

SOLID STATE

SOLID

(Substances which have definite volume and shape)

1. Classification of Solids

Solids are divided into two classes, namely crystalline and amorphous solids. A solid is said to be crystalline if the constituents arrange themselves in regular manner throughout the three-dimensional network. The ordered arrangement of building constituents extends over a large distance (long range order). On the other hand, in amorphous solids, the arrangement of building constituents is not regular (short range order).

Difference between Crystalline and Amorphous Solids :

Crystalline solids

1. They have definite and regular geometry due to definite and orderly arrangement of atoms, ions or molecules in three-dimensional space.
2. They have sharp melting points and change abruptly into liquids
3. Crystalline solids are anisotropic. Some of their physical properties are different in different directions
4. These are considered as true solids
5. Crystalline solids are rigid and their shape is not distorted by mild distorting forces
6. Crystals are bound by plane faces. The angle between any two faces is called interfacial angle. For a given crystalline solid, it is a definite angle and remains always constant no matter how the faces develop. When a crystalline solid is hammered, it breaks up into smaller crystals of the same geometrical shape.
7. Example: NaCl, KCl, Sugar, Quartz, etc.

Amorphous solids

They do not have any pattern of arrangement of atoms, ions or molecules and, thus do not have any definite geometrical shape.

Amorphous solids do not have sharp melting points and donot change abruptly into liquids.

Amorphous solids are isotropic. Their physical properties are same in all direction

These are considered pseudosolids or supercooled liquid.

Amorphous solids are not very rigid. These can be distorted by bending or compressing forces.

Amorphous solids not have well defined planes. When an amorphous solid is broken, the surfaces of the broken pieces are generally not flat and intersect at random angles.
(Amorphous solids do not have any symmetry)

Example :Plastic, Glass, Rubber etc.

Types of crystalline solids

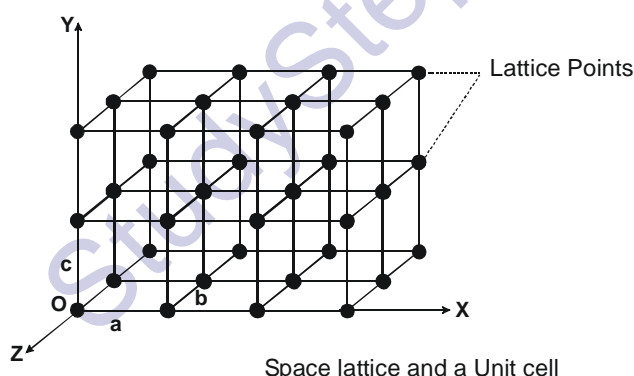
	Ionic	Metallic	Covalent	molecular
Particles occupying lattice points	Anions, cations	Metal ions in electron cloud	Atoms	Molecules (or atoms)
Binding force	Electrostatic attraction	Metallic bonds	Covalent bonds	Van der waals dipole-dipole
Properties	Hard, Brittle, poor thermal and electrical conductors	Soft to very hard, good thermal and electrical conductors	Very hard, poor thermal and electrical conductors	Soft, poor thermal and electrical conductors
Example	NaCl, CaBr ₂ , KNO ₃ , etc	Li, K, Ca, Cu, Na, etc.	C(diamond) SiO ₂ (quartz), etc	H ₂ O, H ₂ , CO ₂ , Ar etc

2. Terms and concepts

(i) Space lattice or crystal lattice

It may be defined as a regular three dimensional arrangement of identical points in space.

The positions which are occupied by atoms, ions or molecules in the crystal lattice are called **lattice points** or **lattice sites**.



(ii) Unit Cell

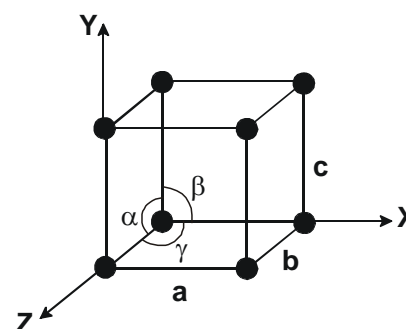
A space lattice can be sub-divided into a number of small cells known as unit cells. It can be defined as the smallest block from which entire crystal can be built up by its translational repetition in three dimensions.

The unit cell shown in figure is characterized by a , b & c along the three edges of the unit cell & the angles α , β & γ between the pair of edges

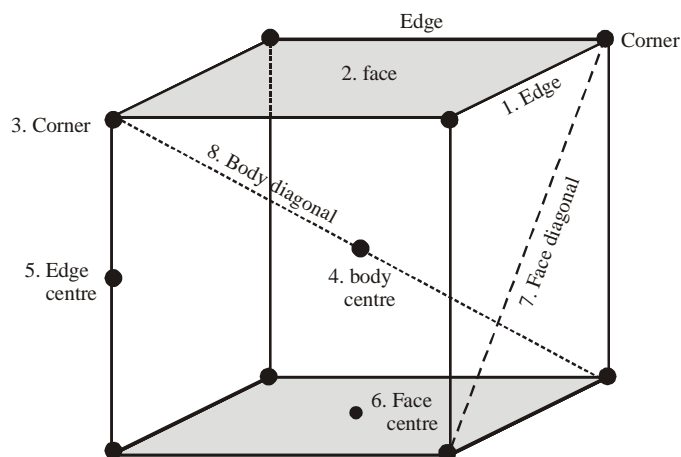
The angle α is between the edges b & c .

Angle β is between the edges c & a

Angle γ is between the edges a & b



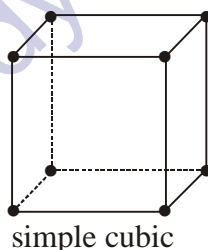
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1. Total number of edges in a cube = 12
2. Total number of faces in a cube = 6
3. Total number of corners in a cube = 8
4. Total number of body centre in a cube = 1
5. Total number of edge centre in a cube = 12
6. Total number of face centre in a cube = 6
7. Total number of face diagonals in a cube = $6 \times 2 = 12$
8. Total number of body diagonals in a cube = 4

3. Types of Lattices and Types of Unit Cell

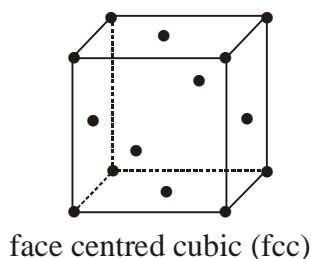
- (i) **Primitive or simple Unit Cells:** In a primitive unit cell, the same type of particles are present at all the corners of the unit cell.



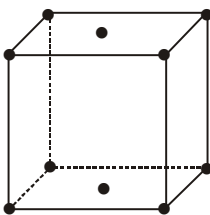
- (ii) **Non-primitive or centered unit cells:**

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

- (a) **Face Centered:** When atoms are present in all 8-corners and six face centres in a cubic unit cell then this arrangement is known as FCC.

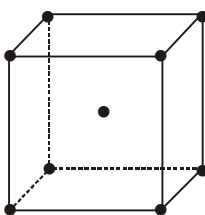


- (b) **End-Centered** : When in addition to particles at the corners, there are particles at the centres of the end faces.



end centred cubic (fcc)

- (c) **Body Centered** : When atoms are present at 8 corners as well as in the body centre in a cubic unit cell then this arrangement is known as BCC.

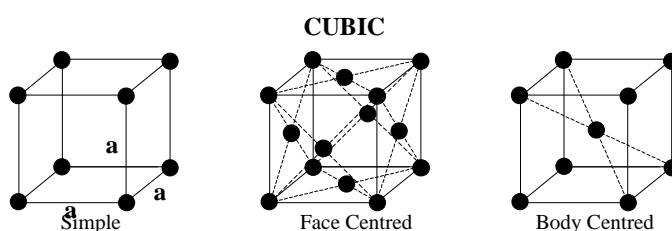


Body centred cubic (bcc)

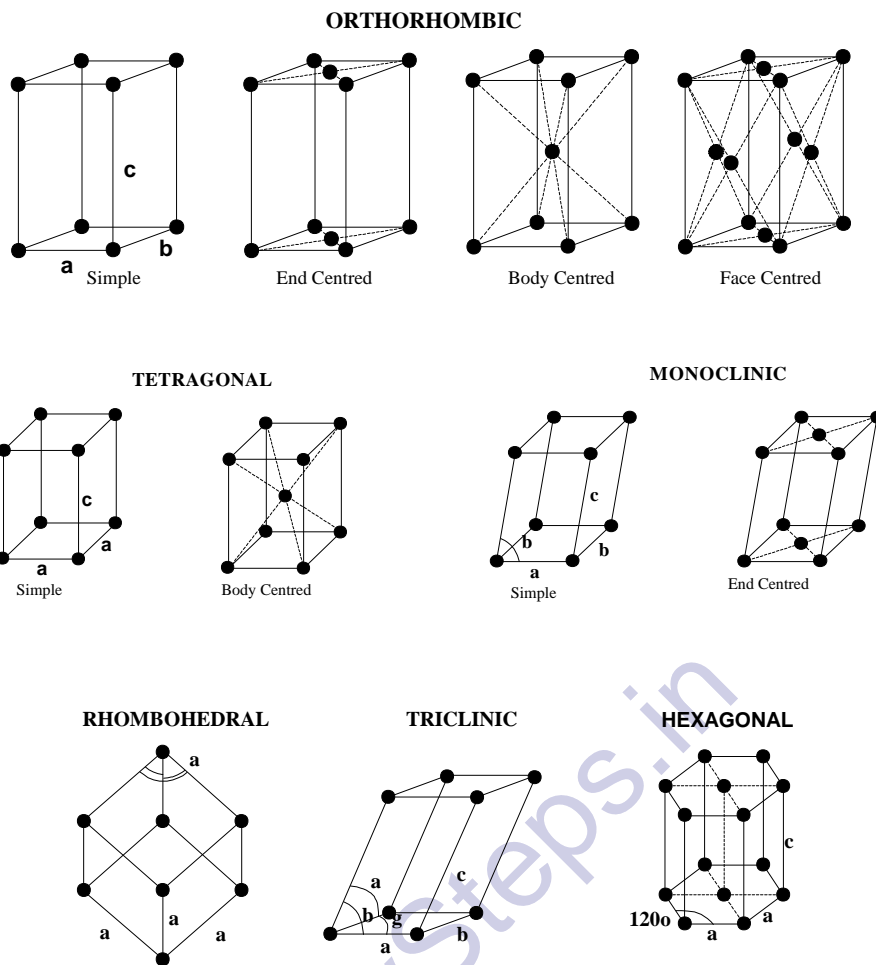
4. Seven Crystal Systems

Crystal System	Bravais Lattices	Parameters of Unit Cell		Example
		Intercepts	Interfacial angle	
1. Cubic	Primitive, Face Centered, Body Centered = 3	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	Pb, Hg, Ag, Au Diamond, NaCl, ZnS
2. Tetragonal	Primitive, Body Centered = 2	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	TiO ₂ , SnO ₂
3. Orthorhombic	Primitive, Face Centered, Body Centered, End Centered = 4	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	KNO ₃ , K ₂ SO ₄
4. Hexagonal	Primitive = 1	$a = b \neq c$	$\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$	Mg, SiO ₂ , Zn, Cd
5. Rhombohedral	Primitive = 1	$a = b = c$	$\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$	As, Sb, Bi, CaCO ₃
6. Monoclinic	Primitive, End Centered = 2	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ$, $\beta \neq 90^\circ$	CaSO ₄ ·2H ₂ O
7. Triclinic	Primitive = 1	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	K ₂ Cr ₂ O ₇ , CaSO ₄ ·5H ₂ O
Total = 14 (Total 14 type of lattices are called Bravais lattices)				

Seven Crystal Systems and Fourteen Bravais Lattice



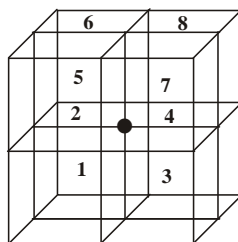
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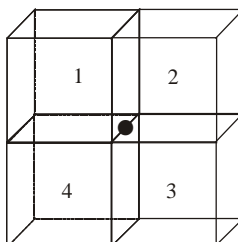
5. Calculation of number of particles in a unit cell (Z)

In a crystal atoms located at the corner and face center of a unit cell are shared by other cells and only a portion of such an atom actually lies within a given unit cell.

