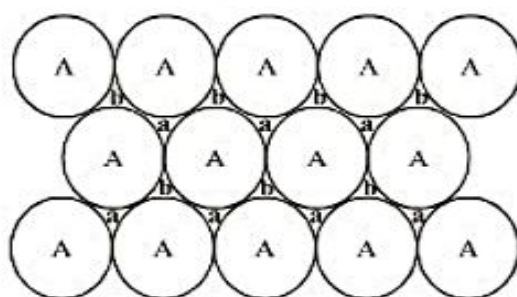
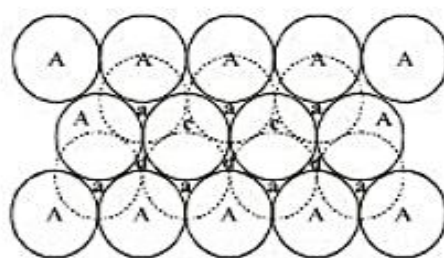


Figure II(a)

All the voids are equivalent, but the spheres of the second layer may be placed either on the voids marked '*a*' or on the other set of voids marked '*b*'. It may be noted that it is not possible to place spheres on both types of voids.

Let us place the spheres on hollows marked '*a*' to make the second layer which may be labelled as '*B*' layer. Obviously, the holes marked '*b*' remain unoccupied while building the second layer. The second layer is indicated in the following figure.

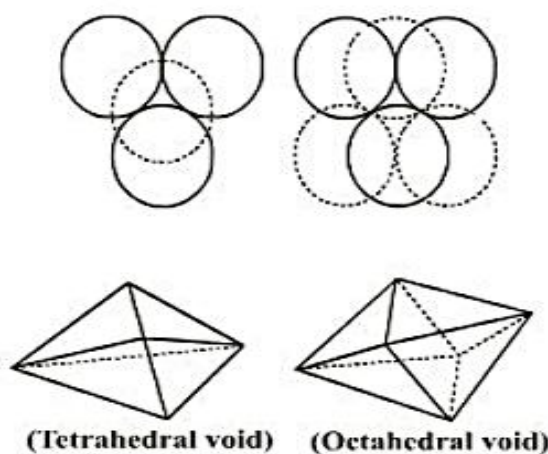


Solid circles represent layer A
Dotted circles represent layer B
Figure II (b)

Now, there are two types of voids in the second layer. These are marked as 'c' and 'd'. The voids 'c' (of the second layer) 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 second of the second layer.

The 'a' and 'b' voids of the first layer are both triangular whereas only 'c' voids of the second layer are triangular. The 'd' voids of the second layer which are a combination of two triangular voids (one each of first and second layer) with the vertex of one triangle upwards and the vertex of other triangle downwards.

A simple triangular void in a crystal is surrounded by four spheres and is called a tetrahedral void or a hole. A double triangular void like 'd' is surrounded by six spheres and is called an octahedral void.



Now, there are two ways of building a third layer.

- (i) When a third layer is placed over the second in such a way that the spheres cover the tetrahedral or 'c' voids, a three dimensional closest packing is obtained, where the spheres in every third layer or alternate layers are vertically aligned. The arrangement is called ABAB pattern or hexagonal close packing (hcp). Mo, Mg, Zn, Cd, Be, etc. have an hcp structure.
- (ii) If the third layer is placed over the second layer in such a way that the spheres cover the octahedral or 'd' voids, a different layer 'C' is formed. In this case, every fourth layer will be vertically aligned. This arrangement is called ABCABC..... pattern or cubic close packing (ccp) Fe, Ni, Cu, Ag, Au, Pt etc. have a ccp structure.

These two arrangements are depicted in figures III and IV. Both hcp and ccp arrangements of packing are equally efficient. In these patterns, the maximum possible space (74% of the available volume) is occupied. Only 26% of the space remains empty. That is why these are referred to as close packings.

In both hcp and ccp, a sphere is in contact with 6 others in its own layer and three spheres in the layer above and three spheres in the layer below. The coordination number is 12 in both the patterns.

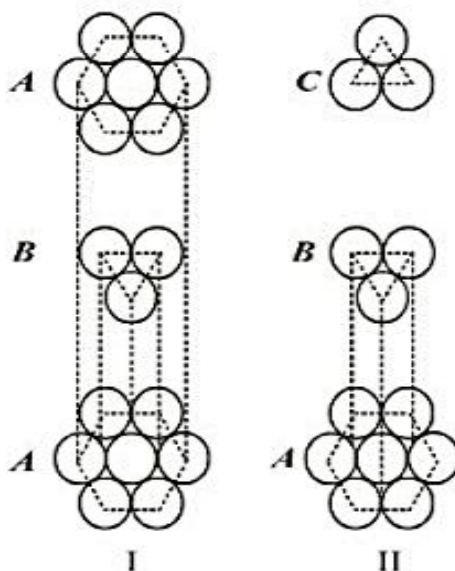
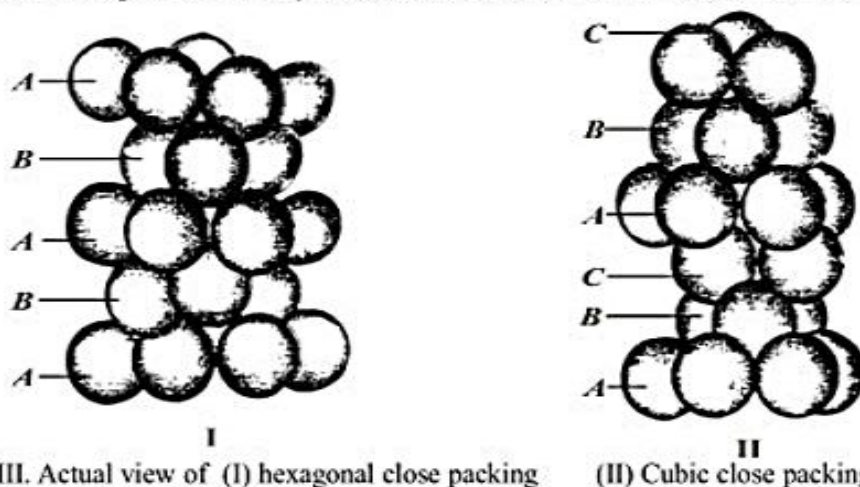


Figure IV. Simplified view of (I) Hexagonal close packing (AB AB....pattern)
(II) Cubic close packing (ABC ABC.... pattern)

In addition to these two types of close packings, a third type of arrangement is found in metals. It is body-centered cubic packing (bcc). This is found in metals like Li, Na, K, Rb, and Cs. In this packing, the spheres are opened up and not touching. 'B' is placed on 'A'. The building of third layer is exactly like the first. The coordination number is 8 and 68% of volume is occupied.



