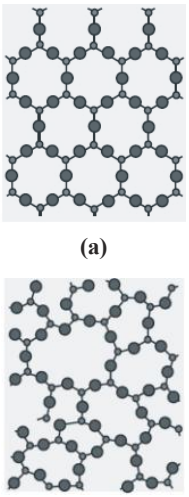
SOLID STATE

1. THE SOLID STATE :

The solid are characterised by incompressibility, rigidity and mechanical strength. The molecules, atoms or ions in solids are closely packed i.e. they are held together by strong forces and can not move about at random. Thus solids have definite volume, shape, slow diffusion, low vapour pressure and possesses the unique property of being rigid.

2. AMORPHOUS AND CRYSTALLINE SOLIDS

Solids can be classified as *crystalline* or *amorphous* on the basis of the nature of order present in the arrangement of their constituent particles. A crystalline solid usually consists of a large number of small crystals, each of them having a definite characteristic geometrical shape. In a crystal, the arrangement of constituent particles (atoms, molecules or ions) is ordered. It has ***long range order*** which means that there is a regular pattern of arrangement of particles which repeats itself periodically over the entire crystal. Sodium chloride and quartz are typical examples of crystalline solids. An amorphous solid (Greek *amorphos* = no form) consists of particles of irregular shape. The arrangement of constituent particles (atoms, molecules or ions) in such a solid has only ***short range order***. In such an arrangement, a regular and periodically repeating pattern is observed over short distances only.



(a) **(b)**

Fig. 1.1 : Two dimensional structure of (a) quartz and (b) quartz glass

Such portions are scattered and in between, the arrangement is disordered. The structures of quartz (crystalline) and quartz glass (amorphous) are shown in Fig. 1.1 (a) and (b) respectively. While the two structures are almost identical, yet in the case of amorphous quartz glass there is no *long range order*. The structure of amorphous solids is similar to that of liquids. Glass, rubber and plastics are typical examples of amorphous solids. Due to the differences in the arrangement of the constituent particles, the two types of solids differ in their properties.

Space for Notes

Crystalline solids have a sharp melting point. On the other hand, amorphous solids soften over a range of temperature and can be moulded and blown into various shapes. On heating they may become crystalline at some temperature. Some glass objects from ancient civilisations are found to become milky in appearance because of some crystallisation. Like liquids, amorphous solids have a tendency to flow, though very slowly. Therefore, sometimes these are called ***pseudo solids*** or ***super cooled liquids*****.** Glass panes fixed to windows or doors of old buildings are invariably found to be slightly thicker at the bottom than at the top. This is because the glass flows down very slowly and makes the bottom portion slightly thicker.

Crystalline solids are ***anisotropic*** in nature, that is, some of their physical properties like electrical resistance or refractive index show different values when measured along different directions in the same crystals. This arises from different arrangement of particles in different directions. This is illustrated in Fig. 1.2. Since the arrangement of particles is different along different directions, the value of same physical property is found to be different along each direction. Amorphous solids on the other hand are ***isotropic*** in nature. It is because there is no *long range* order in them and arrangement is irregular along all the directions. Therefore, value of any physical property would be same along any direction. These differences are summarised in Table below :

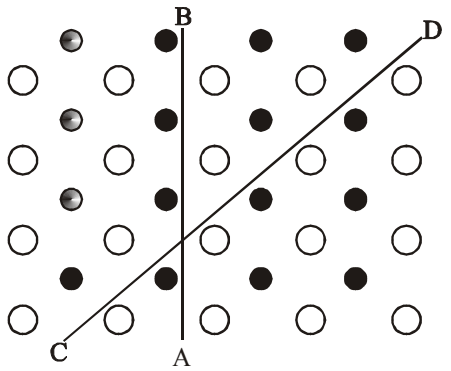


Fig. 1.2 : Anisotropy in crystals is due to different arrangement of particles along different directions.

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Distinction between Crystalline and Amorphous Solids

Property	Crystalline Solids	Amorphous Solids
Shape	Definite characteristic geometrical shape	Irregular shape
Melting point	Melt at a sharp and characteristic temperature	Gradually soften over a range of temperature
Cleavage property	When cut with a sharp edged tool, they split into two pieces and the newly generated surfaces are plane and smooth	When cut with a sharp edged tool, they cut into two pieces with irregular surfaces
Heat of fusion	They have a definite and characteristic heat of fusion	They do not have definite heat of fusion
Anisotropy	Anisotropic in nature	Isotropic in nature
Nature	True solids	Pseudo solids or super cooled liquids
Order in arrangement of constituent particles	Long range order	Only short range order.

Ex.1 Classify the following as amorphous or crystalline solids :

(a) Polyurethane (b) Napthalene

(c) Benzoic acid (d) Teflon

(e) Potassium nitrate (f) Cellophane

(g) Polyvinyl chloride (h) Fibre glass

(i) Copper

Sol. Crystalline : (b) , (c) , (e) , (i)

Amorphous : (a) , (d) , (f) , (g), (h)

Note : Polymeric substances are generally amorphous.

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3. TYPES OF THE CRYSTALLINE SOLID

Types of Solid	Constituent Particles	Bonding/ Attractive forces	Examples	Physical Nature	Electrical Conductivity	Melting Point
(1) Molecular Solids (i) Non polar	Molecules	Disppersion or London forces	Ar, CCl_4, H_2, I_2 CO_2	Soft	Insulator	Very low
(ii) Polar		Dipole-dipole	HCl, SO_2	Soft	Insulator	Low
(iii) Hydrogen bonded		Hydrogen bonding	H_2O (ice)	Hard	Insulator	Low
(2) Ionic Solids	Ions	Coulombic or electrostatic	NaCl, MgO, ZnS, CaF_2	Hard but brittle	Insulator in solid state but conductors in molten state and in aqueous solutions	High
(3) Metallic Solids	Positive ions in a sea of delocalised electrons	Metallic bonding	Fe, Cu, Ag, Mg	Hard but malleable and ductile	Conductors in solid state as well as in molten state	Fairly high
(4) Covalent or network Solids	Atoms	Covalent bonding	SiO_2 (quartz) SiC, C (diomond) AIN,	Hard	Insulators	Very high
			C(graphite)	Soft	Conductor	

Ex.2 ***Classify the following solids in different categories based on the nature of intermolecular forces operating in them :***

(a) Potassium sulphate (K_2SO_4) **(b)** Tin (Sn)

(c) Benzene (C_6H_6) **(d)** Urea (NH_2CONH_2)

(e) Ammonia (NH_3) **(f)** Water (H_2O)

(g) Zinc sulphide (ZnS) **(h)** Graphite (C)