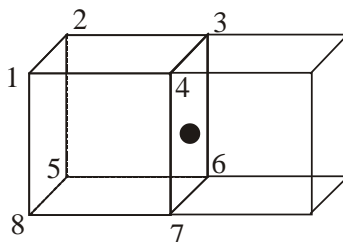
- (i) A point that lies at the corner of a unit cell is shared among eight unit cells and therefore, only one eighth of each such point lies within the given unit cell.



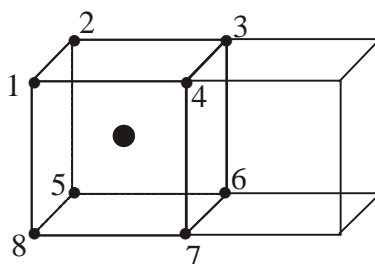
- (ii) A point along an edge is shared by four unit cells and only one-fourth of it lies within any one cell.



- (iii) A face-centered point is shared by two unit cells and only one half of it is present in a given unit cell.



- (iv) A body-centered point lies entirely within the unit cell and contributes one complete point to the cell.



Type of Lattice point	Contribution to one unit cell
Corner	$\frac{1}{8}$
Edge	$\frac{1}{4}$
Face-center	$\frac{1}{2}$
Body Center	1

Calculation of number of particles in a unit cell

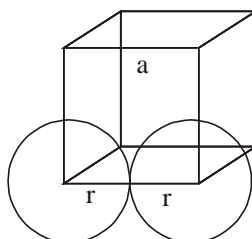
Type of unit cell	Lattice points at corners	Lattice points at face-centered	Lattice points at body centered	Z = no. of lattice points per unit cell
SCC	8	0	0	$8 \times \frac{1}{8} = 1$
BCC	8	0	1	$8 \times \frac{1}{8} + 1 \times 1 = 2$
FCC	8	6	0	$8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$

6. Relation between edge length of unit cell and radius of atoms

- (i) Simple cubic or Primitive –

(a) edge length of unit cell $a = 2r$

(b) atomic radius $r = a/2$

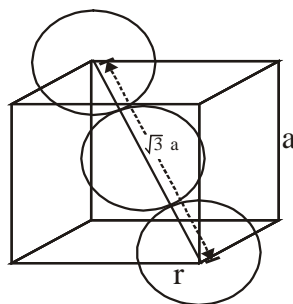


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(ii) Body centre cubic

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

(b) atomic radius, $r = \frac{\sqrt{3} a}{4}$



(iii) Face centre cubic/cubic close packed

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

(b) atomic radius $r = \frac{\sqrt{2} a}{4}$

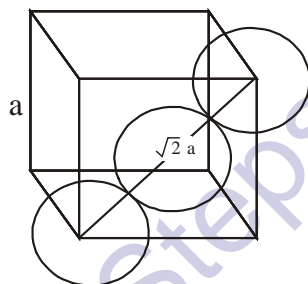


Illustration 1: A solid has a cubic structure in which X atoms are located at the corners of the cube, Y atoms are at the cube centres and O atoms are at the edge centres. What is the formula of the compound?

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

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

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

O atom is present at each of the edge centre (number of edges of cube = 12) And each O atom present at edge centre will make $\frac{1}{4}$ contribution towards the unit cell.

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

The formula of the compound is, therefore XYO_3

Illustration 2: Potassium crystallizes in a body centered cubic lattice. What is the approximate number of unit cells in 4.0g of potassium? Atomic mass of potassium = 39.

Solution: There will be eight atoms at corners of the cube and one atom at the body centre.

$$\therefore \text{Number of atoms per unit cell} = 8 \times \frac{1}{8} + 1 \times 1 = 2$$

$$\text{Number of atoms in 4.0g of potassium} = \frac{4}{39} \times 6.023 \times 10^{23}$$

$$\therefore \text{Number of unit cells in 4.0g of potassium} = \frac{4}{39} \times \frac{6.023 \times 10^{23}}{2} = 3.09 \times 10^{22}$$

7. Fraction of volume occupied by atoms in a cube

Packing Fraction = Volume of atoms in the cube/Total volume of cube)

	Item	Primitive	BCC	FCC
1.	Atoms occupy :	8 corners	8 corners, 1 centre	8 corners, 6 face centres
2.	Each atom contributes			
	(a) corner atom :	$\frac{1}{8} \text{th} \times 8$	$\frac{1}{8} \text{th} \times 8$	$\frac{1}{8} \text{th} \times 8$
	(b) Face centre atom :	nil	nil	$\frac{1}{6} \times 6$
	(c) Body centre atom :	nil	one \times one	nil
3.	\therefore No. of atoms in the cube (Z):	one	two	four
4.	Radius of the atom :	r	r	r
5.	Total volume of atoms :	$1 \times \frac{4}{3} \pi r^3$	$2 \times \frac{4}{3} \pi r^3$	$4 \times \frac{4}{3} \pi r^3$
6.	Edge of the cube :	a	a	a
7.	Edge of the cube in terms of r :	$a = 2r$	$a = \frac{4}{\sqrt{3}} r$	$a = \frac{4r}{\sqrt{2}}$
8.	Total volume of the cube, a^3 :	$(2r)^3$	$\left(\frac{4}{\sqrt{3}} r\right)^3$	$\left(\frac{4}{\sqrt{2}} r\right)^3$
9.	Fraction of volume occupied :	$\frac{4}{3} \pi r^3$	$\frac{8}{3} \pi r^3$	$\frac{16}{3} \pi r^3$
	$= \frac{\text{Total volume of atoms}}{\text{Total volume of cube}}$	$8r^3$	$\frac{64}{3\sqrt{3}} r^3$	$\frac{64}{2\sqrt{2}} r^3$
10.	(or) packing fraction :	$\frac{\pi}{6}$	$\frac{\sqrt{3}}{8} \pi$	$\frac{\sqrt{2}}{6} \pi$
11.	(or) volume occupied by atoms :	0.52	0.6802	0.7405
12.	% volume occupied by atoms :	52%	68.02 %	74.05%
13.	Fraction of void volume :	0.48	0.3198	0.2595
14.	% of void volume in cube :	48%	31.98%	25.95%
15.	% of empty space in cube :	48%	31.98%	25.95%

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Illustration 3: Calculate the packing fraction for the Ca unit cell, given that Ca crystallizes in a face-centered cubic unit cell.

Solution: One-eighth of each corner atom and one-half of each face-centered atom are contained within the unit cell of Ca giving

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

Further, atomic radius, $r = \frac{\sqrt{2}a}{4}$

$$\text{Volume of 4 atoms} = 4 \times \frac{4}{3} \pi r^3 = 4 \times \frac{4}{3} \times \pi \left(\frac{\sqrt{2}a}{4}\right)^3 = \frac{\sqrt{2}\pi a^3}{6}$$

$$\text{Packing fraction} = \frac{\sqrt{2}\pi a^3}{6} / a^3 = \frac{\sqrt{2}\pi}{6} = 0.74$$

8. Density of unit cell

Density of unit cell (and hence density of a crystal)

$$\rho = \frac{Z \times M}{a^3 \times N_0 \times 10^{-30}}$$

where a is edge of unit cell in pm

N_0 = Avogadro number (6.02×10^{23})

M = Atomic mass of element or formula mass of the compound

Z = No. of atoms present per unit cell or formula units. e.g.
for fcc, Z = 4, for bcc, Z = 2, for simple cubic, Z = 1

Item	Symbols and formula
1. Edge of the unit cell	a pm
2. Volume of the unit cell	a^3 pm ³
3. Volume of the unit cell	$a^3 \times 10^{-30}$ cc
4. Atomic mass of element	M
5. Avogadro number	N_A
6. Mass of one atom of element	$\frac{M}{N_A}$
7. No. of atoms in the unit cell	Z
8. Mass of (z atoms in the) unit cell	$\frac{ZM}{N_A}$
9. Density, ρ	$\frac{\text{mass in g}}{\text{vol. in cc}}$
10. Density of unit cell, ρ	$\frac{ZM}{N_A \cdot a^3 \cdot 10^{-30}}$
11. No. of molecules in unit cell z	$\frac{a^3 \rho N_A}{M}$

Illustration 4: Gold has a close-packed structure which can be viewed as-spheres occupying 0.74 of the total volume. If the density of gold is 19.3 g/cc, calculate the apparent radius of a gold ion in the solid

Solution: Gold has a close-packed structure with a packing fraction value of 0.74. This shows that it has a face-centered cubic cell. The number of ions in a face-centered unit cell is 4.

$$\text{Now density} = \frac{Z \times M}{a^3 \times N_A}$$

$$\text{or } 19.3 = \frac{4 \times (197)}{a^3 \times 6.02 \times 10^{23}} \Rightarrow a = 4.07 \times 10^{-8} \text{ cm}$$

In a face-centered cubic cell.

$$\text{radius} = \frac{\sqrt{2}a}{4} = \frac{\sqrt{2} \times 4.07 \times 10^{-8}}{4} = 1.439 \times 10^{-8} \text{ cm}$$

Illustration 5: An element occurs in bcc structure with a cell edge of 288 pm. The density of metal is 7.2 g cm⁻³. How many atoms does 208 g of the element contain?

Solution: Volume of the unit cell = $(288 \times 10^{-10})^3$
= $23.9 \times 10^{-24} \text{ cm}^3$

$$\text{Volume of 208 g of the element} = \frac{208}{7.2} = 28.88 \text{ cm}^3$$

$$\text{Number of unit cells in } 28.88 \text{ cm}^3 = \frac{28.88}{23.9 \times 10^{-24}} = 12.08 \times 10^{23} \text{ unit cells}$$

Each bcc structure contains 2 atoms.

$$\text{So total atoms in } 12.08 \times 10^{23} \text{ unit cells} = 2 \times 12.08 \times 10^{23} = 24.16 \times 10^{23}$$

Illustration 6: When heated above 916°C, iron changes its crystal structure from body-centered cubic to cubic closed packed structure. Assuming that the metallic radius of the atom does not change, calculate the ratio of density of the bcc crystal to that of the ccp crystal.

Solution: In body-centered packing, the efficiency of packing is 67.92%.