It is seen that even in closely packed spheres and most efficient arrangements, certain hollows are left vacant. These holes or voids are called *interstitial sites*. Two important interstitial sites are (a) tetrahedral voids and (b) octahedral voids.

The voids are not tetrahedral or octahedral but the arrangement around it is such that if the spheres are arranged in the voids, the geometric figure generated is like that.

1. In the closest packed system for each sphere, there are two tetrahedral voids and only one octahedral void. The two tetrahedral voids are present above and below each atom and octahedral void is midway between two closely packed layers.
2. In ionic crystals, it is not possible for both cations and anions to have a close packed structure due to their different sizes. However, it is common for the bigger ion (usually anions) alone to approach a close-packed structure and smaller ions to fit into voids in the structure. The radii of interstitial sites that is, the voids in these close-packed structures are related to the sizes of the spheres present in them. If 'R' is the radius of the spheres in the close-packed structures, then

Radius (r) of tetrahedral void = 0.225 R

Radius (r) of octahedral void = 0.414 R.

Therefore, the limiting size of cations which can fill voids without disturbing the closest packing is for

octahedral void = $r_c/r_a = 0.414$, tetrahedral void = $r_c/r_a = 0.225$, and for cubic voids $r_c/r_a = 0.732$

where r_c = radius of cation and r_a = radius of anion.

3. In a close-packed arrangement hcp or ccp, the number of octahedral voids are equal to the number of atoms present in the close-packed arrangement and the number of tetrahedral voids are equal to 2x (number of octahedral voids) and consequently are equal to 2x (number of atoms).

Illustration

1. The packing fraction in fcc and hcp structure is same. Moreover, this is the highest packing fraction of all the possible unit cells with same atoms. Can you explain this?

Sol. The arrangement of atoms in hcp is of ABABAB ... type and in case of fcc is of ABCABCABC... type. Both in hcp and fcc, the layers are formed of same atoms in similar arrangement but the only difference is the placement of layers on top of each other. Hence, both have same packing fraction.

In both the arrangement, the number of atom of same size present around the atom is maximum, i.e., 6. So, the packing fraction is highest.

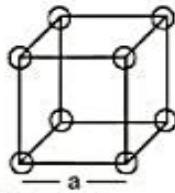
Exercise

1. A compound formed by elements A and B crystallizes in the cubic structure where A atoms are at the corners of a cube and B atoms are at the face centres. The formula of the compound is
(A) AB_3 (B) AB (C) A_3B (D) A_2B_2

Ans. (A)

CALCULATION OF PACKING FRACTIONS

- (i) Consider a simple cubic unit cell. Suppose the edge length of the cell is a and the radius of the sphere is r . As the spheres are touching each other, $a = 2r$.



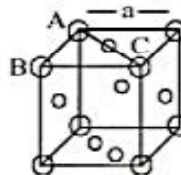
Number of spheres per unit cell = $1/8 \times 8 = 1.0$

Volume of the sphere = $\frac{4}{3} \pi r^3$

Volume of the cube = $a^3 = (2r)^3 = 8r^3$

Packing fraction = $\frac{\frac{4}{3} \pi r^3}{8r^3} = 0.524$ or 52.4 percent occupied.

- (ii) In a face-centred cubic structure.
Spheres on the face are in contact (touching) whereas the one at corners are not touching each other.



Therefore, $AC = 4r$

Also $AC = \sqrt{AB^2 + BC^2}$ (since ABC is right angled triangle)

$$AC = \sqrt{a^2 + a^2}$$

$$AC = \sqrt{2}a = 4r \text{ or } a = \frac{4}{\sqrt{2}}r$$

Volume of unit cell = $a^3 = \left(\frac{4}{\sqrt{2}}r\right)^3 = \frac{32}{\sqrt{2}}r^3$

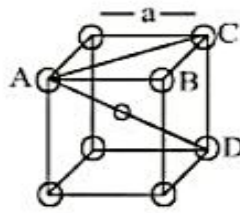
Number of spheres in unit cell = $\frac{1}{8} \times 8 + 6 \times \frac{1}{2} = 4$

Volume of 4 spheres = $4 \times \frac{4}{3} \pi r^3 = \frac{16}{3} \pi r^3$

Therefore, fraction occupied = $\frac{16\pi r^3 / 3}{32r^3 / \sqrt{2}} = 0.74$ or 74% occupied.

- (iii) In a body-centred cubic structure.
 AD is the body diagonal and since the sphere at centre touches the one at corners, $AD = 4r$. Also

$$AD = \sqrt{AC^2 + CD^2}$$



$$\text{Since } AC = \sqrt{AB^2 + BC^2} = \sqrt{a^2 + a^2} = \sqrt{2}a$$

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

$$\text{Or } a = \frac{4r}{\sqrt{3}} \text{ or the volume of the cubic cell} = a^3 = \left(\frac{4r}{\sqrt{3}}\right)^3 = \frac{64r^3}{3\sqrt{3}}$$

$$\text{Number of spheres per unit cell} = \left(8 \times \frac{1}{8} = 1\right) + 1 = 2$$

$$\text{Volume of 2 spheres} = 2 \times \frac{4}{3} \pi r^3 = \frac{8}{3} \pi r^3$$

$$\text{Packing fraction} = \frac{\frac{8}{3} \pi r^3}{\frac{64r^3}{3\sqrt{3}}} = 0.68 \text{ or } 68\% \text{ occupied.}$$

LENGTH OF UNIT CELL AND DENSITY OF A CUBIC CRYSTAL

The density of the crystal can be calculated if the edge size of the cubic crystal and the type of structure possessed by it is known.

If the length of the unit cell is a

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

$$\text{And, density of the unit cell} = \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}} = \frac{\text{Number of atoms in the cell} \times \text{Mass of each atom}}{\text{Volume of unit cell}}$$

$$\text{Density } (\rho) = \frac{Z \times M}{a^3 \times N_a}$$

Z = Effective number of atoms in unit cell

N_a = Avogadro's number

M = Atomic mass

Illustration

1. Sodium has a bcc structure with nearest neighbour distance 365.9 pm. Calculate its density. (Atomic mass of Na = 23)

Sol. For the bcc structure, nearest neighbour distance ($2r$) is related to edge length (a) as

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

$$\therefore a = \frac{2}{\sqrt{3}} \times 2r = \frac{2}{1.732} \times 365.9 = 422.5 \text{ pm}$$

$$M = 23$$

$$\text{For bcc structure, } z = 2 \quad d = \frac{z \times M}{a^3 \times N_0} = \frac{2 \times 23}{(422.5 \times 10^{-10})^3 \times 6.023 \times 10^{23}} = 1.51 \text{ g/cm}^3$$

1. In solid, oxide ions are arranged in ccp. One sixth of the tetrahedral voids are occupied by the cations (A) while one third of the octahedral voids are occupied by the cations (B). What is the formula of the compound. ?