(i) Rubidium (Rb) **(j)** Argon (Ar)

(k) Silicon carbide (SiC) **(*l*)** Bronze

Space for Notes

Sol. Ionic solids : (a), (g)

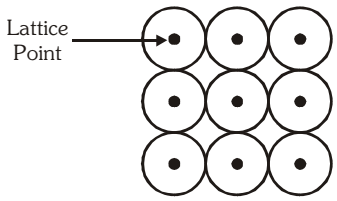
Metallic solids : (b), (i), (*l*)

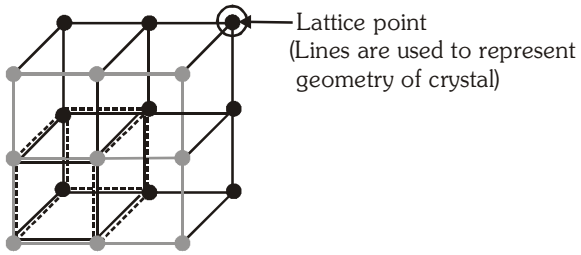
Molecular solids : (c), (d), (e), (f), (j)

Covalent network solids.: (h), (k)

4.0 SOME BASIC DEFINITION :

4.1 SPACE LATTICE (CRYSTAL LATTICE :





The main characteristic of crystalline solids is a regular and repeating pattern of constituent particles. If the three dimensional arrangement of constituent particles in a crystal is represented diagrammatically, in which each particle is depicted as a point, the arrangement is called crystal lattice. Thus, ***a regular three dimensional arrangement of points in space is called a crystal lattice***. A portion of a crystal lattice is shown in Fig. The following are the characteristics of a crystal lattice:

(a) Each point in a lattice is called ***lattice point*** or ***lattice site***.

(b) Each point in a crystal lattice represents one constituent particle which may be an atom, a molecule (group of atoms) or an ion.

(c) Lattice points are joined by straight lines to bring out the geometry of the lattice.

4.2. UNIT CELL :

Unit cell is the smallest portion of a crystal lattice which , when repeated in different directions, generates the entire lattice.

A unit cell is characterized by the edge lengths a, b and c along the three edges of the unit cell and the angles α, β and γ between the pair of edges : bc, ca and ab, respectively.

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TYPE OF UNIT CELLS -

4.2.1 Primitive and Centred Unit cells

Unit cells can be broadly divided into two categories, primitive and centred unit cells.

(a) Primitive Unit Cells (P)

When constituent particles are present only on the corner positions of a unit cell, it is called as **primitive unit cell.**

(b) Centred Unit Cells : When a unit cell contains one or more constituent particles present at positions other than corners in addition to those at corners, it is called a centred unit cell. **Centred unit cells** are of three types :

(i) **Body-Centred Unit Cells (I) :** Such a unit cell contains one constituent particle (atom, molecule or ion) at its body-centre besides the ones that are at its corners.

(ii) **Face-Centred Unit Cells (F) :** Such a unit cell contains one constituent particle present at the centre of each face, besides the ones that are at its corners.

(iii) **End-Centred Unit Cells (E) :** In such a unit cell, one constituent particle is present at the centre of any two opposite faces besides the ones present at its corners.

4.3. THE SEVEN CRYSTAL SYSTEMS

On the basis of the classification of symmetry, the lattice have been divided into seven systems. These can be grouped into 7 crystal systems. These seven systems with the characteristics of their axes (angles and intercepts) along with some examples of each are given in the following table :

Seven Primitive Unit cells and their Possible Variations as Centred Unit Cells

Crystal system	Possible Variations	Axial distance or edge lengths	Axial angles	Examples
Cubic	Primitive, body-centred, Face centre	$a = b = c$	$\alpha = \beta = \gamma = 90°$	NaCl, Zinc blende, Cu
Tetragonal	Primitive, Body-centred	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	White tin, SnO_2,TiO_2, $CaSO_4$
Orthorhombic	Primitive, Body-centred, Face-centred, End-centred	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	Rhombic sulphur, KNO_3, $BaSO_4$
Hexagonal	Primitive	$a = b \neq c$	$\alpha = \beta = 90°$, $\gamma = 120°$	Graphite, ZnO, CdS,
Rhombohedral or Trigonal	Primitive	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	Calcite ($CaCO_3$), HgS (Cinnabar)
Monoclinic	Primitive, End-centred	$a \neq b \neq c$	$\alpha = \gamma = 90°$, $\beta \neq 90°$	Monoclinic sulphur,$Na_2SO_4 \cdot 10H_2O$
Triclinic	Primitive	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	$K_2Cr_2O_7$,$CuSO_4.5H_2O$,H_3BO_3

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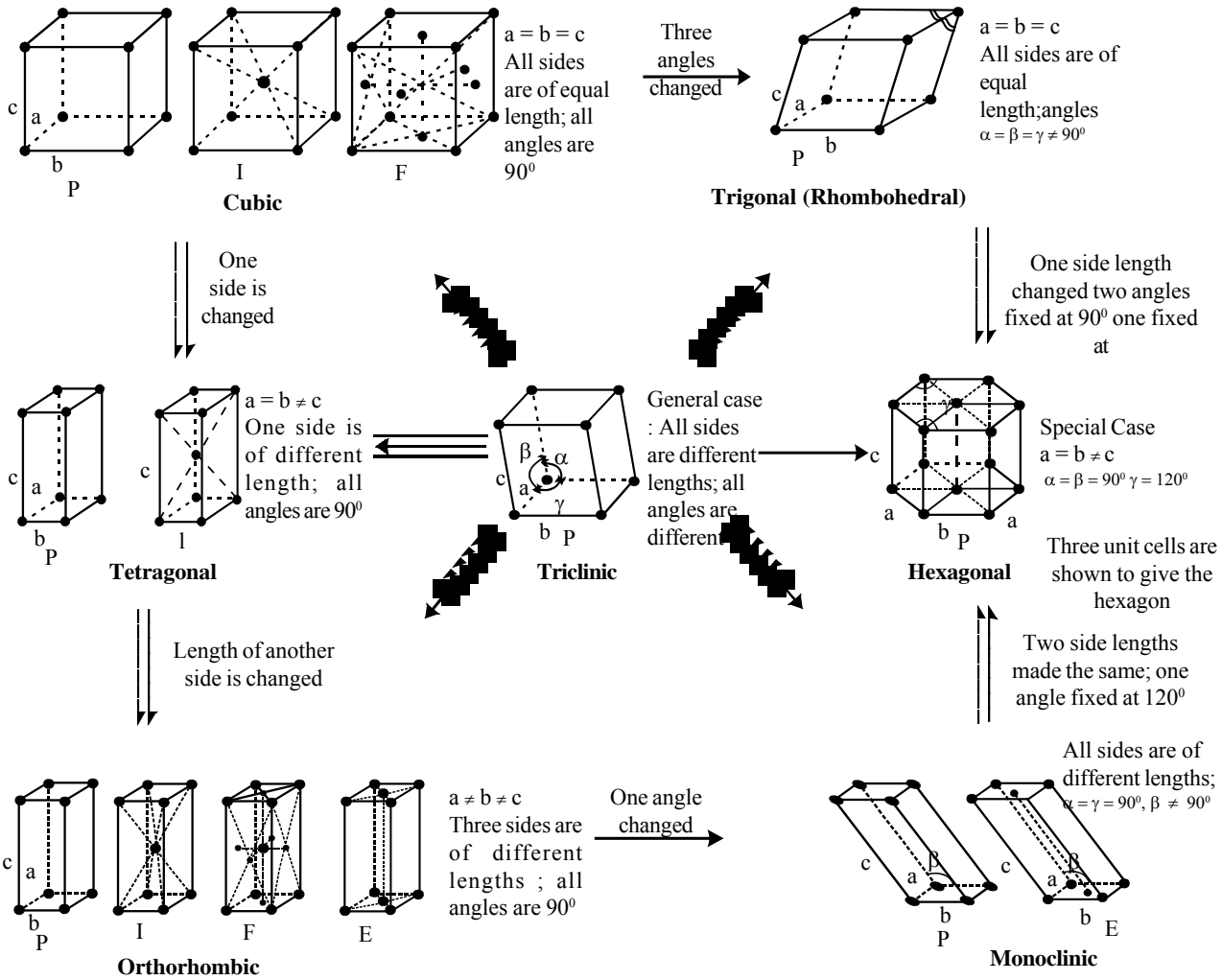
4.4. BRAVAIS LATTICES : There are 14 Bravais lattices :