In the cubic closed packing the packing efficiency is 74.02%

Let d_1 be the density when packing efficiency is 67.92% and d_2 is the density when packing efficiency is 74.02%.

$$\frac{d_2}{d_1} = \frac{67.92}{74.02} = 0.918$$

1. Daily Practice Problem Sheet

1. A compound formed by elements A and B has a cubic structure in which A atoms are at the corners of the cube and B atoms are at the face centres. Derive the formula of the compound.
2. A cubic solid is made up of two elements P and Q. Atoms Q are present at the corners of the cube and atoms P at the body centre. What is the formula of the compound.
3. A compound formed by elements X and Y crystallizes 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.
4. A compound formed by elements X and Y crystallizes in the cubic structure where Y atoms are at the corners of the cube and X atoms are at the alternate edge centres. What is the formula of the compound?
5. Calculate the number of atoms in a cubic based unit cell having one atom on each corner and two atoms on each body diagonal.
6. A compound made up of elements A and B crystallises in the cubic structure. Atoms A are present on the corners as well as face centres whereas atoms B are present on the edge centres as well as body centre. What is the formula of the compound.
7. Xenon crystallises in the face centered cubic lattice and the edge of the unit cell is 620 pm. What is the nearest neighbour distance and what is the radius of xenon atom.
8. If the radius of an atom of an element is 75 pm and the lattice type is body centered cubic, what is the edge of the unit cell.
9. The radius of an atom of an element is 500 pm. If it crystallizes as a face centered cubic lattice, what is the length of the side of the unit cell.
10. A face centered cubic element (atomic mass 60) has a cell-edge of 400 pm. What is its density.
11. An element occurs in the BCC structure with cell edge of 288 pm. The density of the element is 7.2 g/cm^3 . How many atoms of the element does 208 g of the element contain.
12. Sodium has a bcc structure with nearest neighbour distance 365.9 pm. Calculate its density
13. Gold crystallizes in a face-centered cubic lattice. If the length of the edge of the unit cell is 407 pm, calculate the density of gold as well as its atomic radius assuming it to be spherical. [Au = 197 amu].
14. An element crystallizes in a structure having fcc unit cell of an edge 200 pm. Calculate the density if 200 g of this element contains 24×10^{23} atoms.
15. Use the data given below to find the type of cubic lattice to which the crystal of iron belongs :
a = 286 pm, $\rho = 7.86 \text{ g cm}^{-3}$. Atomic mass of iron = 56 amu.
16. The density of a face centered cubic element (atomic mass = 60.2 amu) is 6.25 g cm^{-3} . Calculate the length of the edge of the unit cell.
17. A body centered cubic element cubic lattice whose density 10.3 g cm^{-3} has a cell edge of 314 pm. Calculate the atomic mass of the element.
18. Chromium crystallizes in a body-centered cubic lattice whose density is 7.20 g/cm^3 . The length of the edge of the unit cell is 288.4 pm. Calculate Avogadro's number.
19. An element occurs in BCC structure. It has a cell edge of 250 pm. Calculate its molar mass if its density 8.0 g cm^{-3} .

9. Close packing in crystals

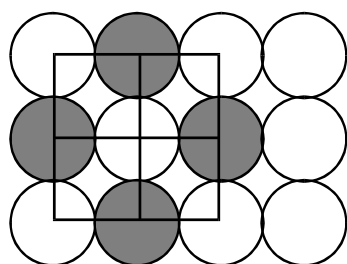
(i) Close packing in two dimensions

There are two ways to build a crystal plane

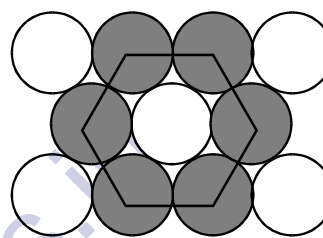
- (a) Spheres are packed in such a way that the rows have a horizontal as well as vertical alignment. In this arrangement, the spheres are found to form square. This type of packing is also called **square close packing**.

The number of spheres which are touching a given sphere is called the co-ordination number. Thus, the coordination number of each sphere in (a) is four.

- (b) The spheres are packed in such a way that the spheres in the second row are placed in the depressions between the spheres of the first row and so on. This gives rise to hexagonal close packing of spheres and the coordination number of each sphere is six.



(a) square close packing
(coordination number 4)

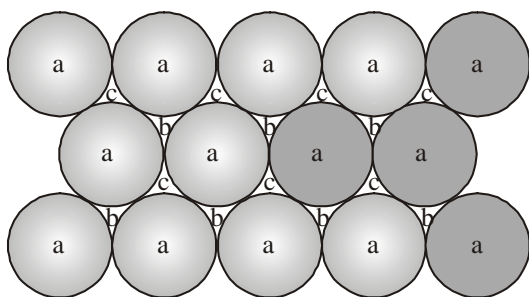


(b) Hexagonal close packing
(coordination number 6)

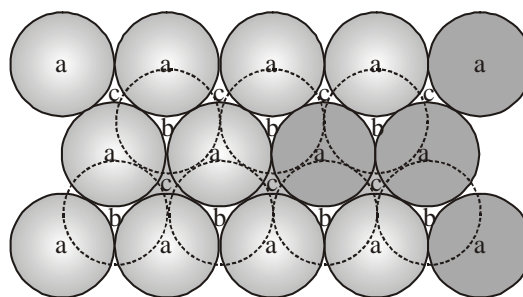
(ii) Close packing in three dimensions

It is clear from the figure (a) that there are two types of voids or hollows in the first layer. These are marked as b and c. All the hollows are equivalent but the sphere of second layer may be placed either on hollows which are marked b or on the other set of hollows marked c. It may be noted that it is not possible to place spheres on both types of hollows so the second layer is indicated as dotted in circles in figure b.

When a third layer is to be added, again there are two types of hollows available. One type of hollows marked 'a' are unoccupied hollows of the first layer. The other type of hollows are hollows in the second layer (marked c). Thus, there are two alternatives to build the third layer.



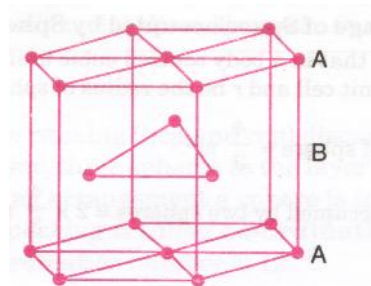
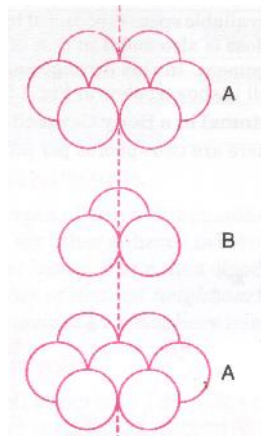
(a)



(b)

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- (i) When the third layer is placed over the second layer so as to cover the tetrahedral or 'c' voids, a three-dimensional closest packing is obtained where the spheres in every third layer are vertically aligned to the first layer. This arrangement is called ABAB,... pattern or hexagonal (HCP) close packing (calling first layer as A and second layer B).

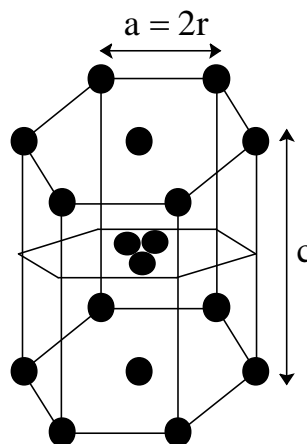
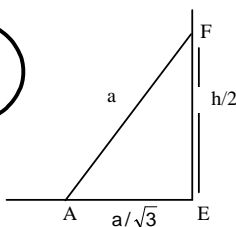
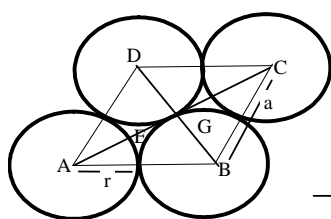


Hexagonal close packing (hcp)

- (a) For HCP geometry Coordination number = 12
 (b) For HCP geometry no. of atoms per unit cell
- $$= 12 \text{ (corners)} \times \frac{1}{6} + 2 \text{ (face centres)} \times \frac{1}{2} + 3 \text{ (inside the body)} \times 1 = 6$$
- (c) For HCP geometry packing efficiency = 74 %

Calculation of Packing efficiency for HCP geometry : Each corner atom would be common to 6 other unit cells, therefore their contribution to one unit cell would be $1/6$. Total number of atom in 1 hcp unit

$$\text{cell} = \frac{12}{6} \text{ (from 12 corners)} + \frac{2}{2} \text{ (from 2 face centered)} + \frac{3}{1} \text{ (from body centre)}$$



ABCD is the base of hexagonal unit cell

$AD = AB = a$. The sphere in the next layer has its centre F vertically above E it touches the three spheres whose centres are A, B and D.

$$\text{Hence } FE = \frac{h}{2} = \sqrt{(2r)^2 - \left(\frac{2r}{\sqrt{3}}\right)^2}$$

$$\therefore \text{The height of unit cell (h)} = 4r\sqrt{\frac{2}{3}}$$

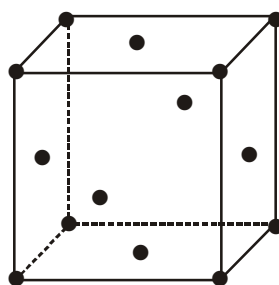
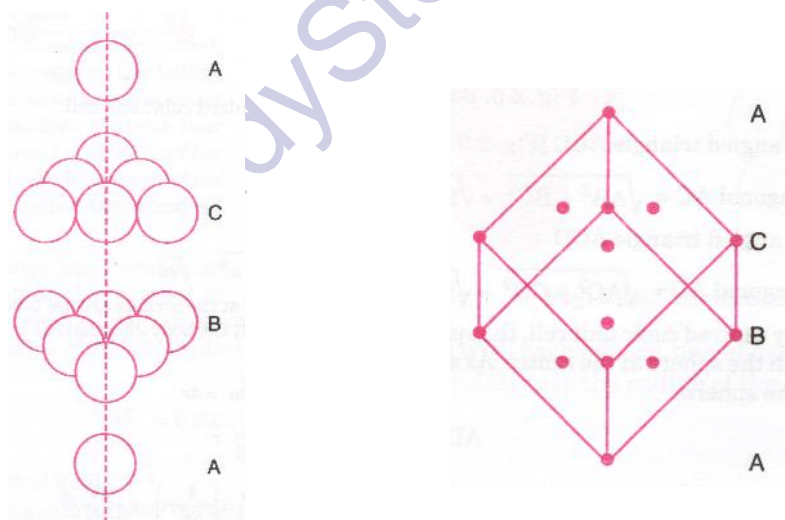
The area of the base is equal to the area of six equilateral triangles, $= 6 \times \frac{\sqrt{3}}{4} (2r)^2$.

The volume of the unit cell $= 6 \times \frac{\sqrt{3}}{4} (2r)^2 \times 4r\sqrt{\frac{2}{3}}$.

$$\text{Therefore, } PF = \frac{6 \times \frac{4}{3} r^3}{6 \times \frac{\sqrt{3}}{4} (2r)^2 \times 4r\sqrt{\frac{2}{3}}} \approx \mathbf{0.74}; \quad \therefore VF \approx 0.26$$

- (ii) When the third layer is placed over the second layer such that the spheres cover the octahedral or 'd' voids, a layer C different from A and B is formed. This pattern is called ABCABC..... pattern or cubic close packing (CCP).

The ABCABC peaking has cubic symmetry and is known as cubic close packing (ccp). The cubic close packing close packing has face centered cubic (fcc) unit cell.