Sol. Let, number of O^{2-} ions be 90

Then octahedral voids = 90

Tetrahedral voids = 180

Number of cations (A) = $1/6 \times 180 = 30$

Number of cations (B) = $1/3 \times 90 = 30$

\therefore Ratio A : B : O^{2-} = 30 : 30 : 90 = 1 : 1 : 3

The formula of the compound is ABO_3

Exercise

1. An element crystallizes as face centred cubic lattice with density 5.20 g/cm^3 and edge length of the side of unit cell as 300 pm. Calculate the mass of the element which contains 3.01×10^{24} atoms.

Sol. 105.65 g

1. A compound formed by elements X and Y, Crystallizes in the cubic structure where X is at the corners of the cube and Y is at the six face centre. What is the formula of the compound ? If side length is 5 Å, estimate the density of the solid assuming atomic weight of X and Y as 60 and 90 respectively.

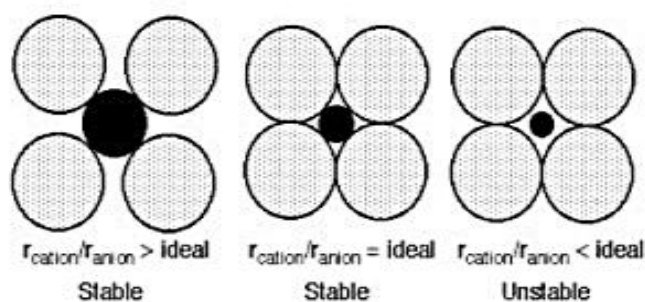
Ans. 4.38 gm/cm^3

RADIUS RATIO RULES

Following conditions must be satisfied simultaneously during the stacking of ions of different sizes in an ionic crystal:

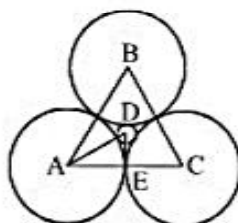
- (a) An anion and a cation are assumed to be hard spheres always touching each other.
- (b) Anions generally will not touch but may be close enough to be in contact with one another in a limiting situation.
- (c) A cation should surround itself with as many anions as possible. Each ion tends to surround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

RADIUS RATIO



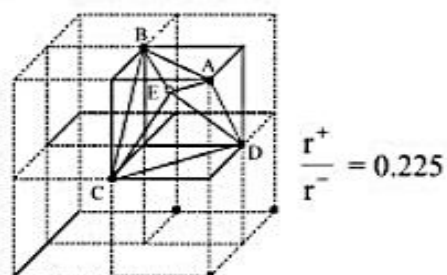
Radius ratio for co-ordination number 3

(Triangular Arrangement): $\frac{r^+}{r^-} = 0.155$



Radius ratio for coordination number 4

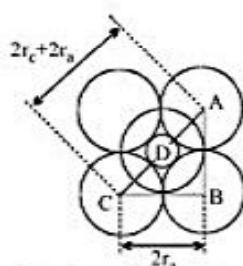
(Tetrahedral arrangement):



Radius ratio for coordination number 6:

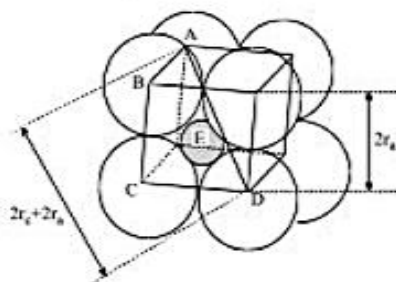
(Octahedral Arrangement)

$$\frac{r^+}{r^-} = 0.414$$



Top view of octahedral arrangement

**Radius ratio for coordination number 8 :
(Body centered cubic crystal)**



$$\frac{r^+}{r^-} = 0.732$$

Ligancy as a function of radius ratio in 1 : 1 or AB-type structure

S.No.	Ligancy or coordination number	Range of radius ratio	Configuration	Structure type	Examples
1.	2	$0.0 < \frac{r^+}{R} < 0.155$	Linear	—	—
2.	3	$0.155 \leq \frac{r^+}{R} < 0.225$	Triangular	—	—
3.	4	$0.225 \leq \frac{r^+}{R} < 0.414$	Tetrahedral	ZnS	CuCl, CuBr, CuI, BaS, HgS
4.	6	$0.414 \leq \frac{r^+}{R} < 0.732$	Octahedral	NaCl	MgO, NaBr, CaS, MnO, KBr, CuO
5.	8	$0.732 \leq \frac{r^+}{R} < 1.0$	Cubic	CsCl	CsI, CsBr, TlBr, NH ₄ Br
6.	12	$\frac{r^+}{R} = 1.0$	fcc or hcp	—	—

* r = radius of cation ; R = radius of anion

Illustration

Q.1 A solid A^+B^- has a sodium-chloride-type close-packed structure. If the anion has a radius of 250 pm, what should be the radius of the cation? Can a cation C^+ having a radius of 180 pm be slipped into the tetrahedral site of the crystal A^+B^- ?

Sol. As A^+B^- has a sodium-chloride-type packing, A^+ ions will be present in octahedral voids. The ideal radius of the cation will be equal to the radius of the octahedral void as then the cation will touch the anions and the arrangement will be close packed.

$$\text{Radius of octahedral void} = r_{A^+} = 0.414 \times r_{B^-}$$

Therefore, $r_{A^+} = 0.414 \times 250 \text{ pm} = 103.4 \text{ pm}$

The radius of tetrahedral site is $= 0.225 \times r_{B^-} = 0.225 \times 250 \text{ pm}$
 $= 56.25 \text{ pm}$

Obviously, cation C^+ of 180 pm dimension cannot be slipped into the tetrahedral site.

Exercise

1. What is the simplest formula of a solid whose cubic unit cell has the atom A at each corner, the atom B at each face centre and C atom at the body centre
 (A) AB_2C (B) A_2BC (C) AB_3C (D) ABC_3
 Ans. (C)

Effect of Temperature and Pressure on Crystal Structure

On applying a high pressure, sodium chloride structure (6 : 6 coordination) changes to cesium chloride structure (8 : 8 coordination). Similarly, cesium chloride structure on heating to 760 K changes to sodium chloride structure. Obviously, an increase in pressure enhances the coordination number whereas an increase in temperature causes a reverse effect.

Structure of Some Ionic Crystals

Sodium Chloride (NaCl) Type AB. (Rock Salt)



$r_{Na^+} / r_{Cl^-} = 0.524$ suggests octahedral voids.