4.5. CO-ORDINATION NUMBER :

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

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4.6. PACKING EFFICIENCY OR PACKING DENSITY (P.E.) :

Packing efficiency is defined as the ratio of volume occupied by the constituent particles to the total volume of the crystalline substance.

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

$$\text{P.E.} = \frac{\text{Volume occupied by particles present in unit cell}}{\text{Volume of Unit Cell}}$$

$$\text{P.E.} = \frac{Z \times (4/3)\pi r^3}{V}$$, where Z = number of atoms present in unit cell

4.7. *DENSITY OF THE CRYSTAL :*

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

Mass of the unit cell = Number of particles present in a unit cell × Mass of one particles = Z × m

$$\text{But mass of one particles (m)} = \frac{\text{Particle mass}}{\text{Avogadro Number}} = \frac{M}{N_A}$$

$$\text{Mass of an unit cell} = Z \times \frac{M}{N_A}$$

$$\text{Density of an unit cell} = \frac{Z \times \frac{M}{N_A}}{V}$$

$\therefore$ **Density of Crystal, d = Density of an unit cell = $\frac{Z \times M}{V \times N_A}$ g cm^{-3}**

5.0 ANALYSIS OF CUBIC CRYSTAL :

5.1. GEOMETRY OF A CUBE

Number of corners = 8

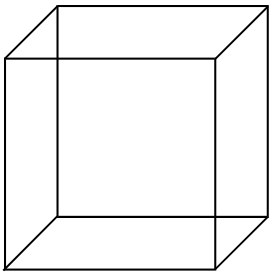
Number of faces = 6

Number of edges = 12

Number of cube centre = 1

Number of cube diagonals = 4

Number of face diagonals = 12



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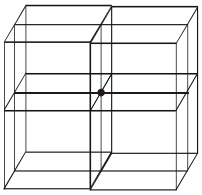
5.2 CONTRIBUTION OF A CONSTITUENT PARTICLE AT DIFFERENT SITES OF CUBE :

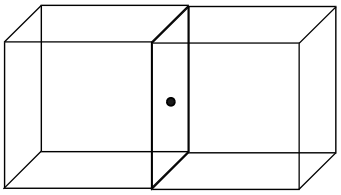
5.2.1 A corner of a cube is common in 8 cubes.

So $\frac{1}{8}$ th part of a particle is present at this corner of cube.



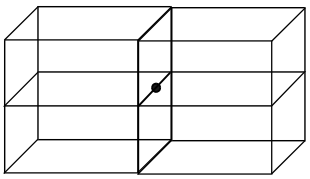
5.2.2 A face of a cube is common is 2 cubes.

So $\frac{1}{2}$ th part of a particle is present at the face of a cube.



5.2.3 An edge of a cube is common in four cubes,

so $\frac{1}{4}$ th part of particle is present at the edge of a cube

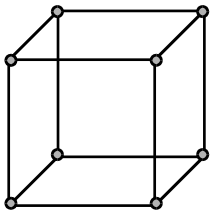


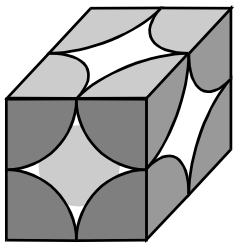
5.3 TYPE OF CUBIC UNIT CELL :

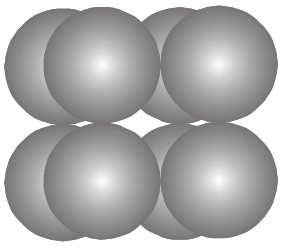
5.3.1 Simple/Primitive/Basic Unit cell (Simple cubic, SC) ;

A unit cell having lattice point only at corners called as primitive or simple unit cell. In this case there is one particle at each of the eight corners of the unit cell.

Considering a particles at one corner as the centre, it will be found that this atom is surrounded by six equidistant neighbours (particles) and thus the co-ordination number will be six. If 'a' is the side of the unit cell, then the distance between the nearest neighbours shall be equal to 'a'.





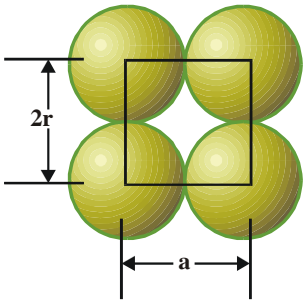


Space for Notes

(a) Relationship between Edge length 'a' and Particle radius 'r' :-

a = 2r

i.e., $\boxed{r = \frac{a}{2}}$



(One face of SC)

(b) Number of particles present in unit cell (Z) : In this case one particle lies at each corner. Hence simple cubic unit cell contains a total of $\frac{1}{8}\times 8 = 1$ particle /unit cell.