Cubic close packing (ccp)

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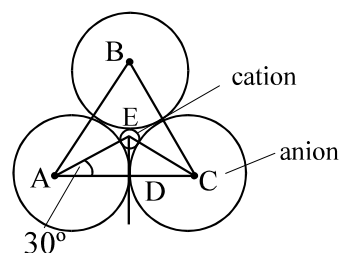
- (i) For CCP geometry coordination number = 12
- (ii) For CCP geometry no. of atoms per unit cell = 4 (as calculated before)
- (iii) For CCP geometry packing efficiency = 74 % (as calculated before)

In the close packing of spheres, certain hollows are left vacant. These holes or voids in the crystals are called interstitial sites or interstitial voids. Two important interstitial sites are

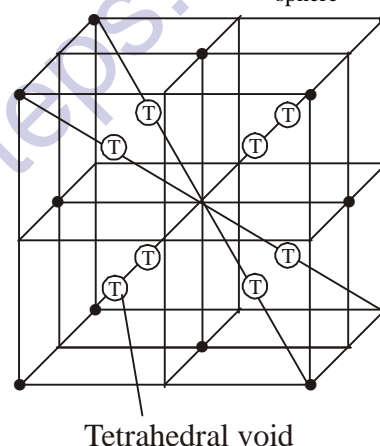
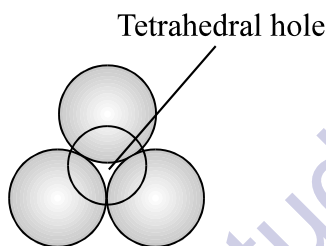
- (i) triangular
- (ii) tetrahedral
- (iii) octahedral
- (iv) cubical void

- (i) **Triangular :** The vacant space (void) formed by touching three spheres.

$$\frac{r_{\text{void}}}{r_{\text{sphere}}} = 0.155$$

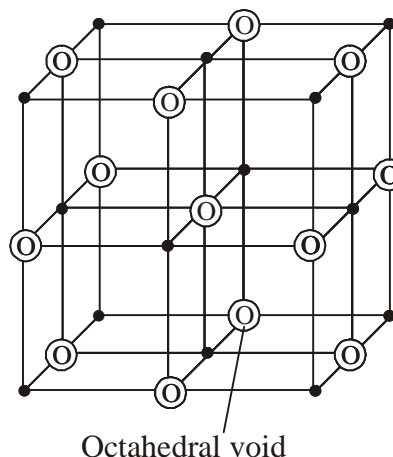
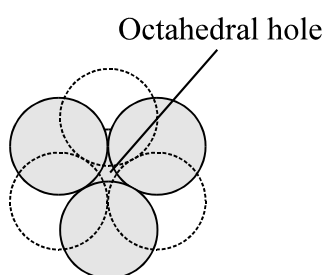


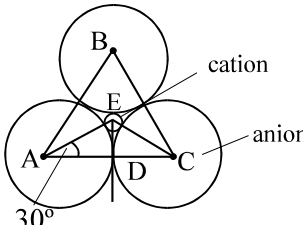
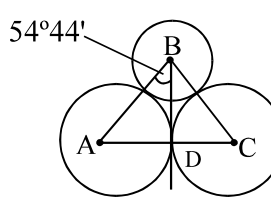
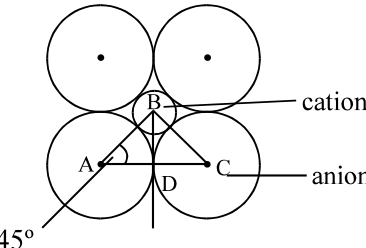
- (ii) **Tetrahedral** – The vacant space among four spheres having tetrahedral arrangement is called tetrahedral site or tetrahedral hole. For tetrahedral void $\frac{r_{\text{void}}}{r_{\text{sphere}}} = 0.225$.



- (iii) **Octahedral** – This type of site is formed at the centre of six sphere. The void formed by two equilateral triangles with apices in opposite direction is called octahedral site or octahedral hole.

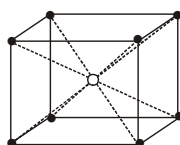
For octahedral void $\frac{r_{\text{void}}}{r_{\text{sphere}}} = 0.414$



LIMITING RATIO TRIGONAL	LIMITING RATIO TETRAHEDRAL	LIMITING RATIO OCTAHEDRAL
<p style="text-align: center;">Co-ordination no. 3</p>  <p> $\angle AEC = 120^\circ$ $AD = r_a$ $AE = r_a + r_c$ $\angle BAD = 60^\circ$ ($\because \Delta ABC$ is equilateral) $\angle DAE = 30^\circ$ $\cos \hat{D}AE = \cos 30^\circ$ In ΔAED $\frac{AD}{AE} = \cos 30^\circ$ $\frac{r_a}{r_a + r_c} = 0.866$ $\frac{r_c}{r_a} + 1 = \frac{1}{0.866}$ $\frac{r_c}{r_a} + 1 = 1.155$ $\frac{r_c}{r_a} = 0.155$ </p>	<p style="text-align: center;">Co-ordination no. 4</p>  <p> $\angle ABC = 109^\circ 28'$ $AD = r_a$ $AB = r_a + r_c$ $\frac{1}{2}$ tetrahedral angle $\angle ABD = 54^\circ 44'$ $\sin \hat{A}BD = \sin 54^\circ 44'$ In ΔABD $\frac{AD}{AB} = \sin 54^\circ 44'$ $\frac{r_a}{r_a + r_c} = 0.8164$ $\frac{r_c}{r_a} + 1 = \frac{1}{0.864}$ $\frac{r_c}{r_a} + 1 = 1.225$ $\frac{r_c}{r_a} = 0.225$ </p>	<p style="text-align: center;">Co-ordination no. 6</p>  <p> $\angle ABC = 90^\circ$ $AD = r_a$ $AB = r_a + r_c$ $\angle BAD = 45^\circ$ $\cos \hat{B}AD = \cos 45^\circ$ In ΔABD $\frac{AD}{AB} = \cos 45^\circ$ $\frac{r_a}{r_a + r_c} = 0.7071$ $\frac{r_c}{r_a} + 1 = \frac{1}{0.7071}$ $\frac{r_c}{r_a} + 1 = 1.414$ $\frac{r_c}{r_a} = 0.414$ </p>

(iv) **cubical void** : The vacant space (void) formed by touching eight spheres.

$$\frac{r_{\text{void}}}{r_{\text{sphere}}} = 0.732$$



Note : If a close packing (array) is made up of n number of atoms or ions then it has n no. of octahedral voids and $2n$ no. of tetrahedral voids.

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Illustration 8: In a cubic lattice, the closed packed structure of mixed oxides of the lattice is made up of oxide ion; one eighth of the tetrahedral voids are occupied by divalent ions (A^{2+}) while one half of the octahedral voids are occupied by trivalent ions (B^{3+}). What is the formula of the oxides?

Solution: Let there be n no. of O^{2-} in the crystal.

\therefore Octahedra voids = n

Tetrahedral voids = $2n$

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

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

\therefore formula is AB_2O_4 .

11. Radius ratio rules

In ionic crystals, the coordination numbers as well as the geometrical shapes of the crystals depend mainly on the relative sizes of the ions. The ration of the radii of the positive and negative ions is called radius ratio.

$$\text{Radius ratio} = \frac{\text{Radius of postive ion (cation)}}{\text{Radius of negative ion (anion)}} = \frac{r_c^+}{r_a^-}$$

Common coordination numbers are 3, 4, 6 and 8.

Limiting $\frac{r_a}{r_c}$ radius ratio	Co-ord. No.	Shape	
Example			
< 0.155	2	Linear	BeF_2
$0.155 - 0.225$	3	Trigonal planar	B_2O_3
$0.225 - 0.414$	4	Tetrahedral	ZnS
$0.414-0.732$	4	square planar	$PtCl_4^{-2}$
$0.414-0.732$	6	octahedral	$NaCl$
$0.732 - 0.999$	8	B.C.C.	$CsCl$

12. Structure of ionic compounds

Simple ionic compounds are of the type AB or AB_2 where A and B represent the positively and negatively charged ions respectively. (In any solid of the type A_xB_y , the ratio of co-ordination number of A to B would be $y : x$).

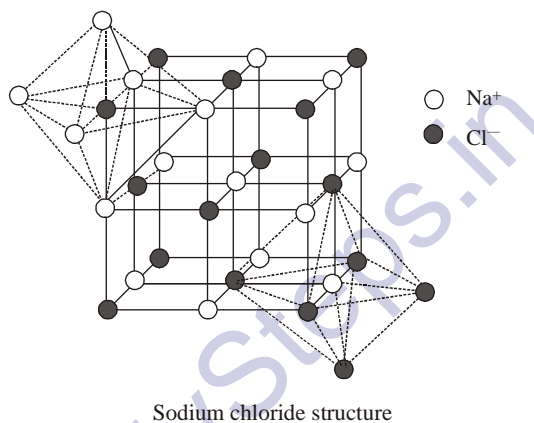
(i) Structures of Type AB:

Ionic compounds of the type AB means compounds having the positively and negatively charged ions in the ratio 1:1. These compounds can have following three type of structures.

1. Rock salt ($NaCl$) type
2. Cesium chloride ($CsCl$) type
3. Zinc blende (ZnS) type

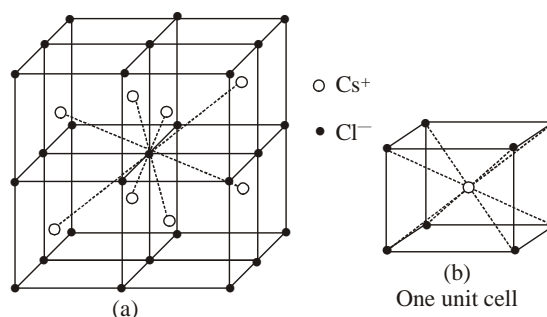
1. Rock salt structure (NaCl) :

- (a) Cl^- is forming a FCC unit cell in which Na^+ is in the octahedral voids. The co-ordination number of Na^+ is 6 and that of Cl^- would also be 6.
- (b) Ratio of ionic radii = $\left(\frac{r_{\text{Na}^+}}{r_{\text{Cl}^-}} = 0.525 \right)$
- (c) No. of sodium ions = $12 \text{ (At edge centre)} \times \frac{1}{4} + 1 \text{ (At body centre)} \times 1 = 4$
 No. of chloride ions \Rightarrow
 $= 8 \text{ (At corners)} \times \frac{1}{8} + 6 \text{ (At face centres)} \times \frac{1}{2} = 4$ (Thus formula is Na_4Cl_4 i.e. NaCl)
- (d) Most of the halides of alkali metals and oxides of alkaline-earth metal have this type of structure. e.g. NaI, KCl, RbI and RbF. FeO also has rock-salt structure in which oxide ions are arranged in ccp and Fe^{2+} ions occupy octahedral voids.



2. Caesium chloride structure (CsCl)

- (a) CsCl has body-centered cubic (bcc) arrangement. This structure has 8 : 8 co-ordination, i.e., each Cs^+ ion is touching eight Cl^- ions and each Cl^- ions in touching eight Cs^+ ions. (bcc)
- (b) $\frac{r_{\text{Cs}^+}}{r_{\text{Cl}^-}} = 0.93$.