- (a) It has face-centred cubic (fcc) arrangements (also called cubic close packing ccp). Cl^- are large and present at the corners and face centres whereas Na^+ (in octahedral holes) are present at the body centre and edge centre.
- (b) Since the number of octahedral holes is equal to the number of anions, the formula is NaCl. In this packing, each Na^+ is surrounded by six Cl^- and each Cl^- is surrounded by 6 Na^+ . (In this packing, there are six octahedral holes.) Therefore, the coordination number of Na^+ and Cl^- is six, that is, this structure has 6 : 6 coordination.
- (c) In the unit cell, Cl^- are at the corners and at the face centres; therefore, the number of Cl^- per unit cell is

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

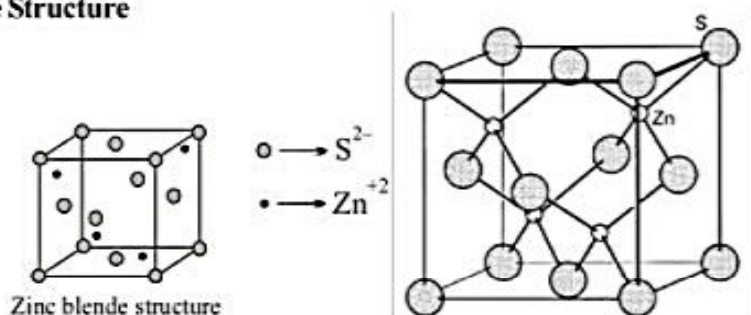
Similarly, Na^+ are at the body centre and edge centre.

$$\text{Total number of } \text{Na}^+ \text{ per unit cell} = 1 + 12 \times \frac{1}{4} = 4.$$

Thus, there are four NaCl units per unit cell.

Other crystals which have a similar structure are AgCl, AgBr, oxides and sulphides of alkaline earth metals (except BeS) and halides of K, Rb and NH_4Cl , NH_4Br and NH_4I .

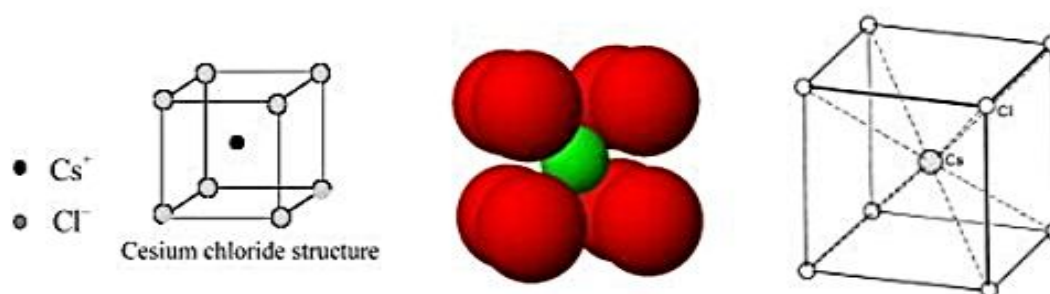
Zinc Blende (ZnS)-Type Structure



$r_{\text{Zn}^{2+}} / r_{\text{S}^{2-}} = 0.40$, that is, a tetrahedral arrangement.

- (a) The crystal has a cubic close packing (ccp) in which S^{2-} form a face-centred cubic structure and thus are present at the corners and at the centre of each face, whereas Zn^{2+} occupy the tetrahedral holes.
- (b) For every atom or ion closely packed, there are two tetrahedral holes and only half are occupied by Zn^{2+} to have the formula ZnS (1 : 1 stoichiometry). Only alternate holes are occupied by Zn^{2+} .
- (c) Each Zn^{2+} in a tetrahedral hole is surrounded by 4 sulphide ions and each sulphide ion is surrounded by four Zn^{2+} . Thus, the coordination number of both ions is 4 or it has 4 : 4 coordination.
- (d) In a unit cell
 Out of 8 tetrahedral voids, Zn^{2+} occupy four.
 Therefore, the number of Zn^{2+} per unit cell = 4.
 Sulphide ions occupy the corners and face centres.
 So, the number of sulphide ions is $8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$.
 So, there are four ZnS units per unit cell.
- (e) BeS, AgI, and halides of copper have a similar structure.

Caesium Chloride (CsCl)-Type Structure



- (a) It has a body-centred cubic (bcc) arrangement plus a hole (cubic).
- (b) Cl^- form a simple cubic arrangement and occupy corners of a cube and Cs^+ is present in the body in interstitial hole.
- (c) Each Cs^+ is surrounded by 8 Cl^- and each Cl^- is surrounded by 8 Cs^+ . The coordination number is 8 : 8.
- (d) In a unit cell,

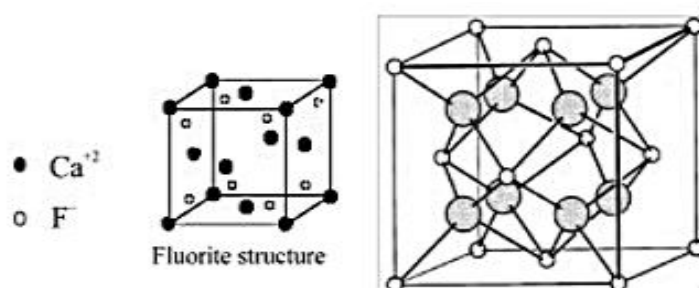
$$\text{the total number of } \text{Cl}^- \text{ is } 8 \times \frac{1}{8} = 1$$

$$\text{and the total number of } \text{Cs}^+ = 1$$

Therefore, there is one unit of Cs Cl per unit cell.

- (e) Cs Br, Cs I, Tl Cl, Tl Br, Tl I, and Tl CN have a similar structure.

Calcium Fluoride (CaF_2) (Fluorite)



- (a) This is also a ccp or fcc structure. Each Ca^{2+} is present at corners plus centre of each face. F^- occupy tetrahedral sites.
- (b) Since there are two tetrahedral holes for each Ca^{2+} , there would be two F^- per calcium ion. The stoichiometry is 1 : 2.
- (c) Each Ca^{2+} is surrounded by 8 F^- and each F^- (in tetrahedral hole) has 4 Ca^{2+} around it. Therefore, the coordination number of Ca^{2+} is 8 and that of F^- is 4, or the coordination number of the crystal is 8 : 4.
- (d) The unit cell has

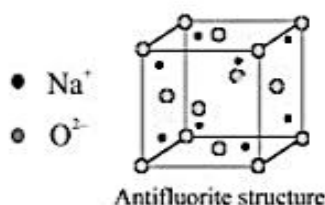
$$\text{Ca}^{2+} = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$$

$\text{F}^- = 8$ within the body

Therefore, there are 4 CaF_2 units per unit cell.

- (e) PbF_2 , BaCl_2 , BaF_2 , SrF_2 , SrCl_2 , CdF_2 , and ThO_2 have this type of structure.

Antifluorite Structure (Reverse of Fluorite)



Examples are Li_2O , Na_2O , etc.