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

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

$$P.E. = \frac{1\times\frac{4}{3}\times\pi\times\left(\frac{a}{2}\right)^3}{a^3} = \frac{\pi}{6} = 0.52 \text{ or } 52\% \qquad \left[r = \frac{a}{2} \text{ and } V = a^3, Z = 1\right]$$

In SC, 52% of total volume is occupied by particles.

$\therefore$ Void space $\approx$ (100 – 52)= 48 %

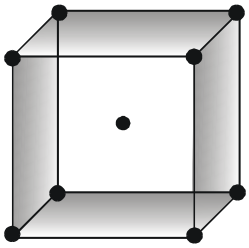
(d) Coordination number (CN)

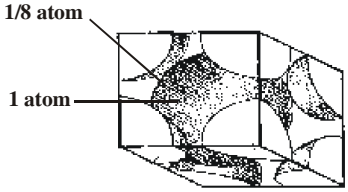
Nearest neighbour	Distance	Number
1	a	6
2	$\sqrt{2}$a	12
3	$\sqrt{3}$a	8

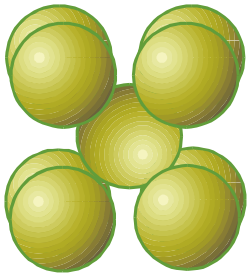
Space for Notes

5.3.2. Body Centred Cubic unit cell (BCC):

A unit cell having lattice point at the body centre in addition to the lattice points at every corner is called as body centered unit cell. Here the central particle is surrounded by eight equidistant particles and hence the co-ordination number is eight. The nearest distance between two particles will be $\frac{a\sqrt{3}}{2}$

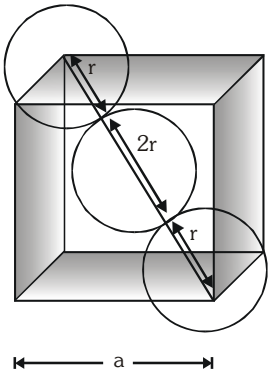






(a) Relationship between edge length 'a' and particle radius 'r' :

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



So, $\sqrt{3}a = 4r$

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

(b) Number of particle present in unit cell (Z):

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

(Corner) (Body centre)

In this case one particle lies at the each corner of the cube. Thus contribution of the 8 corners is $\left(\frac{1}{8}\times 8\right) = 1$, while that of the body centred is 1 in the unit cell. Hence total number of particles per unit cell is 1 + 1 = 2

Space for Notes

(c) Packing efficiency :

$$\text{P.E.} = \frac{Z \times \frac{4}{3}\pi r^3}{V} = \frac{2 \times \frac{4}{3} \times \pi \left(\frac{\sqrt{3}a}{4}\right)^3}{a^3} = \frac{\sqrt{3}\pi}{8} = 0.68 \text{ or } 68\% \qquad \left[Z = 2, r = \frac{\sqrt{3}a}{4}, V = a^3\right]$$

In BCC, 68% of total volume is occupied by particles.

$\therefore$ Void space = 100 – 68 = 32 %

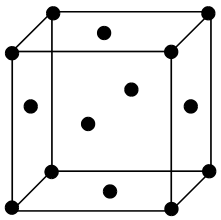
(d) Coordination number (CN)

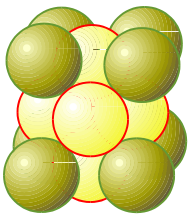
Nearest neighbour	Distance	Number
1	$\sqrt{3}\frac{a}{2}$	8
2	a	6
3	$\sqrt{2}a$	12

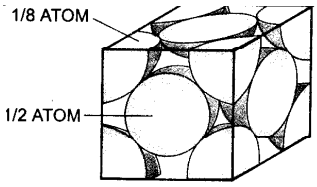
5.3.3 Face Centred Cubic unit cell (FCC):

A unit cell having lattice point at every face centre in addition to the lattice point at every corner called as face centred unit cell.

In this case there are eight particles at the eight corners of the unit cell and six particles at the centre of six faces. Considering a particle at the face centre as origin, it will be found that this face is common to two cubes and there are twelve points surrounding it situated at a distance which is equal to half the face diagonal of the unit cell. Thus the co-ordination number will be twelve and the distance between the two nearest particles will be $\frac{a}{\sqrt{2}}$.







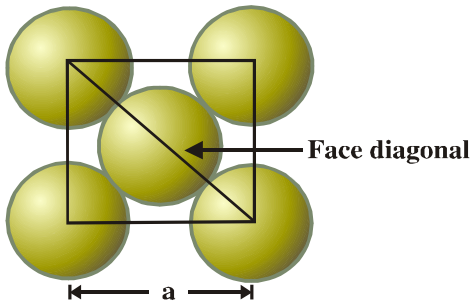
Space for Notes

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

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

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

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



(b) Number of particles per unit cell : (Z)

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

In this case, one particle lies at the each corner of the cube and one particle lies at the centre of each face of the cube. It may noted that only 1/2 of each face sphere lie within the unit cell and there are six such faces. The total contribution of 8 corners is $\left(\frac{1}{8}\times 8\right) = 1$, while that of 6 face centred particles is $\left(\frac{1}{2}\times 6\right) = 3$ in the unit cell.

Hence, total number of particles per unit cell is $1 + 3 = 4$

(c) Packing efficiency :

$$\text{P.E.} = \frac{Z\times\frac{4}{3}\pi r^3}{V} \qquad [Z = 4,\ r = \frac{a}{2\sqrt{2}},\ V = a^3]$$

$$= \frac{4\times\frac{4}{3}\pi\times\left(\frac{a}{2\sqrt{2}}\right)^3}{a^3} = \frac{\pi}{3\sqrt{2}} = 0.74 \text{ or } 74\%$$

In FCC, 74% of total volume is occupied by particles. This is maximum for crystals having identical particles.