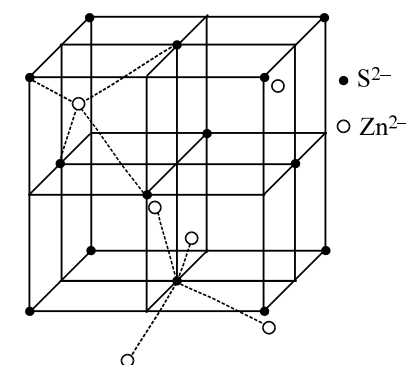
- (c) No. of Cl^- ions = $8 \text{ (At corners)} \times \frac{1}{8} = 1$
 No. of Cs^+ ions = $1 \text{ (At the body centre)} \times 1 = 1$
 No. of CsCl unit per unit cell = 1
- (d) Compounds having this type of structure are CsBr, CsI, TlCl, and TlBr.

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3. Zinc blende structure or sphalarite structure (ZnS)

(a) Sulphite ions are face centered and zinc is present in alternate tetrahedral voids.

(b) $\frac{r_{\text{Zn}^{2+}}}{r_{\text{S}^{2-}}} = 0.40$



Zinc blende structures of zinc sulphide

(c) In unit cell no. of S^{2-} ions

$$= 8 \text{ at corners} \times \frac{1}{8} + 6 \text{ at face centres} \times \frac{1}{2} = 4$$

(Formula is Zn_4S_4 , i.e. ZnS)

No. of Zn^{2+} ions = 4 (within the body) $\times 1 = 4$

\therefore No. of ZnS units per unit cell = 4

(d) Ionic solids having zinc blende structure are CuCl , CuBr , CuI & AgI

(ii) Structure of Ionic Compounds of the Type AB_2 :

These are the ionic compounds having cations and anions in the ratio 1 : 2.

4. Fluorite structure (CaF_2)

(a) The cations are arranged in cubic close packing (ccp) while the anion occupy all the tetrahedral voids. Calcium fluoride has 8 : 4 co-ordination. (ccp)

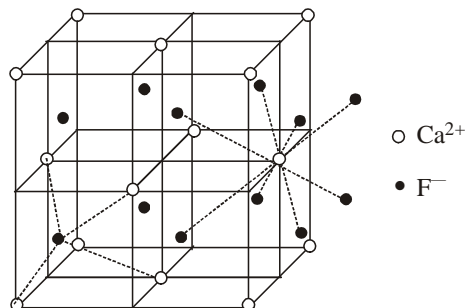
(b) In unit cell no. of calcium ions

$$= 8 \text{ at corners} \times \frac{1}{8} + 6 \text{ at face centres} \times \frac{1}{2} = 4$$

No. of fluoride ions = 4 (within the body) $\times 1 = 4$

\therefore No. of CaF_2 units per unit cell = 4

(c) Compounds having fluorite structure are SrF_2 , BaCl_2 , BaF_2 , PbF_2 and CdF_2 .



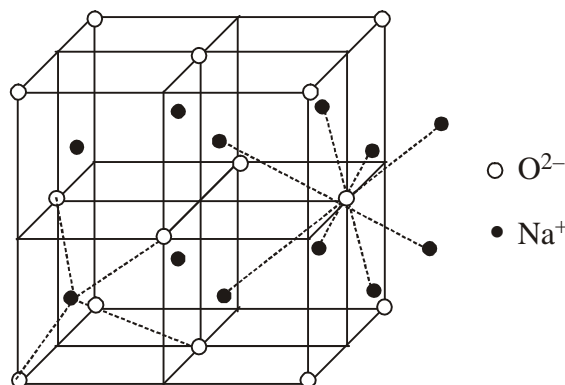
Structure of calcium fluoride

(iii) Structure of Ionic Compounds of the Type A_2B :

5. Antifluorite structure.

In antifluorite structure e.g., (Na_2O)

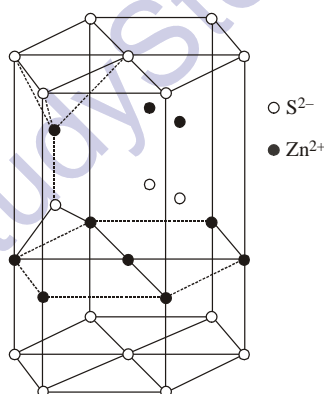
- (a) The anions are arranged in cubic close packing (ccp) while the cations occupy all the tetrahedral voids.
- (b) Na_2O has 4 : 8 co-ordination
- (c) Compounds having antifluorite structures are : Li_2O , K_2O , Rb_2O and Rb_2S



(iv) Some special structures

6. WURTZITE structure

- (a) Sulphide ions have hcp arrangement and zinc ions occupy tetrahedral voids.
- (b) Structure has 4 : 4 coordination



Unit cell representation
of Wurtzite structure

7. Spinal structure

- (a) A spinel is an important class of oxide consisting of two types of metal ions with the oxide ions.
- (b) General formula of compound is AB_2O_4
e.g., MgAl_2O_4 , ZnFe_2O_4
- (c) Oxide ions are arranged in ccp arrangement. Divalent cations are in tetrahedral sites and trivalent ions are in octahedral sites.
- (d) Spinel type structures are important magnetic material used in telephones or memory loops in computers.

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Property	Rock-salt	CsCl (BCC)	Corundum	Antifluorite	Zinc blende	Fluorite	Spinel
Type	FCC-anions	BCC-cations	HCP-anions	CCP-anions	CCP-anions	CCP-cations	CCP-oxides
Void	octahedral void-cation	BCC-anions	$\frac{2}{3}$ octahedral void-cation	tetrahedral void-cations	$\frac{1}{2}$ tetrahedral void-cations	tetrahedral holes-anions	$\frac{1}{8}$ the tetrahedral void A^{+2} $\frac{1}{2}$ tetrahedral void B^{+3}
Ratio A : B	4 : 4	1 : 1	2 : 3	8 : 4	4 : 4	1/8 : 1/4	$A^{+2} : B^{+3} : O^{-2} = 1 : 2 : 4$
formula	A_4B_4	AB	A_2B_3	A_8B_4	A_4B_4 , AB	$A_{1/8}B_{1/4}$, AB_2	$A_1B_2O_4$
Example	NaCl, MgO	CsCl	Fe_2O_3 , Al_2O_3	Li_2O , Rb_2O	BeO, ZnS	UO_2 , CaF_2	$ZnAl_2O_4$, $ZnFe_2O_4$
r^+ / r^-	0.414 – 0.736	0.732 – 0.999	0.414 – 0.736	0.225 – 0.414	0.225 – 0.414	0.225 – 0.414	0.225 – 0.414
Neighbrous	12	8	12	12			
co-ord-no.	6 each	8 each	6	4	cation-4 anion-8	cations-8 anions-4	4

2. Daily Practice Problem Sheet

1. 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 of 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.
2. A solid AB has NaCl structure. If the radius of the cation A is 100 pm, what is the radius of the anion B?
3. A solid AB has NaCl structure. If the radius of cation A^+ is 170 pm, calculate the maximum possible radius of the anion B^- .
4. A solid A^+B^- has NaCl type close packed structure. If the anion has a radius of 241.5 pm, what should be the minimum radius of the cation? Can a cation C^+ having radius of 50 pm be fitted into the tetrahedral hole of the crystal A^+B^- ?
5. In a crystalline solid, anions B are arranged in a cubic close packing. Cations A are equally distributed between octahedral and tetrahedral voids. If all the octahedral voids are occupied, what is the formula of the solid?
6. In corundum, oxide ions are arranged in hexagonal close packing and aluminium ions occupy two-third of the octahedral voids. What is the formula of corundum?
7. The two ions A^+ and B^- have radii 88 and 200 pm respectively. In the close packed crystal of compound AB, predict the co-ordination number of A^+ .
8. If the radius of Mg^{2+} ion, Cs^+ ion, O_2^- ion, S^{2-} ion and Cl^- ion are 0.65 Å, 1.69 Å, 1.40 Å, 1.84 Å and 1.81 Å respectively, calculate the co-ordination numbers of the cations in the crystals of MgS, MgO and CsCl.
9. Predict the structure of MgO crystal and co-ordination number of its cation in which cation and anion radii are equal to 65 pm and 140 pm respectively.
10. In the compound AX, the radius of A^+ ion is 95 pm and that of X^- ion is 181 pm. Predict the crystal structure of AX and write the co-ordination number of each of the ions.
11. Predict the close packed structure of an ionic compound A^+B^- in which the radius of the cation = 148 pm and radius of anion = 195 pm. What is the co-ordination number of the cation?
12. The compound CuCl has ZnS (cubic) structure. Its density is 3.4 g/cm^3 . What is the length of the edge of the unit cell? (At masses Cu = 63.5, Cl = 35.5)
13. KF has NaCl structure. What is the distance between K^+ and F^- in the KF, if the density is 2.48 g cm^{-3} ?
14. The density of KBr is 2.75 g cm^{-3} . the length of the edge of the unit cell is 654 pm. Show that KBr has a face centered cubic structure.
15. A crystal of Lead (II) sulphide has NaCl structure. In this crystal the shortest distance between the Pb^{2+} ion and S^{2-} ion is 297 pm. What is the length of the edge of the unit cell in lead sulphide? Also calculate the unit cell volume.
16. The edge length of NaCl unit cell is 564 pm. What is the density of NaCl in g/cm^3 ?
[Na = 6.02×10^{23} , Na = 23.0 and Cl = 35.5]

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17. A compound AB crystallises in bcc lattice with the unit cell edge length of 380 pm. Calculate
 - (i) the distance between oppositely charged ions in the lattice.
 - (ii) radius of B^- if the radius of A^+ is 190 pm.
18. Write the co-ordination number of each ion in the following crystals
 - (i) NaCl (ii) CsCl (iii) ZnS (iv) CaF_2 (v) Na_2O
19. The density of KBr is 2.75 g/cm^3 . The length of the unit cell is 654 pm. Atomic mass of K = 39, Br = 80. Then what is the true about the predicted nature of the solid ?
 - (A) unit cell is fcc (B) $Z = 4$
 - (C) there are four constituents/unit cells
 - (D) there are 8 ions at corners and 6 at the centres of the faces
20. What is true about BCC unit cell ?
 - (A) No. of atoms in the unit cell is 2
 - (B) In addition to an atom at the centred of the body of the unit cell there are 8 atoms at 8 different corner
 - (C) $\frac{1}{8}$ atom at a corner of the unit cell (D) none of these
21. What is true about simple cubic type of unit cells ?
 - (A) Eight constituents are at different corners of the cube (B) $Z = 1$
 - (C) contribution by one corner is $\frac{1}{8}$ th of an atom (D) none of these
22. A solid has a structure in which W atoms are located at the corners of a cubic lattice, O atoms at the centre of the edges and Na atom at centre of the cube. The formula for the compound is
 - (A) $NaWO_2$ (B) $NaWO_3$ (C) Na_2WO_3 (D) $NaWO_4$
23. The number of octahedral sites per sphere in fcc structure is
 - (A) 8 (B) 4 (C) 2 (D) 1

13. Imperfections or defects in solids

At absolute zero, crystals tend to have a perfectly ordered arrangement. This arrangement corresponds to state of lowest energy. As the temperature increases, the crystals start deviating from the perfectly ordered arrangement. Any deviation from the perfectly ordered arrangement constitutes a defect or imperfection. These defects are sometimes called **thermodynamic defects** because the number of these defects depends on the temperature. Crystals may also possess addition defects due to the presence of impurities. Many properties of crystalline solids such as electrical conductivity and mechanical strength can be explained in terms of imperfections. Imperfections not only modify the properties of solids but also give rise to new properties.