In this, the oxide ions form a cubic arrangement and Na^+ or Li^+ is in tetrahedral hole. The oxide ions are surrounded by 8 Li^+ or Na^+ whereas each Li^+ or Na^+ is surrounded by four oxide ions. So, the coordination number of Li or Na is 4 and that of oxide is 8 or it has 4 : 8 coordination.

Metals like Al, Ag, Au, Cu, Ni and Pt have a ccp structure and Be, Cd, Mg, Co and Zn have a hcp structure.

Illustration

- The radius of a calcium ion is 94 pm and of an oxide ion is 146 pm. Predict the crystal structure of calcium oxide.

Sol. The ratio $\frac{r^+}{r^-} = \frac{94}{146} = 0.644$

The prediction is an octahedral arrangement of the oxide ions around the calcium ion. Because the ions have equal but opposite charges, there must also be an octahedral arrangement of calcium ions around oxide ions. Thus, we would expect a rock salt (NaCl) structure.

Exercise

- Radii of A^+ and that of X^- and Y^- have been given as
 $\text{A}^+ = 1.00 \text{ pm}$
 $\text{X}^- = 1.00 \text{ pm}$
 $\text{Y}^- = 2.00 \text{ pm}$

Assign structure of AX and AY crystals and also determine the volume of unit cells of AX and AY crystals.

Ans. volume (a^3) = 216 pm^3

2. The density of CaO is 3.35 gm/cm^3 . The oxide crystallizes in one of the cubic systems with an edge of 4.80 \AA . How many Ca^{2+} ions and O^{2-} ions belong to each unit cell, and which type of cubic system is present?

Ans. Cubic system is FCC type.

3. In LiI crystal, I^- ions form a cubical closest packed arrangement and Li^+ ions occupy octahedral holes. What is the relationship between the edge-length of the unit cells and the radii of the I^- ions? Calculate the limiting ionic radii of Li^+ and I^- if $a = 600 \text{ pm}$.

Ans. 87.84 pm

Noble gases (except He, which has a hcp structure) have a ccp structure.

Structure of FeO , Fe_2O_3 , and Fe_3O_4

- (a) **FeO.** This oxide is non-stoichiometric and has a composition Fe_xO (Generally 'x' varying from 0.92 to 0.97). The oxide ions form a cubic close packing. The octahedral voids are occupied by Fe^{2+} but a small number of Fe^{2+} are replaced by Fe^{3+} ions. Three Fe^{2+} will be replaced by two Fe^{3+} to maintain electrical neutrality but then what we obtain is an iron-deficient crystal.
- (b) **Fe_2O_3 .** If all Fe^{2+} are replaced by Fe^{3+} , the ratio between Fe:O will be 2 : 3 (since 3 Fe^{2+} are replaced by 2 Fe^{3+}) and not 1 : 1. As such, we obtain Fe_2O_3 .
- (c) **Fe_3O_4 .** This is obtained by replacing exactly two thirds of Fe^{2+} by Fe^{3+} (in FeO structure). The remaining Fe^{2+} ions and 50% of Fe^{3+} ions occupy the octahedral voids. The remaining Fe^{3+} ions occupy tetrahedral voids.

If in the structure of Fe_3O_4 , the Fe^{2+} ions are replaced by divalent cations such as Mg^{2+} , Zn^{2+} , etc., the compounds obtained are called *ferrites*. In ferrites, divalent cations occupy tetrahedral voids and trivalent cations occupy octahedral voids. This structure is called *spinel structure*.

IMPERFECTIONS IN SOLID

Any deviation from the perfectly ordered arrangement constitutes a defect or imperfection. These defects sometimes called thermodynamic defects because the number of these defects depends on the temperature. Crystals may also possess additional defect due to the presence of impurities. Imperfection not only modify the properties of solids but also give rise to new properties.

Electronic imperfection

Generally, electrons are present in fully occupied lowest energy states. But at high temperatures, some of the electrons may occupy higher energy state depending upon the temperature.

For example, in the crystals of pure Si or Ge some electrons are released thermally from the covalent bonds at temperature above 0 K. These electrons are free to move in the crystal and are responsible for electrical conductivity. This type of conduction is known as intrinsic conduction.

The electron deficient bond formed by the release of an electron is called a hole. In the presence of electric field the positive holes move in a direction opposite to that of the electrons and conduct electricity.

Atomic imperfection

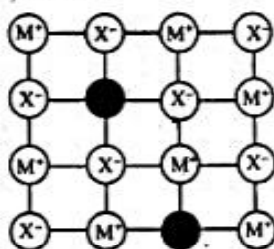
The compounds in which the number of irregularity present in the arrangement of atoms or ions are called- atomic imperfections. It is of two types -

STOICHIOMETRIC DEFECTS

Those compounds in which the number of positive and negative ions are exactly in the ratio indicated by their chemical formula are called stoichiometric compounds. eg NaCl (1 : 1)

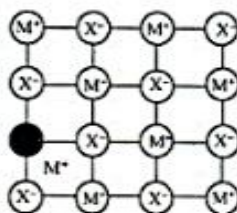
These solids show following types of defects:

- (a) **Schottky defect** : This type of defect is created when same number of positive ion and negative ion are missing from their respective positions leaving behind a pair of holes. Schottky defect is more common in ionic compounds with high co-ordination number and where the size of positive and negative ions are almost equal. The presence of large number of schottky defects in crystal results in significant decrease in its density. Eg. NaCl, KCl, CsCl, KBr etc.



Schottky Defect

- (b) **Interstitial Defect** : This type of defect is caused due to the presence of ions in the normally vacant interstitial sites in the crystal.
- (c) **Frenkel Defect** : This type of defect is created when an ion leaves its correct lattice site and occupies an interstitial site. Frenkel defects are common in ionic compounds which have low co-ordination number and in which there is large difference in size between positive and negative ions. Eg. ZnS, AgCl, AgBr, Ag etc.



Frenkel Defect

Non Stoichiometric Defect Frenkel Defect

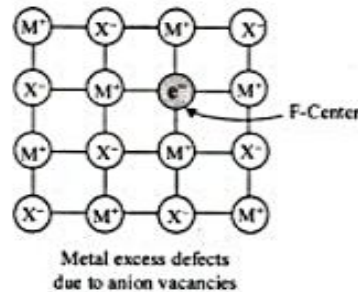
There are many compound in which the ratio of positive and negative ions present in the compound differs from that required by ideal formula of the compound. Such compounds are called Nonstoichiometric compounds. eg. VO_x (Where x can vary between 0.6 to 1.3.)

In these compounds balance of positive and negative charges is maintained by having extra electrons or extra positive charge.

So, these defects are of following types:

- (a) **Metal excess defects due to anion vacancies**
- A compound may have excess metal ion if a negative ion is absent from its lattice site, leaving a hole which is occupied by electron to maintain electrical neutrality.
- The holes occupied by electrons are called F-centres and are responsible for the colour of the compound.
- Eg.
- The excess sodium in NaCl makes the crystal appears yellow.
 - Excess potassium in KCl makes it violet.
 - Excess lithium in LiCl makes it Pink.