$\therefore$ Void space = 100 – 74 = 26 %

Space for Notes

(d) Coordination number (CN)

Nearest neighbour	Distance	Number
1	$\frac{a}{\sqrt{2}}$	12
2	a	6
3	$\sqrt{\frac{3}{2}}a$	24

5.4 SUMMARY OF CUBIC CRYSTAL :

Unit cell	No. of particles per unit cell (Z)	2r =	CN	Volume occupied by particles (%)
Simple cube (SC)	1	a	6	52
Body centred cube (BCC)	2	$\frac{a\sqrt{3}}{2}$	8	68
Face centred cube (FCC)	4	$\frac{a}{\sqrt{2}}$	12	74

CLASS ILLUSTRATION - 01

1. ***A solid crystallises in cubic crystal in which 'X' atoms occupy all the corners and body centres and 'Y' atoms occupy all the face-centres. What is the simplest formula of solid?***
2. ***A metal has bcc structure and the edge length of its unit cell is 3.04 Å. The volume of the unit cell in cm^3 will be***
3. ***The density of Al is 5.4 g/cm^3. If it crystallise in fcc lattice, determine its atomic radius.***
4. ***An element (atomic mass = 60) having face centred cubic crystal has a density of 6.23 g cm^{-3}. What is the edge length of the unit cell ?***

   (Avogadro constant, $N_A = 6.02 \times 10^{23}$ mol^{-1})

Space for Notes

5. *An element (molar mass = 60 gm/mole) crystallises in CCP lattice. If density is 6.25 gm/cm^3 and the distance between next nearest neighbour is dÅ, then the value of 'd' is ($N_A = 6 \times 10^{23}$).*

6. *Potassium crystallizes in a body-centred cubic lattice with edge length, a = 5.2 Å.*

   (a) What is the distance between nearest neighbours?

   (b) What is the distance between next-nearest neighbours?

   (c) How many nearest neighbours does each K atom have?

   (d) How many next-nearest neighbours does each K atom have?

   (e) What is the density of crystalline potassium?

   (Given : K = 39, $(5.2)^3 = 140$)

7. *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 2.4×10^{24} atoms. ($N_A = 6 \times 10^{23}$)*

8. *Iron crystallizes in several modifications. At about 910°C, the body-centred cubic 'α' form undergoes a transition to the face-centred cubic 'γ' form. Assuming that the distance between nearest neighbours is the same in the two forms at the transition temperature, the ratio of the density of γ iron to that of α iron at the transition temperature, x : 1, then the value of $(3\sqrt{6x})$ is.*

9. *An element crystallizes into a structure which may be described by a cubic type of unit cell having one atom on each corner of the cube and two extra atoms on one of its body diagonal. If the volume of this unit cell is 2.4×10^{-23} cm^3 and density of element is 7.2 g cm^{-3}, calculate the number of atoms present in 288 g of element.*

6. CLOSE PACKING OF IDENTICAL SOLID SPHERES

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

Space for Notes

To clearly understand the packing of these spheres, the packing can be categorised as :

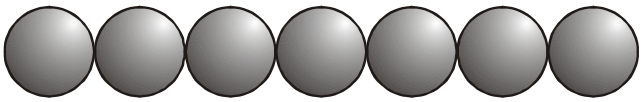
(i) Close packing in one dimension.

(ii) Close packing in two dimension.

(iii) Close packing in three dimension.

6.1 CLOSE PACKING IN ONE DIMENSION :

In one dimension , only one arrangement of spheres is possible as shown in fig.



Close packing of spheres in one dimension

Each sphere is touched by other two spheres, hence coordination numbers of packing is two.

6.2 CLOSE PACKING IN TWO DIMENSION :

Two possible types of two dimensional packing are

(i) Square close packing in two dimension.

(ii) Hexagonal close packing in two dimension.

(i) Square close packing in two dimension :

When two rows are placed in such a manner, that spheres of one row are placed immediately below of the other, the resulting packing is called two dimensional square close packing.

(i) Since all the rows are identical, the packing is called AAA ..... type packing.

(ii) Each sphere is touched by four other, hence coordination number is four.

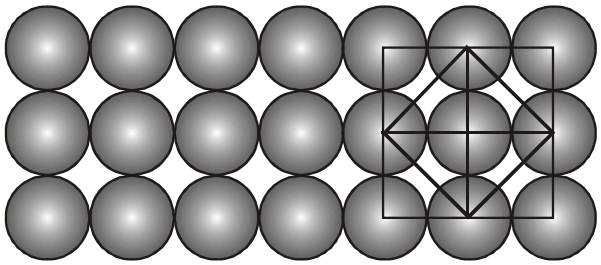
(iii) If centres of spheres are connected, square cells are formed , hence it also called two dimensional square packing.

(iv) This type of packing is not very effective in terms of utilisation of space.

(v) Packing efficiency in 2-D $= \frac{1 \times \pi r^2}{a^2} = \frac{1 \times \pi (a/2)^2}{a^2} = \frac{\pi}{4} = 0.78$ or 78%

(vi) Packing efficiency in 3-D $= \frac{1 \times \frac{4}{3}\pi\left(\frac{a}{2}\right)^3}{a^3} = 0.52$ or 52% [In 3-D, its unit cell is simple cubic]

Space for Notes



(ii) Hexagonal close packing in two dimension :

If various one dimensional close pack rows are placed in such a way that spheres of top row fits in depression of bottom row spheres, the resulting packing is called two dimensional hexagonal close packing.

(i) Every third row sphere comes exactly at top of first row sphere, hence the packing is called ABABAB ..... packing.

(ii) If centres are joined, hexagonal unit cells are formed. Hence this is called two dimensional hexagonal close packing.

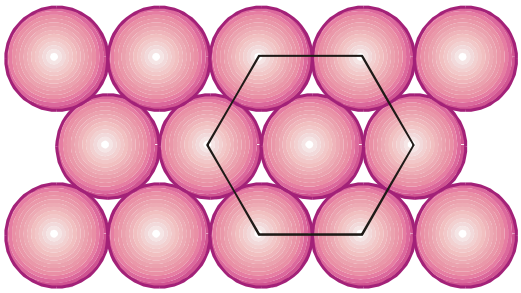
(iii) This packing is most efficient in utilising space in two dimensional arrangement.

(iv) Each sphere is touched by six other, hence coordination number is six.

(v) Packing efficiency in 2-D $= \dfrac{3\times\pi\left(\frac{a}{2}\right)^2}{\frac{a^2\sqrt{3}}{4}\times 6} = \dfrac{\pi}{2\sqrt{3}} = 0.90$ or 90%

(vi) Packing efficiency in 3-D $= \dfrac{3\times\frac{4}{3}\pi\left(\frac{a}{2}\right)^3}{\frac{a^2\sqrt{3}}{4}\times 6\times a} = \dfrac{\pi}{3\sqrt{3}} = 0.60$ or 60%

Space for Notes



6.3 CLOSE PACKING IN THREE DIMENSIONS :

When two dimensional packing structure are arranged one above the other, depending upon type of two dimensional arrangement in a layer, and the relative positions of spheres in above or below layer, various types of three dimensional packing results. To define 3-D lattice, six lattice parameters are required - 3 edge lengths & 3 angles.

(i) Simple cubic packing (A A A A .....)

(ii) Hexagonal close packing (AB AB AB .....)

(iii) Cubic close packing or face centred cubic (ABC ABC...)