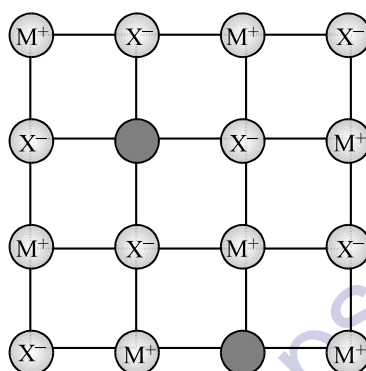
The defects which arises due to the irregularity in the arrangement of atoms or ions are called **atomic imperfections**. The atomic defects caused by missing or misplaced ions are called **point defects**. If the deviations from periodicity extend over microscopic regions of the crystal they are called lattice imperfections. Lattice imperfections may extend along lines (line defects) or planes (plane defects). Line defects are also called dislocations. Various types are as follows :

(i) Stoichiometric point defects

The compounds in which the numbers of positive and negative ions are exactly in the ratios indicated by their chemical formulae are called stoichiometric compounds. The defects that do not disturb the stoichiometry (the ratio of numbers of positive and negative ions) are called stoichiometric defects. These are of following types

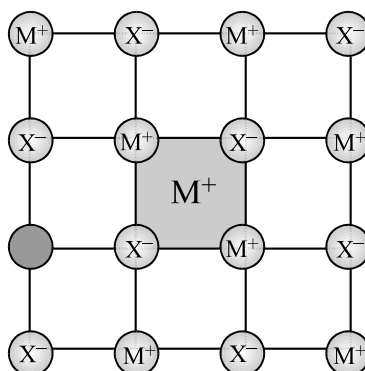
- (a) **Schottky Defects** : This type of defect is created when one positive ion and one negative ion are missing from their respective positions leaving behind a pair of holes. Schottky defects are more common in ionic compounds with high co-ordination number, and where the sizes of positive and negative ions are almost equal. For example, NaCl, KCl, CsCl and KBr.

The presence of large number of Schottky defects in crystal results in significant decrease in its density.



Schottky defect

- (b) **Interstitial Defects** – This type of defect is caused due to the presence of ions in the normally vacant interstitial sites in the crystal. The ions occupying the interstitial sites are called **interstitials**. The formation of interstitial defects is determined by the size of the interstitial ion.
- (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. For example, ZnS, AgCl, AgBr and AgI.



Frenkel defect

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Consequences of stoichiometric defects

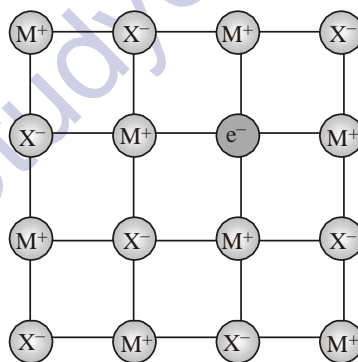
- (i) The presence of those defects in the crystal makes them good electrical conductors.
- (ii) The presence of holes in the Schottky type defects lowers their density.
- (iii) The presence of ions in interstitial sites in the Frenkel defects increases the dielectric constant of the crystals.

(ii) Non Stoichiometric defects

There are many compounds in which the ratio of positive and negative ions present in the compound differs from that required by ideal chemical formula of the compound. Such compounds are called non-stoichiometric or Bertholloid compounds. In these compounds composition may vary over a wide range. The defects which disturb the stoichiometry of the compound are called non-stoichiometric defects. These defects are either due to the presence of excess metal ions or excess non-metal ions.

(a) Metal excess Defects due to Anion Vacancies.

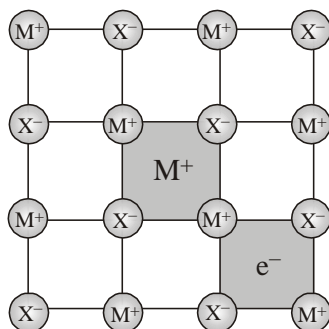
A compound may have excess metal ion if a negative ion is absent from its lattice site, leaving a 'hole', which is occupied by electron to maintain electrical neutrality. This type of defects are found in crystals which are likely to possess Schottky defects. Anion vacancies in alkali halides are produced by heating the alkali halide crystals in an atmosphere of alkali metal vapours. Under these conditions alkali metal atoms deposit on the surface of the alkali halide crystal, halide ions move to the surface and combine with metal ions. The electrons released during conversion of metal atoms into ions diffuse into the crystal and occupy the sites vacated by anions. The 'holes' occupied by electrons are called F-centres (or colour centres) and are responsible for the colour of the compound and many other interesting properties. For example, the excess sodium in NaCl makes the crystal appear yellow, excess potassium in KCl makes it violet and excess lithium in LiCl makes it pink. Greater the number of F-centres, greater is the intensity of colour. Solids containing F-centres are paramagnetic because the electrons occupying the 'holes' are unpaired.



(a) Metal excess defect due to anion vacancies

(b) Metal Excess Defects due to Interstitial Cations

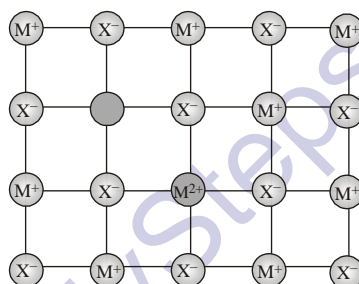
Another way in which metal excess defects may occur is, if an extra positive ion is present in an interstitial site. Electrical neutrality is maintained by the presence of an electron in the interstitial site. This type of defects are exhibited by the crystals which are likely to exhibit 'Frenkel' defects. For example, when ZnO is heated, it loses oxygen reversibly. The excess metal is accommodated in interstitial sites, with electrons trapped in the neighbourhood. The yellow colour and the electrical conductivity of the non-stoichiometric ZnO is due to these trapped electrons.



(b) Metal excess defect due to interstitial cation

(c) **Metal Deficiency due to cations vacancies.**

The non-stoichiometric compounds 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. It may be mentioned here that metal excess compounds and metal deficient compounds both act as semi-conductors. Metal excess compounds conduct electricity through normal electron conduction mechanism and are therefore n-type semiconductors. Metal deficient compounds conduct electricity through positive hole conduction mechanism and are therefore p-type semiconductors.

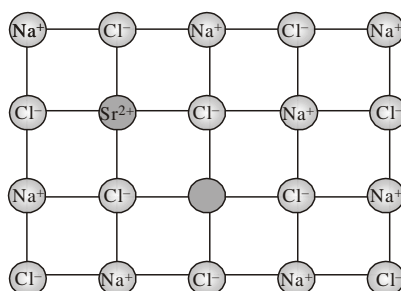


Metal deficiency due to cation vacancy

(iii) **Point Defects due to the Presence of Foreign Atoms (Impurity defect)**

Foreign atoms can occupy interstitial sites in a crystal example non-stoichiometric cuprous oxide (Cu_2O) can be prepared in laboratory. In this oxide copper to oxygen ratio is slightly less than 2 : 1. This is due to the reason that some of the positions which were to be occupied by Cu^+ ions are vacant whereas some positions are occupied by Cu^{2+} ions. Defects in the ionic solids may be introduced by adding impurity ions. If the impurity ions have different valence state than that of the host ions, vacancies are created. For example addition of SrCl_2 to NaCl yields solids solution where the divalent cation occupies Na^+ sites and produces cation vacancies equal to the number of the divalent ions occupying substitutional sites.

Similarly, AgCl crystals can be doped with CdCl_2 to produce impurity defects in a likewise manner.



Introduction of cation vacancy in NaCl by substitution of Na^+ with Sr^{2+} ion.

14. Properties of Solids

(i) Electrical Properties :

Solids can be broadly classified into three types, on the basis of electrical conductivity.

(a) Metals (conductors) (b) Insulators (c) Semi-conductors

Electrical conductivity of metals is very high and is of the order of $10^6 - 10^8 \text{ ohm}^{-1} \text{ cm}^{-1}$ whereas for insulators, it is of the order of $10^{-12} \text{ ohm}^{-1} \text{ cm}^{-1}$. Semi-conductors have intermediate conductivity in the range of $10^2 - 10^{-9} \text{ ohm}^{-1} \text{ cm}^{-1}$. Electrical conductivity of solids may arise through the motion of electrons and holes (positive) or through the motion of ions. The conduction through electrons is called n-type conduction and through (positive) holes is called p-type conduction. Pure ionic solids where conduction can take place only through movement of ions are insulators. The presence of defects in the crystal structure increases their conductivity.

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 decrease.

(ii) Magnetic Properties

Diamagnetic Materials : Those materials which are weakly repelled by the magnetic field are called diamagnetic materials. e.g. Cu^+ , TiO_2 , NaCl and benzene. They do not have unpaired electrons.

Paramagnetic Materials : The materials which are weakly attracted by magnetic field are called paramagnetic materials. These materials have permanent magnetic dipoles due to presence of atoms, ions or molecules with unpaired electron. e.g. O_2 , Cu^{2+} , Fe^{2+} etc. But these materials lose their magnetism in the absence of magnetic field.

Ferromagnetic Materials : The materials which show permanent magnetism even in the absence of magnetic field are called ferromagnetic materials. These materials are strongly attracted by the magnetic field. e.g. Fe, Co, Ni and CrO_2 . Ferromagnetism arises due to spontaneous alignment of magnetic moments of ions or atoms in the same direction.

Alignment of magnetic moments in opposite directions in a compensatory manner and resulting in zero magnetic moment gives rise to anti-ferromagnetism



for example, MnO , Mn_2O_3 and MnO_2 .

Alignment of magnetic moments in opposite directions resulting in a net magnetic moment due to unequal number of parallel and anti-parallel magnetic dipoles give rise to ferri-magnetism e.g. Fe_3O_4 . Ferromagnetic and ferrimagnetic substances change into paramagnetic substances at higher temperature due to randomisation of spins. Fe_3O_4 is ferrimagnetic at room temperature and becomes paramagnetic at 850 K.

(iii) Dielectric Properties

The electrons in insulators are closely bound to the individual atoms or ions and thus they do not generally migrate under the applied electric field. However, due to shift in charges, dipoles are created which results in polarisation. The alignment of these dipoles in different ways i.e. compensatory way (zero dipole) or non-compensatory way (net dipole) impart certain characteristic properties to solids.

If the dipoles align in such a way that there is net dipole moment in the crystals, these crystals are said to exhibit piezoelectricity or piezoelectric effect i.e. when such crystals are subjected to pressure

or mechanical stress, electricity is produced. Conversely, if an electric field is applied to such a crystal, the crystal gets deformed due to generation of mechanical strain. This is called inverse piezoelectric effect.

Some crystals which on heating, acquire electric charges on opposite faces, are said to exhibit pyroelectric effect.

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

Ferroelectric solids – Barium titanate (BaTiO_3), sodium potassium tartrate (Rochelle salt) and potassium hydrogen phosphate (KH_2PO_4). Anti-ferroelectric – Lead Zirconate (PbZrO_3).

Super Conducting Materials : The material which offer no resistance to the passage of electricity is called superconductor or super conducting material. In this state, the materials become diamagnetic and are repelled by the magnets. Most of the metals become super conducting at low temperatures ($2 - 5\text{K}$). Highest temperature at which super conductivity is known is 23K in alloys of niobium (e.g. Nb_3Ge). Many complex metal oxides have been found to possess super-conductivity at somewhat higher temperatures.