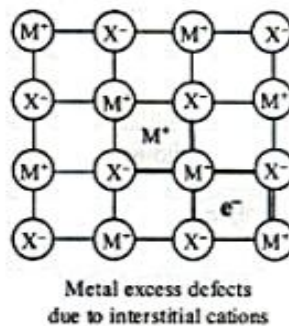
Greater the number of F-centres greater is the intensity of colour. This type of defects are found in crystal which are likely to possess schottky Defects.



(b) Metal excess defects due to interstitial cations

It may occur if an extra positive ion is present in an interstitial site. Electrically neutrality is maintained by the presence of an electron in the interstitial site.

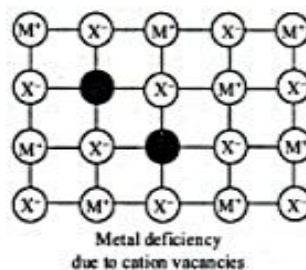
This type of defects are exhibited by the crystals which are likely to exhibit "Frenkel defects". Eg. Yellow colour of ZnS.



(c) Metal deficiency due to cation vacancies

The non-stoichiometric compound may have metal deficiency due to the absence of a metal ion from its lattice site. The charge is balanced by an adjacent ion having higher positive charge.

This type of defects are generally shown by compounds of transition metals.



Illustration

1. Analysis shows that nickel oxide has the formula $\text{Ni}_{0.98}\text{O}$. What fractions of the nickel exist as Ni^{2+} and Ni^{3+} ?

Sol. 98 Ni atoms are associated with 100 O atoms. Out of 98 Ni atoms, suppose Ni present as $\text{Ni}^{2+} = x$
Then Ni present as $\text{Ni}^{3+} = 98 - x$
Total charge on $x \text{ Ni}^{2+}$ and $(98 - x) \text{ Ni}^{3+}$ should be equal to total charge on 100 O^{2-} ions.

$$\text{Hence, } 2 \times x + 3 \times (98 - x) = 100 \times 2$$

$$\text{or } 2x + 294 - 3x = 200$$

$$\therefore x = 94$$

$$\therefore \text{Fraction of Ni present as } \text{Ni}^{2+} = \frac{94}{98} \times 100 = 96\%$$

$$\text{Fraction of } \text{Ni}^{3+} \text{ present as } \text{Ni}^{3+} = \frac{4}{98} \times 100 = 4\%$$

Exercise

1. Calcium crystallizes in a face centred cubic unit cell with $a = 0.556 \text{ nm}$. Calculate the density if it contains.
(i) 0.1% Frenkel defect
(ii) 0.1% Schottky defect

Ans. (i) 1.5463 g/cm^3 (ii) 1.5448 g/cm^3

PROPERTIES OF SOLIDS

Electrical properties of solids :

On the basis of electrical conductivity, solids are classified into three types.

i. metals

ii. semi-conductors

iii. insulators

Electrical conductivity of metals is very high and is of the order of $10^6 - 10^8 \text{ ohm}^{-1} \text{ cm}^{-1}$.

Electrical conductivity of solids is due to the movement of electrons and positive holes or through the motion of ions.

The conduction through electrons is called n-type conduction and through positive ions is called p-type conduction.

Pure ionic solids, where conduction takes place only through motion of ions, are insulators.

The presence of defects in the crystal structure increases their conductivity.

The solids whose conductivity lies between those of metallic conductors and insulators are called semi-conductors.

Semi - conductors have conductivity which lies in the range of $10^2 - 10^9 \text{ ohm}^{-1} \text{ cm}^{-1}$.

The solids which do not allow the passage of electric current through them are called insulators.

Eg: Wood, rubber, sulphur, phosphorus etc..

The conductivity of semi conductors and insulators is mainly due to the presence of interstitial electrons and positive holes in the solids due to imperfections.

The conductivity of semi conductors and insulators increases with increase in temperature while that of metals decreases.

Magnetic properties of solids :

The substances which are weakly repelled by magnetic field are called **diamagnetic** substances.

Eg : TiO_2 , NaCl, benzene etc..

Diamagnetism arises when all the electrons are paired.

The substances which are weakly attracted by magnetic field are called **paramagnetic substances**.

Atoms, ions or molecules with unpaired electrons exhibit paramagnetism.

Paramagnetic substances lose their magnetism in the absence of magnetic field.

Eg : TiO , VO_2 , CuO etc.

The substances which are strongly attracted by magnetic field are called **ferromagnetic substances**.

Ferromagnetic substances show permanent magnetism even in the absence of magnetic field.

Eg : Iron, cobalt, nickel, CrO_2 etc.

Ferromagnetism arises due to spontaneous alignment of magnetic moments in the same direction.

Anti ferromagnetism arises due to the alignment of magnetic moments in opposite direction in a compensatory manner and resulting in a zero magnetic moment.

Eg : MnO , MnO_2 , Mn_2O_3 .

Ferrimagnetism arises due to alignment of magnetic moments in opposite directions resulting in a net magnetic moment.

Eg : Fe_3O_4 , $\text{M}^{2+}\text{Fe}_2\text{O}_4$; (M = Mg, Cu, Zn etc.)

Ferromagnetic and ferrimagnetic substances change into paramagnetic substances at higher temperatures due to randomisation of spins.

Dielectric Properties :

A dielectric is a substance in which an electric field gives rise to no net flow of electric charge. The electrons in a dielectric are tightly held by individual atoms.

Due to shift in charges, dipoles are created which result into polarisation.

The dipoles may align in an ordered manner such that there is some resultant dipole moment in the crystals.

The dipoles may align in such a way that the dipole moments cancel each other and resultant dipole moment is zero.

There may be no dipoles in the crystal but only ions are present.

Depending upon the alignment of the dipoles, the properties of crystals are:

- i. Piezoelectricity ii. Ferroelectricity iii. Anti-ferroelectricity iv. Pyroelectricity

i. Piezoelectricity :

The crystals in which the dipoles may align in an ordered way having some dipole are referred to as piezoelectrics and such crystals exhibit **piezoelectricity**.

Piezoelectric crystals act as mechanical-electrical transducers.

When these crystals are subjected to a pressure or mechanical stress, electricity is produced. These crystals are used as pickups in record players by the application of pressure.

ii. Ferroelectricity :

The solids, in which dipoles are spontaneously aligned in a particular direction, even in the absence of electric field, are called ferroelectric substances and the phenomenon is called ferroelectricity.

The direction of polarisation in these substances can be changed by applying electric field.