6.3.1 Three dimensional close packing from square two dimensional packing (Simple cubic packing in three dimension)

The two dimensional square close packed layer are placed, in such a manner that spheres in each layer comes immediately on top of below layer, simple cubic packing results. Important points :

(i) Spheres all aligned vertically and horizontally in all directions.

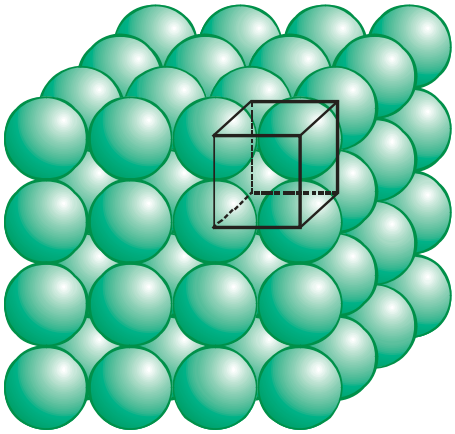
(ii) The unit cell for this packing is simple cubic unit cell.

(iii) In this packing, only 52% of available space is occupied by spheres.

(iv) Each sphere is in contact will six spheres and hence coordination number is 6.

(v) Packing efficiency $= \frac{1 \times \frac{4}{3}\pi r^3}{(2r)^3} = \frac{\pi}{6} \approx 0.52$

Space for Notes

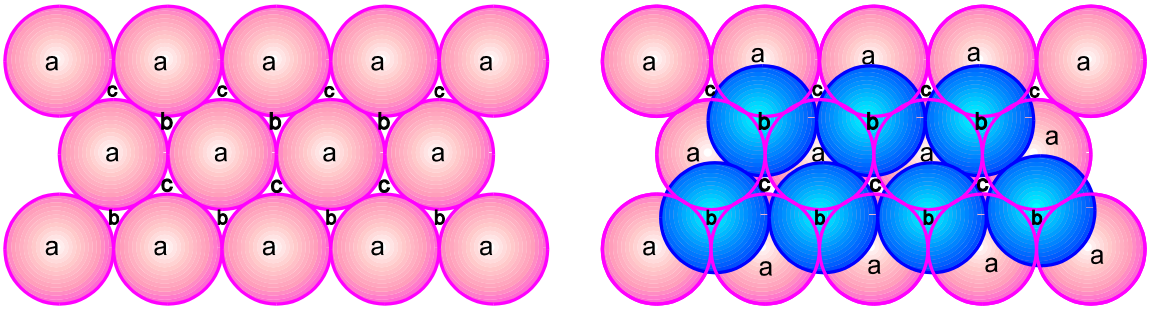


Simple cubic lattice formed by
A A A ... arrangement

Coordination number = 6
First neighbour = 6 at a distance = a
Second neighbour = 12 at ($\sqrt{2}$a) distance
Third neighbour = 8 at ($\sqrt{3}$a) distance

6.3.2 Three dimensional close packing from hexagonal two dimensional packing :

In hexagonal close packing, there are two types of the voids (open space or space left) which are divided into two sets 'b' and 'c' for convenience. The spaces marked 'c' are curved triangular spaces with tips pointing upwards whereas spaces marked 'b' are curved triangular spaces with tips pointing downwards.



Now we extend the arrangement of spheres in three dimensions by placing second close packed layer (hexagonal close packing) (B) on the first layer (A). The spheres of second layer may placed either on space denoted by 'b' or 'c'. It may be noted that it is not possible to place spheres on both types of voids (i.e. b and c). Thus half of the voids remain unoccupied by the second layer. The second layer also have voids of the types 'b' and in order to build up the third layer, there are following ways :

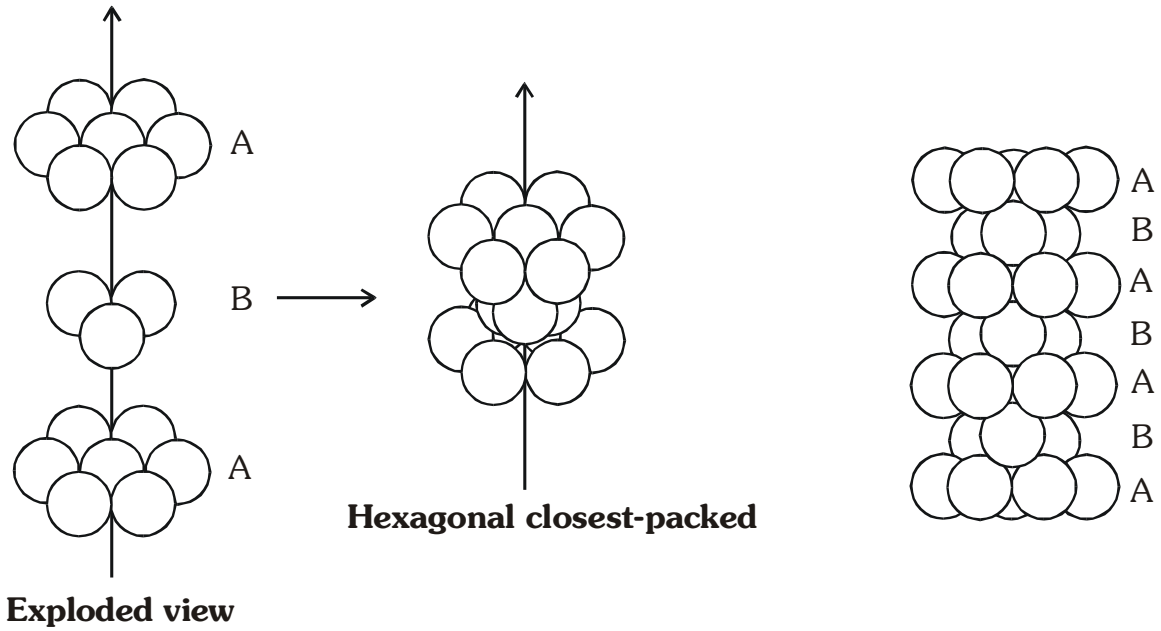
Space for Notes

(I) Hexagonal close packing (HCP)

(i) In one way, the spheres of the third layer lie on the spaces of second layer (B) in such a way that they lie directly above those in the first layer(A). In other words we can say that the third layer becomes indentical to the first layer. Such arrangement is called AB AB AB ....type packing or hexagonal close packing (hcp).

(ii) Maximum possible space is occupied by spheres.

(iii) Each sphere is touched by 12 other spheres in 3D (6 is one layer, 3 in top layer and 3 in bottom) and hence the coordination number is 12.