Material	Temperature
Nb_3Ge	23 K
$\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_{10}$	105 K
$\text{Ti}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_{10}$	125 K

15. Amorphous Solids

Solids, which do not have an ordered arrangement of their constituent atoms or ions but have a disordered or random arrangement are called amorphous solids e.g. ordinary glass.

Properties of Amorphous Solids

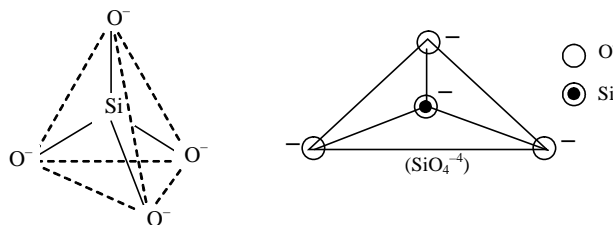
- (i) **Short range order :** Amorphous solids have a short range order like liquids i.e. the order does not extend to large three dimensional network.
- (ii) **No sharp melting point :** These solids melt over a range of temperature. This property is used in moulding and giving desired shape to the articles of glass.
- (iii) **Conversion into crystalline form on heating :** Amorphous solids, when heated and cooled slowly, become crystalline at certain temperature.

Use of Amorphous Solids

- (i) Amorphous solids, in the form of inorganic glasses, find application in construction, house-ware, laboratory ware etc.
- (ii) These solids are used in making tyres, shoe soles etc., in the form of rubber.
- (iii) Large number of plastics are being used in articles of daily use.
- (iv) These are used in photo voltaic cells (for converting sunlight into electricity).

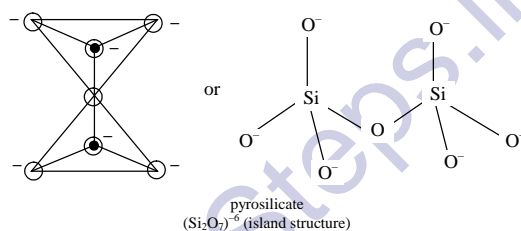
16. Silicates

Silicates are the compounds in which anions present are either discrete SiO_4^{4-} tetrahedra or a number of such units joined together through corners. The tetrahedral structure of SiO_4^{4-} is shown as

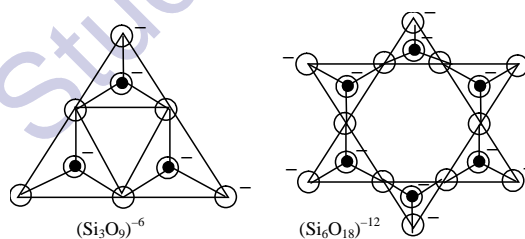


Types of Silicates : Silicates can be classified into different types depending upon the corners (0, 1, 2, 3, or 4) of the SiO_4^{4-} tetrahedron shared with other tetrahedra. If some of silicon atoms in SiO_4^{4-} are replaced by aluminium, we get aluminosilicates.

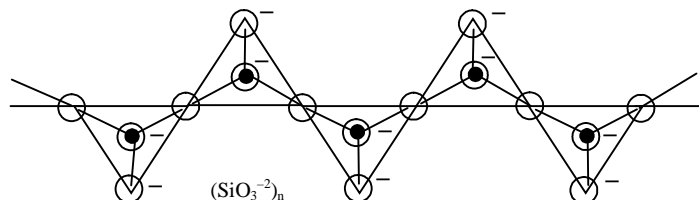
1. **Orthosilicate :** Simple silicates containing discrete SiO_4^{4-} tetrahedra e.g. ZrSiO_4 .
2. **Pyrosilicate :** Two SiO_4^{4-} tetrahedra sharing one corner.



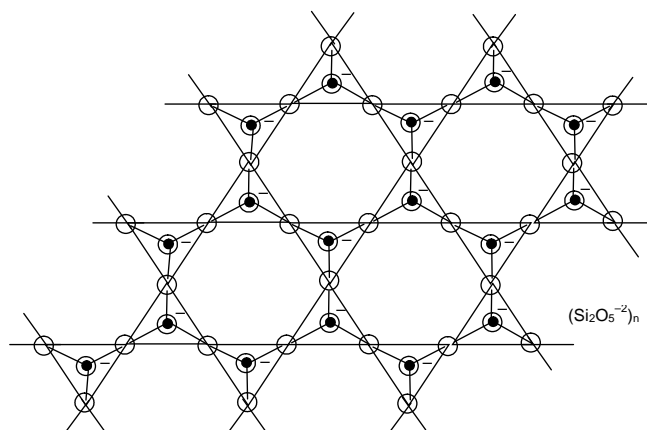
3. **Cyclic or ring silicate :** Two oxygen atoms per tetrahedron sharing to form closed rings with general formula $(\text{SiO}_3^{2-})_n$ or $(\text{SiO}_3)_n^{2n-}$ e.g. $\text{Ca}_3\text{Si}_3\text{O}_9$.



4. **Chain silicates :** Two oxygen atoms per tetrahedron sharing to form long linear single strand chain of general formula $(\text{SiO}_3)_n^{2n-}$ e.g. $\text{CaMg}(\text{SiO}_3)_2$.



5. **Sheet Silicates :** Sharing of three corners (i.e. three oxygen of each tetrahedron) resulting in an infinite two dimensional sheet structure of formula $(\text{Si}_2\text{O}_5)_n^{2-}$ or $(\text{Si}_2\text{O}_5^{2-})_n$
e.g. clay contains these anions.



6. **Three dimensional silicates :** If all the four corners are shared with other tetrahedra forming three dimensional network.

SOLVED PROBLEMS

SUBJECTIVE

Problem 1 :

A compound formed by elements A and B crystallizes in cubic structure where A atoms are at the corners of a cube and B atoms are at the face center. What is the formula of the compound?

Solution : A atom are eight corners of the cube. Hence no. of A atoms $= 8 \times \frac{1}{8} = 1$
B atoms are at the face centre of six faces. Hence no. of B atoms $= \frac{6}{2} = 3$
The formula is AB_3

Problem 2 :

NH_4Cl crystallizes in a body centred cubic lattice, with a unit cell distance of 387 pm. Calculate :

- (a) *the distance between the appositively charged ions in the lattice,* *and*
(b) *the radius of the NH_4^+ ion if the radius of the Cl ion is 181pm.*

Solution :

- (a) In a body centred cubic lattice, oppositely charged ions touch each other along the cross-diagonal of the cube. So, we can write,

$$2r^+ + 2r^- = \sqrt{3}a \quad \Rightarrow \quad r^+ + r^- = \frac{\sqrt{3}}{2}a = \frac{\sqrt{3}}{2}(387 \text{ pm}) = 335.15 \text{ pm}$$

- (b) Now, since $r^- = 181 \text{ pm}$
We have, $r^+ = (335.15 - 181) \text{ pm} = 154.15 \text{ pm}$

SOLID STATE

Problem 3 :

Iron occurs as BCC as well as FCC unit cell. If the effective radius of an atom of iron is 124 pm, compute the density of iron in both these structures.

Solution : In a body centred unit cell, atoms touch each other along the cross diagonal.

$$\text{Hence, } 4r = \sqrt{3}a$$

$$\Rightarrow a = \frac{4}{\sqrt{3}}r = \frac{4}{\sqrt{3}}(124 \text{ pm}) = 286.4 \text{ pm}$$

for BCC lattice, $Z = 2$, Hence

$$\rho = \frac{ZM}{a^3 N_A} = \frac{2 \times 55.8}{(286.4 \times 10^{-12})^3 \times 6.023 \times 10^{23}} = 7.887 \times 10^6 \text{ gm}^{-3} = 7.886 \text{ g cm}^{-3}$$

In a face centred unit cell, atoms touch each other along the face diagonals.

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

$$a = \frac{4}{\sqrt{2}}r = \frac{4}{\sqrt{2}}(124 \text{ pm}) = 350.7 \text{ pm}$$

For FCC lattice, $Z = 4$, hence,

$$\rho = \frac{4}{(350.7 \times 10^{-12})^3} \times \frac{55.8}{6.023 \times 10^{23}} = 8.89 \times 10^6 \text{ g m}^{-3} = 8.89 \text{ g cm}^{-3}$$

Problem 5 :

Silver has a cubic unit cell with a cell edge of 408 pm. Its density is 10.6 g cm^{-3} . How many atoms of silver are there in the unit cell? What is the structure of silver?

Solution : Length of the edge of unit cell = 408 pm,
 Volume of unit cell = $(408 \text{ pm})^3 = 67.92 \times 10^{-24} \text{ cm}^3$
 Mass of unit cell = Density \times Volume
 $= 10.6 \text{ g cm}^{-3} \times 67.92 \times 10^{-24} \text{ cm}^3 = 7.20 \times 10^{-24} \text{ g}$
 Mass of unit cell = No. of atoms in unit cell \times Mass of each atom

$$\text{Now, mass of each atom} = \frac{\text{Atomic mass}}{\text{Avogadro number}} = \frac{108}{6.023 \times 10^{23}} = 1.79 \times 10^{-22} \text{ g}$$

Let the unit cell contains 'n' atoms, so that

$$\text{Mass of unit cell} = n \times 1.79 \times 10^{-22} = 7.20 \times 10^{-22}$$

$$n = \frac{7.20 \times 10^{-22}}{1.79 \times 10^{-22}} = 4.02, \quad \therefore \text{Number of atoms present in a unit cell} = 4$$

Since the unit cell contains 4 atoms per unit cell, silver has face centred cubic lattice.

Problem 6 :

If NaCl is doped with 10^{-3} mol percent of SrCl_2 , what is the concentration of cation vacancy?

Solution: \square Concentration of cation vacancies = concentration of Sr^{2+} ion in the crystal

$$\begin{aligned} \therefore \text{Number of cationic vacancies per mol} &= \frac{10^{-3} \times 6.023 \times 10^{23}}{100} \\ &= 6.023 \times 10^{18} \text{ vacancies per mole} \end{aligned}$$

Problem 7 :

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 of 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 :

As $A^+ B^-$ has NaCl structure, A^+ ions will be present in the octahedral voids. Ideal radius of the cation will be equal to the radius of the octahedral void because in that case it will touch the anions and the arrangement will be close packed. Hence

$$\text{Radius of the octahedral void} = r_{A^+} = 0.414 \times r_{B^-} = 0.414 \times 250 = 103.4 \text{ pm}$$

$$\text{Radius of the tetrahedral site} = 0.225 \times r_{B^-} = 0.225 \times 250 \text{ pm} = 56.25 \text{ pm}$$

As the radius of the cation C^+ (180 pm) is larger than the size of the tetrahedral site, it cannot be slipped into it.

Problem 8 :

Calculate the void space in a primitive unit cell and also the fraction of the total volume occupied.

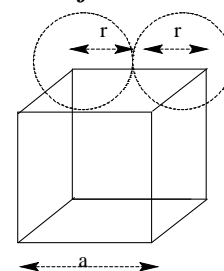
Solution :

$$\text{Volume of the cube} = a^3 = (2r)^3 = 8r^3$$

$$\text{Packing fraction} = \frac{\text{Volume of one atom}}{\text{Volume of the cube}} = \frac{\left(\frac{4}{3}\pi r^3\right)}{8r^3} \quad \begin{matrix} a = 2r \\ \left(\frac{4}{3}\pi r^3\right) \end{matrix}$$

$$= \frac{\pi}{6} = 0.52$$

$$\therefore \text{Void fraction} = 1 - 0.52 = 0.48 \quad , \quad \therefore \text{Void space} = 48\%$$



Problem 9 :

The density of solid argon is 1.65 g/mL at -233°C . If the argon atom is assumed to be sphere of radius $1.54 \times 10^{-8} \text{ cm}$, what percentage of solid argon is apparently empty space? (At. wt. of Ar = 40).