The examples are barium titanate (Ba TiO_3), sodium potassium tartrate (Rochelle salt) and potassium dihydrogen phosphate (KH_2PO_4).

iii. Anti-ferroelectricity :

If the alternate dipoles are in opposite direction, then the net dipole moment will be zero and the crystal is called anti-ferroelectric and the phenomenon is **antiferroelectricity**.

iv. Pyroelectricity :

Some of the polar crystals when heated produce small electric current. This phenomenon is called **pyroelectricity**.

Super Conducting Materials

- Super conducting materials are those which offer no resistance to the passage of electricity. Electrical resistance decreases with decrease in temperature and becomes almost zero near the absolute zero.
 - In this state, the materials become diamagnetic and are repelled by the magnets.
 - Most metals become super conducting at very low temperatures (2 - 5K).
 - The highest temperature at which superconductivity was known is 23K in alloys of niobium (e.g. Nb_3Ge).
 - Some organic compounds also become super conducting at temperatures below 5 K.
 - Some complex metal oxides pass super conductivity at higher temperatures.
- Super conductors are used in electronics, building magnets, power transmission, levitation transportation, (trains which move in air without rails).

SOLVED EXAMPLE

Q.1 Fraction of total volume occupied by atoms in a simple cube is -

- (A) $\frac{\pi}{2}$ (B) $\frac{\sqrt{3}\pi}{2}$ (C) $\frac{\sqrt{2}\pi}{6}$ (D) $\frac{\pi}{6}$

Ans. (D)

Sol. In a simple cubic system, number of atoms $a = 2r$

$$\therefore \text{Packing fraction} = \frac{\text{Volume occupied by one atom}}{\text{Volume of unit cell}} = \frac{\frac{4}{3}\pi r^3}{a^3} = \frac{\frac{4}{3}\pi r^3}{(2r)^3} = \frac{\pi}{6}$$

Q.2 In a crystal both ions are missing from normal sites in equal number. This is an example of -

- (A) F-centres (B) Interstitial defect (C) Frenkel defect (D) Schottky defect

Ans. (D)

Sol. Schottky defects are arised when one positive ion and one negative ion are missing from their respective position leaving behind a pair of holes. These are more common in ionic compounds with high coordination number and having almost similar size of cations and anions.

Q.3 Xenon crystallizes in face centre cubic lattice and the edge of the unit cell is 620 PM, then the radius of Xenon atom is -

- (A) 219.20 PM (B) 438.5 PM (C) 265.5 PM (D) 536.94 PM

Ans. (A)

Sol. For fcc lattice

$$4r = \sqrt{2} a \quad \text{where } a = 620 \text{ PM}$$

$$\text{or } r = \frac{1}{2\sqrt{2}} \times a = \frac{1}{2\sqrt{2}} \times 620 \text{ PM} = 219.20 \text{ PM.}$$

Q.4 The edge length of cube is 400 PM. Its body diagonal would be -

- (A) 500 PM (B) 693 PM (C) 600 PM (D) 566 PM

Ans. (B)

Sol. Since in body centre cubic, the body diagonal

$$= \sqrt{3} a = \sqrt{3} \times 400 \text{ PM} = 692.82 \text{ PM or say } 693 \text{ PM}$$

Q.5 A compound alloy of gold and copper crystallizes in a cube lattice in which the gold atoms occupy the lattice points at the corners of cube and copper atoms occupy the centres of each of the cube faces. The formula of this compound is -

- (A) AuCu (B) AuCu₂ (C) AuCu₃ (D) None

Ans. (C)

Sol. One-eighth of each corner atom (Au) and one half of each face centered atom (Cu) are contained with in the unit cell of the compound.

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

$$\text{the number of Cu atoms per unit cell} = 6 \times \frac{1}{2} = 3. \text{ The formula of the compound is AuCu}_3.$$

Q.6 Lithium borohydride (LiBH_4), crystallises in a orthorhombic system with 4 molecules per unit cell. The unit cell dimensions are : $a = 6.81 \text{ \AA}$, $b = 4.43 \text{ \AA}$, $c = 7.17 \text{ \AA}$. If the molar mass of LiBH_4 is 21.76 g mol^{-1} . The density of the crystal is -

- (A) $.668 \text{ g cm}^{-3}$ (B) $.585 \text{ g cm}^{-2}$ (C) 1.23 g cm^{-3} (D) None

Ans. (A)

Sol. We know that,

$$\rho = \frac{ZM}{N_A V} = \frac{4 \times (21.76 \text{ g mol}^{-1})}{(6.023 \times 10^{23} \text{ mol}^{-1})(6.81 \times 4.43 \times 7.17 \times 10^{-24} \text{ cm}^3)} = 0.668 \text{ g cm}^{-3}$$

Q.7 The unit cell of a metallic element of atomic mass 108 gm/mole and density 10.5 g/cm^3 is a cube with edge length of 409 pm . The structure of the crystal lattice is -

- (A) fcc (B) bcc (C) hcp (D) None

Ans. (A)

Sol. $\rho = \frac{Z \times M}{N_A \times a^3}$

Here, $M = 108$, $N_A = 6.023 \times 10^{23}$

Put on these values and solving we get -

$a = 409 \text{ pm} = 4.09 \times 10^{-8} \text{ cm}$, $\rho = 10.5 \text{ g/cm}^3$

$Z = 4$ = number of atoms per unit cell

So, The structure of the crystal lattice is fcc.

Q.8 Copper metal has a face-centred cubic structure with the unit cell length equal to 0.361 nm . Picturing copper ions in contact along the face diagonal. The apparent radius of a copper ion is -

- (A) 0.128 nm (B) 1.42 nm (C) 3.22 nm (D) 4.22 nm

Ans. (A)

Sol. For a face-centred cube, we have

$$\text{Radius} = \frac{\sqrt{2}a}{4} = \frac{\sqrt{2} \times 0.361}{4} \text{ nm} = 0.128 \text{ nm}.$$

Q.9 The unit cell cube length for LiCl (NaCl structure) is 5.14 \AA . Assuming anion-anion contact, calculate the ionic radius for chloride ion.

Sol. In a face centred cubic lattice, anions touch each other along the face diagonal of the cube.

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

$$\therefore r_{\text{Cl}^-} = \frac{\sqrt{2}}{4} \times a$$

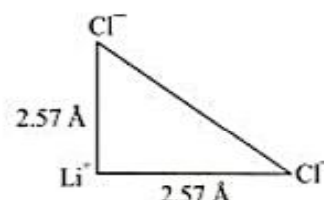
$$= \frac{\sqrt{2}}{4} \times 5.14 = 1.82 \text{ \AA}$$

Alternatively

$$\text{Distance between } \text{Li}^+ \text{ and } \text{Cl}^- \text{ ion} = \frac{5.14}{2} = 2.57 \text{ \AA}$$

$$\text{This distance between two chloride ions} = \sqrt{(2.57)^2 + (2.57)^2} = 3.63$$

$$\therefore r_{\text{Cl}^-} = \frac{3.63}{2} = 1.82 \text{ \AA}$$



- Q.10** The density of potassium bromide crystal is 2.75 gm/cm^3 and the length of an edge of unit cell is 654 pm . The unit cell of KBr is one of the three types of cubic unit cells. How many of formula units of KBr are there in a unit cell? Does the unit cell have a NaCl or LiCl structure?