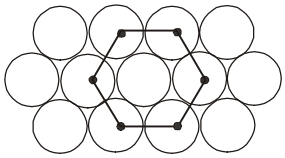


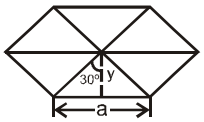
Space for Notes

(iv) Packing efficiency of HCP units

Relation between a, b, c and R :

$a = b = 2R$

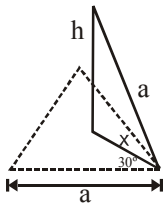




$\tan 30^\circ = \frac{a}{2 \times y}$ So $y = \frac{a \times \sqrt{3}}{2 \times 1} = \frac{\sqrt{3}}{2} a.$

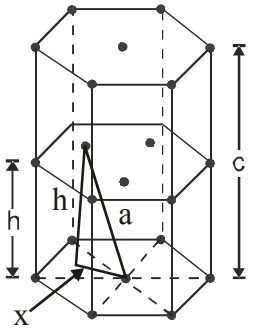
$$\text{Base Area} = 6\left[\frac{1}{2} a \times \frac{\sqrt{3}}{2} a\right] = \frac{6\sqrt{3}a^2}{4}$$

Calculation of c :



$\cos 30^\circ = \frac{a}{2 \times x}$ $x = \frac{2a}{2 \times \sqrt{3}} = \frac{a}{\sqrt{3}}$

Applying pythogoras theorem : $x^2 + h^2 = a^2$



So $h^2 = a^2 - x^2 = a^2 - \frac{a^2}{3} = \frac{2}{3} a^2$

$h = \sqrt{\frac{2}{3}} a$ so $c = 2h = 2\sqrt{\frac{2}{3}} a$

So volume of hexagon = area of base × height

$$= \frac{6.\sqrt{3}}{4} \times a^2 \times 2\sqrt{\frac{2}{3}} a = \frac{6.\sqrt{3}}{4} \times (2R)^2 + 2\sqrt{\frac{2}{3}} \times (2R) = 24\sqrt{2} R^3$$

Space for Notes

(v) Effective no. of particles (Z)

$$Z = 3 + 2 \times \frac{1}{2} + 12 \times \frac{1}{6} = 3 + 1 + 2 = 6.$$

It must be noted that all three spheres of 'B' layer are not exactly inside the unit cell. But the contribution of three spheres are taken because the same volume of other spheres in that layer is also inside the unit cell.

(vi) Packing efficiency $= \frac{6 \times \frac{4}{3}\pi \ R^3}{24\sqrt{2} \ R^3} = \frac{\pi}{3\sqrt{2}} = 0.74$ or 74%.

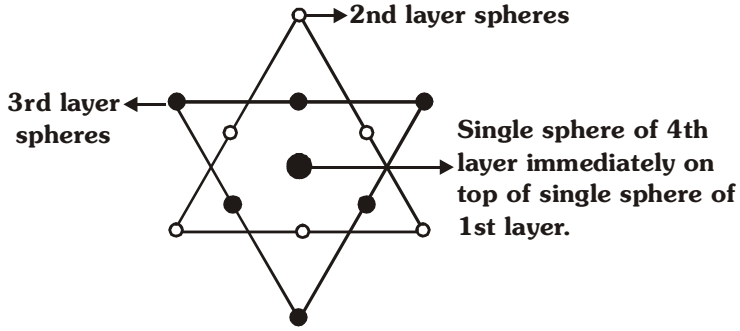
(vii) Density (d) $= \frac{\text{mass}}{\text{volume}} = \left[\frac{Z \times M}{N_A \times \text{volume}}\right]$

(II) Cubic close packing (CCP) or face centered cubic (FCC)

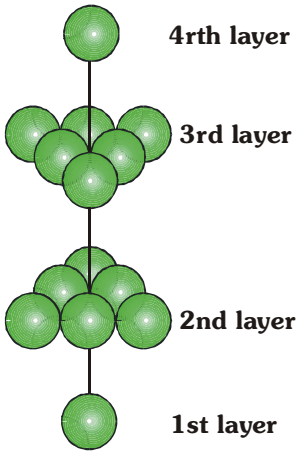
In second way, the spheres of the third layer (C) lie on the second layer (B) in such a way that they lie over the unoccupied spaces 'C' of the first layer(A). If this arrangement is continued in the same order every fourth layer becomes identical to the first. Such arrangement of particle is called ABC ABC ABC.... or cubic close packing (ccp) or face centered cubic (fcc).

It may be noted that in ccp (or fcc) structures, each sphere is surrounded by 12 spheres hence the coordination number of each sphere is 12. The spheres occupy 74% of the total volume and 26% of is the empty space in both (hcp and ccp) structures.

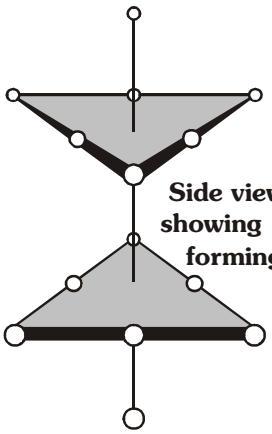
Space for Notes



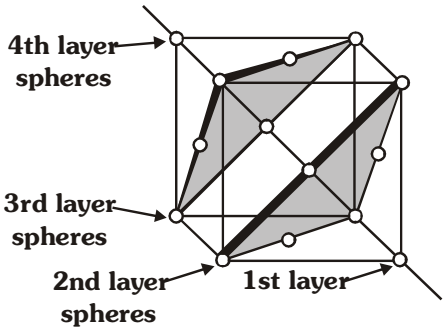
Open structure show top view of 14 spheres forming ccp packing.



Side view exploded space filling diagram showing 14 selected atom forming ccp packing



Side view open structure showing 14 selected atoms forming ccp packing



fcc unit cell showing 14 spheres

(i) Relation between 'a' and 'R' :

$a \neq 2R$

$\sqrt{2}a = 4R$ (sphere are touching along the face diagonal)

(ii) Effective no. of particles per unit cell (Z)

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

Space for Notes

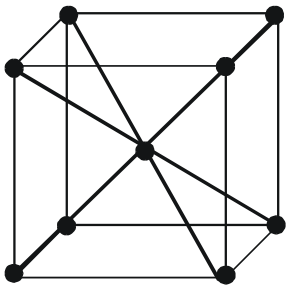
(iii) Packing fraction :

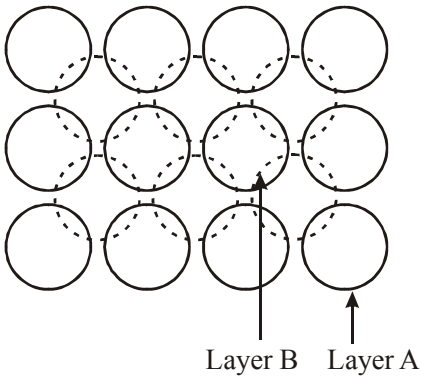
$$\text{P.F.} = \frac{4 \times \frac{4}{3}\pi R^3}{4 \times 4 \times 4 R^3} \times \sqrt{2} \times 2 = \frac{\pi}{3\sqrt{2}} = 0.74 \text{ or } 74\%$$

(iv) Density (d) $= \frac{Z \times M}{N_A \times a^3}$

6.3.3 Body centred cubic (bcc):

There is another possible arrangement of packing of spheres known as body centred cubic (bcc) arrangement. This arrangement is observed in square close packing in which there is suitable space between the spheres in each layer. In bcc arrangement, the spheres of the second layer lie at the space (hollows or voids) in the first layer.