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

$$\text{Also, No. of atoms in 1.65g} = \frac{1.65}{40} \times 6.023 \times 10^{23}$$

$$\therefore \text{Total volume of all atoms of Ar in solid state} = \frac{4}{3}\pi r^3 \times \frac{1.65}{40} \times 6.023 \times 10^{23}$$

$$= \frac{4}{3} \times \frac{22}{7} \times (1.54 \times 10^{-8})^3 \times \frac{1.65}{40} \times 6.023 \times 10^{23} = 0.380 \text{ cm}^3$$

$$\text{Volume of solid argon} = 1 \text{ cm}^3$$

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

SOLID STATE

Problem 10 :

An element crystallizes as body centred cubic lattice. Its density is 7.12 g cm^{-3} and the length of the side of the unit cell is 2.88 \AA . Calculate the number of atoms present in 288 g of the element.

Solution :

$$\text{Volume of unit cell} = a^3 = (2.88 \text{ \AA})^3 = (2.88 \times 10^{-8} \text{ cm})^3 = 23.887 \times 10^{-24} \text{ cm}^3$$

$$\text{Volume of } 288 \text{ g of the element} = \frac{\text{Mass}}{\text{Density}} = \frac{288 \text{ g}}{7.12 \text{ g cm}^{-3}} = 40.449 \text{ cm}^3$$

Number of unit cells in the given volume of the element

$$= \frac{\text{volume of the element}}{\text{volume of the unit cell}} = \frac{40.449}{23.887 \times 10^{-24}} = 1.693 \times 10^{24}$$

Q Each unit cell of b.c.c. lattice contains 2 atoms

\therefore Number of atoms in 288 g of element

$$= \text{No. of unit cells} \times \text{no. of atoms per unit cell} = 1.693 \times 10^{24} \times 2 = 3.386 \times 10^{24}$$

Problem 11 :

Calculate the value of Avogadro number from the internuclear distance of adjacent ions in NaCl, 0.282 nm and the density of solid NaCl is $2.17 \times 10^3 \text{ kg/m}^3$. A unit cell contains 4 NaCl formula units.

Solution :

To calculate Avogadro number, that is, number of NaCl formula units per mol, let us assume 1 mole of NaCl.

$$\text{Volume of 1 mole of NaCl} = \frac{\text{mass of 1 mole}}{\text{density}} = \frac{58.5 \times 10^{-3}}{2.17 \times 10^3} = 2.7 \times 10^{-5} \text{ m}^3$$

$$\text{Volume of 1 unit cell} = a^3 = (0.564 \times 10^{-9})^3 = 1.79 \times 10^{-28} \text{ m}^3$$

$$\therefore \text{Number of unit cells per mol} = \frac{2.7 \times 10^{-5}}{1.79 \times 10^{-28}} = 1.51 \times 10^{23}$$

Since 1 unit cell of NaCl has 4 NaCl formula units,

$$\text{Avogadro number (formula units per mol)} = 4 \times (1.51 \times 10^{23})$$

$$= 6.04 \times 10^{23}$$

Problem 12 :

An ionic solid $A^+ B^-$ crystallizes as a body centred cubic structure. The distance between cation and anion in the lattice is 338 pm . Calculate the edge length of the unit cell.

Solution :

In a body centred cubic unit cell, the distance between the cation and anion ($r_+ + r_-$) is related to the edge length (a) by

$$r^+ + r^- = \sqrt{3} \times \frac{a}{2}, \quad \therefore a = \frac{2}{\sqrt{3}}(r^+ + r^-), \quad \text{It is given that } (r^+ + r^-) = 338 \text{ pm}$$

$$\therefore a = \frac{2}{\sqrt{3}} \times 338 \text{ pm} = \frac{676}{1.732} = 390.3 \text{ pm}$$

OBJECTIVE

Problem 1 :

A compound XY crystallizes in BCC lattice with unit cell edge length of 480 pm, if the radius of Y⁻ is 225 pm, then the radius of X⁺ is:

- (A) 190.70 pm (B) 225 pm (C) 127.5 pm (D) None

Solution : (A)

$$\text{For BCC lattice } 2(r^+ + r^-) = \sqrt{3}a \text{ or } r^+ = (\sqrt{3} \times 480) - 225 = 190.7 \text{ pm}$$

Problem 2 :

If the edge length of the unit cell of sodium chloride is 600 pm, and the ionic radius of Cl⁻ ion is 190 pm, then the ionic radius of Na⁺ ion is

- (A) 310 pm (B) 110 pm (C) 220 pm (D) None

Solution : (B)

$$r_{\text{Na}^+} + r_{\text{Cl}^-} = \frac{600}{2} = 300 \qquad r_{\text{Na}^+} = 300 - 190 = 110 \text{ pm}$$

Problem 3 :

In a cubic packed structure of mixed oxides, the lattice is made up of oxide ions, one fifth of tetrahedral voids are occupied by divalent (X²⁺) ions, while one half of the octahedral voids are occupied by trivalent ions (Y³⁺), then the formula of the oxide is:

- (A) XY₂O₄ (B) X₂YO₄ (C) X₄Y₅O₁₀ (D) X₅Y₄O₁₀

Solution : (C)

In CCP anions occupy primitives of the cube while cations occupied voids. In CCP there are two tetrahedral voids and one octahedral holes.

For one oxygen atom there are two tetrahedral holes and one octahedral hole. Since one fifth of the tetrahedral voids are occupied by divalent cations (X²⁺).

$$\therefore \text{ number of divalent cations in tetrahedral voids} = 2 \times \frac{1}{5}$$

Since half of the octahedral voids are occupied by trivalent cations (Y³⁺)

$$\therefore \text{ number of trivalent cations} = 1 \times \frac{1}{2}$$

So the formula of the compound is X_{2/5}Y_{1/2}O or X₄Y₅O₁₀

Problem 4 :

In a metal M having BCC arrangement edge length of the unit cell is 400 pm. The atomic radius of the metal is:

- (A) 100 pm (B) 141 pm (C) 173 pm (D) 200 pm

Solution : (C)

In a BCC lattice, an atom at the centre of the cube is in contact with atoms at the corners. Thus diagonal of the cube is

$$a\sqrt{3} = 4 \times \text{atomic radius} \Rightarrow r = 400 \times \frac{\sqrt{3}}{4} = 173 \text{ pm}$$

Problem 5 :

The ratio of closed packed atoms to tetrahedral holes in cubic close packing is

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

Solution : (B)

Every constituent has two tetrahedral voids

$$\text{In CCP lattice no. of atoms} = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$$

$$\therefore \text{ tetrahedral voids} = 4 \times 2 = 8 \qquad \text{Thus, ratio} = 4:8 \text{ i.e. } 1:2$$

SOLID STATE

Problem 6 :

In a face centred cubic arrangement of A and B atoms whose A atoms are at the corner of the unit cell and B atoms at the face centres. One of the B atoms is missing from one of the face in unit cell. The simplest formula of compound is :

- (A) AB_3 (B) A_8B_5 (C) A_2B_5 (D) $AB_{2/5}$

Solution : (C)

A face centred atom contributes $1/2$ atom in one unit cell. Therefore, missing one B atoms
..... $2/5$ or A_2B_5 .

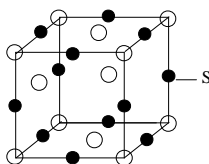
Problem 7 :

For the structure given below, the site marked as S is:

- (A) Cubic void (B) Tetrahedral void
(C) Octahedral void (D) None of these

Solution : (C)

Cubic voids are octahedral or tetrahedral, but for face centred cubic (FCC) lattice we have octahedral void.



Problem 8 :

An element occupying a BCC structure has 12.08×10^{23} unit cells. The total number of atoms of the element in the cells will be

- (A) 24.16×10^{23} (B) 36.18×10^{23}
(C) 6.04×10^{23} (D) 12.08×10^{23}

Solution : (A)

BCC unit cell contains 2 atoms

No. of atoms is 12.08×10^{23} unit cells $= 2 \times 12.08 \times 10^{23} = 24.16 \times 10^{23}$

Problem 9 :

The basic unit of all silicates is

- (A) SiO_2 (B) SiO_4^{2-} (C) SiO_3^{2-} (D) SiO_4^{4-}

Solution : (D)

SiO_4^{4-} is the basic unit of all silicates

Problem 10 :

A binary solid (A^+B^-) has a zinc blende structure with B^- ions constituting the lattice and A^+ ions occupying 25% tetrahedral holes. The formula of solid is:

- (A) AB (B) A_2B (C) AB_2 (D) AB_4

Solution : (C)

$$B^- \text{ ions in the unit cell} = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$$

$$A^+ \text{ ions occupy 25\% of the tetrahedral holes} = \frac{8 \times 25}{100} = 2$$

Thus formula is A_2B_4 or AB_2

1. Daily Practice Problem Sheet

- | | | | | |
|---|--|---------------------------------|-----------------------------|----------|
| 1. $[AB_3]$ | 2. $[PQ]$ | 3. $[XY]$ | 4. $[XY]$ | 5. $[9]$ |
| 6. $[AB]$ | 7. $[438.5 \text{ pm}]$ | 8. $[173.2 \text{ pm}]$ | 9. $[1414 \text{ pm}]$ | |
| 10. $[6.23 \text{ g/cm}^3]$ | 11. $[24.17 \times 10^{23} \text{ atoms}]$ | | 12. $[1.02 \text{ g/cm}^3]$ | |
| 13. $[19.4 \text{ g/cm}^3, 143.9 \text{ pm}]$ | | 14. $[41.67 \text{ g cm}^{-3}]$ | 15. $[BCC]$ | |
| 16. $[400 \text{ pm}]$ | 17. $[96.0]$ | 18. $[6.02 \times 10^{23}]$ | 19. $[37.6]$ | |

2. Daily Practice Problem Sheet

- | | | |
|--|--------------------------------|---|
| 1. $[103.4 \text{ pm}, \text{Cannot}, 56.25 \text{ pm}]$ | 2. $[241 \text{ pm}]$ | 3. $[410.6 \text{ pm}]$ |
| 4. $[100 \text{ pm}, \text{Yes}]$ | 5. $[A_2B]$ | 6. $[Al_2O_3]$ |
| 7. $[6]$ | | |
| 8. $[4, 6, 8]$ | 9. $[6, \text{octahedral}]$ | 10. $[6, \text{octahedral}]$ |
| 11. $[8, \text{body-centered cubic}]$ | | |
| 12. $[578 \text{ pm}]$ | 13. $[268.8 \text{ pm}]$ | 14. $[N = 6.023 \times 10^{23} \text{ mol}^{-1}, \text{At. mass ; K} = 39, \text{Br} = 80]$ |
| 15. $[a = 5.94 \times 10^{-8} \text{ cm}, V = a^3 = 2.096 \times 10^{-22} \text{ cm}^3]$ | 16. $[2.16 \text{ g cm}^{-3}]$ | |
| 17. $[(i) 329 \text{ pm} (ii) 458.9 \text{ pm}]$ | 19. $[(A) (B), (C), (D)]$ | |
| 20. $(A) (B), (C)$ | 21. $(A) (B), (C)$ | 22. (B) |
| | | 23. (D) |

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