Sol.
$$\rho = \frac{Z \times M}{N_0 \times a^3}$$

$$\therefore Z = \frac{d \times a^3 \times N_0}{M}$$

$$= \frac{2.75 \times (654 \times 10^{-10})^3 \times 6.023 \times 10^{23}}{119}$$

$$= 3.89 \approx 4$$

Number of formula units = 4
It is NaCl type crystal (FCC)

- Q.11** A metal (atomic mass = 50) has a body centre cubic crystal structure. The density of the metal is 5.96 g/cm^3 . Find the volume of unit cell. ($N_0 = 6.023 \times 10^{23} \text{ atoms mol}^{-1}$)

Sol. Mass of the unit cell = mass of one atom \times No. of atom present per unit cell = $\frac{50}{6.023 \times 10^{23}} \times 2$

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

$$= \frac{50 \times 2}{6.023 \times 10^{23}} \times \frac{1}{5.96} = 2.78 \times 10^{-23} \text{ cm}^3$$

- Q.12** The unit cell length of NaCl is observed to be 0.5627 nm by X-ray diffraction studies; the measured density of NaCl is 2.164 cm^{-3} . Calculate the different of observed and calculated density and calculate % of missing Na^+ and Cl^- ions.

Sol. Density (ρ) = $\frac{Z \times M}{N_0 \times a^3}$

$$= \frac{4 \times 58.5}{6.023 \times 10^{23} \times (0.5627 \times 10^{-7})^3}$$

$$= 2.1805 \text{ g/cm}^3$$

Observed density = 2.164 g/cm^3 which is less than calculated density because some ions are missing.
Actual constant units per unit cell can be calculated as :

$$Z = \frac{\rho \times N_0 \times a^3}{M} = \frac{2.164 \times 6.023 \times 10^{23} \times (0.5627 \times 10^{-7})^3}{58.5} = 3.969$$

Missing units = $4 - 3.969 = 0.031$

$$\therefore \% \text{ missing of } \text{Na}^+ \text{ and } \text{Cl}^- = \frac{0.031}{4} \times 100 = 0.775\%$$

Q.13 Compute the percentage void space per unit volume of unit cell in zinc fluoride structure.

Sol. Since anions occupy fcc position and half of the tetrahedral voids are occupied by cations, there are 4 anions and 8 tetrahedral voids per unit cell. The fraction of volume occupied by spheres per unit volume of the unit cell is

$$= \frac{4 \times \left(\frac{4}{3} \pi r_a^3 \right) + \frac{1}{2} \times 8 \times \left(\frac{4}{3} \pi r_c^3 \right)}{16\sqrt{2}r_a^3} = \frac{\pi}{3\sqrt{2}} \left\{ 1 + \left(\frac{r_c}{r_a} \right)^3 \right\}$$

$$= \frac{\pi}{3\sqrt{2}} \{ 1 + (-0.225)^3 \} = 0.7496 \left(\text{For tetrahedral voids, } \frac{r_c}{r_a} = 0.225 \right)$$

\therefore Void volume = $1 - 0.7496 = 0.2504$ /unit volume of unit cell

% void space = 25.04%

Q.14 Copper has fcc crystal structure. Assuming an atomic radius of 130 pm for copper atom ($\text{Cu} = 63.54$)

(a) What is the length of unit cell of Cu ?

(b) What is the volume of the unit cell ?

(c) How many atoms belong to the unit cell ?

(d) Find the density of Cu

Sol. As we know

$$\rho = \frac{n \times M_m}{N_0 \times a^3}$$

(a) For FCC structure

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

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

$$= 2 \sqrt{2} \times 130 \text{ pm} = 367.64 \text{ pm}$$

(c) Volume of unit cell $a^3 = \frac{n \times M_m}{N_0 \times \rho} = (3.67 \times 10^{-8})^3 = 4.94 \times 10^{-23} \text{ cm}^3$

(c) $n = 4$

(d) $\rho = \frac{4 \times 63.54}{6.03 \times 10^{23} \times (3.67 \times 10^{-8})^3} = 8.54 \text{ gm/cm}^3$

Q.15 A metal crystallizes in two cubic phases, face centre cubic (fcc) and body centred cubic (bcc) whose unit cell length are 3.5 and 3.0 Å respectively. Calculate the ratio of density of fcc and bcc.

Sol. $\rho = \frac{n \times M_m}{N_0 \times a^3}$

For FCC

$n = 4, a = 3.5 \text{ Å}$

$\therefore \rho(\text{fcc}) = \frac{4 \times M_m}{N_0 \times (3.5)^3} \dots\dots(i)$

For bcc lattice
 $n = 2, a = 3.0 \text{ \AA}$

$$\rho_{\text{bcc}} = \frac{2 \times M_m}{N_A \times (3.0)^3} \quad \dots(ii)$$

Comparing eqs. (i) and (ii), we get

$$\therefore \frac{\rho_{\text{fcc}}}{\rho_{\text{bcc}}} = \frac{4}{2} \times \frac{3^3}{(3.5)^3} = \frac{4 \times 3 \times 3 \times 3}{2 \times 3.5 \times 3.5 \times 3.5} = 1.259$$

Q.16 Prove that void space in fluorite structure per unit volume of unit cell is 0.251.

Sol. Cations form cubical closest packing and anions occupying the tetrahedral holes.
 There are 4 cations and 8 anions per unit cell.

Here, face diagonal

$$4r^+ = \sqrt{2} a$$

where, r^+ = radius of cation

$$\therefore a = 2 \sqrt{2} r^+$$

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

$$\text{Volume of unit cell} = 16 \sqrt{2} (r^+)^3$$

Fraction of volume occupied per unit volume of unit cell

$$\text{i.e. Packing fraction} = \frac{4 \times \left(\frac{4}{3} \pi r^{3+} \right) + 8 \times \left(\frac{4}{3} \pi r^{3-} \right)}{16 \sqrt{2} r^{3+}}$$

$$= \frac{\pi}{3 \sqrt{2}} \left[1 + \left(\frac{2r^{3-}}{r^{3+}} \right) \right]$$

Here in fluorite structure, for tetrahedral hole

$$\frac{\text{Radius of anion}}{\text{Radius of cation}} = \frac{r^-}{r^+} = 0.225$$

$$\text{Packing fraction} = \frac{\pi}{3 \sqrt{2}} \{ 1 + 2(0.225)^3 \} = 0.749$$

$$\therefore \text{Void space} = 1 - 0.749$$

$$\text{Void fraction} = 0.251$$