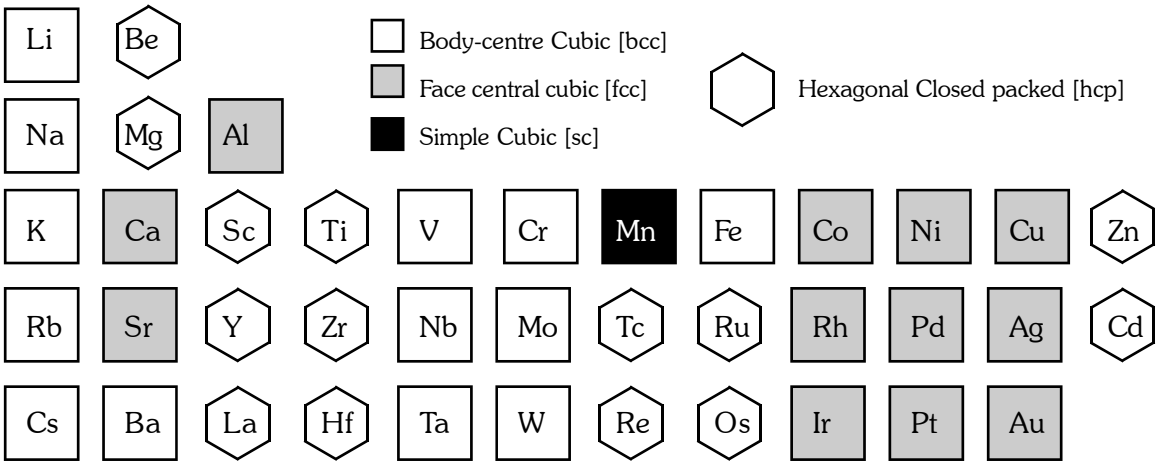




Thus each sphere of the second layer touches four spheres of the first layer. Now spheres of the third layer are placed exactly about the spheres of first layer. In this way each sphere of the second layer touches eight spheres (four of 1st layer and four of IIIrd layer). Therefore coordination number of each sphere is 8 in bcc sturcture. The spheres occupy 68% of the total volume 32% of the volume is the empty space.

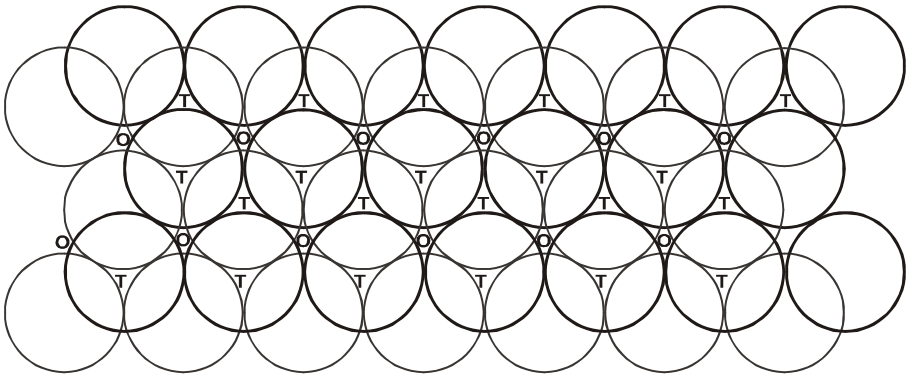
Space for Notes

7. STRUCTURES OF VARIOUS ELEMENTS



8. INTERSTICES OR VOIDS OR HOLES IN CRYSTALS

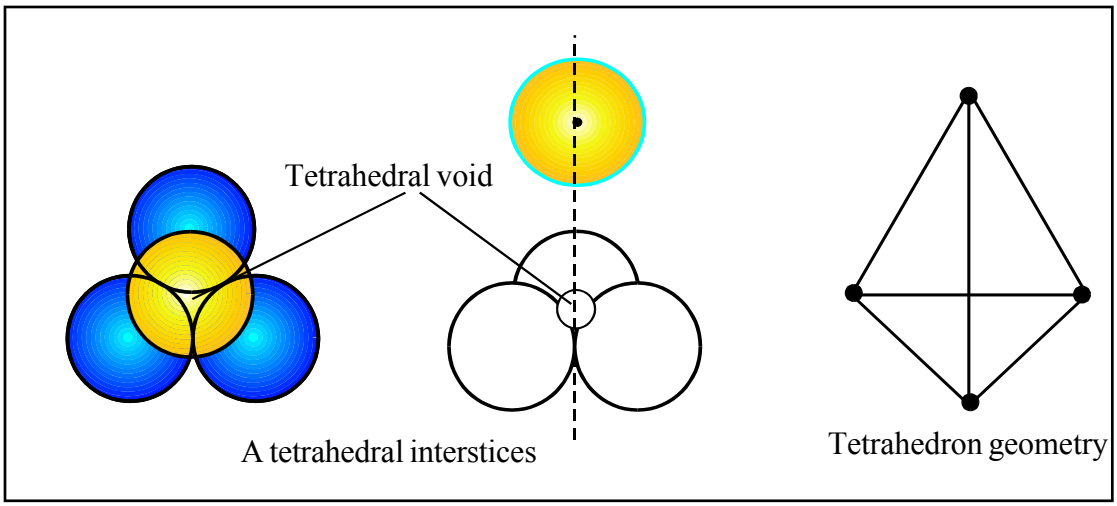
It has been shown that the particles are closely packed in the crystals even than there is some empty space left in between the spheres. This is known as interstices (or interstitial site or hole or empty space or voids). In three dimentional close packing (CCP & HCP) the interstices are of two types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



A stack of two layers of close packed spheres and voids generated in them. T = Tetrahedral void; O = Octahedral void

Space for Notes

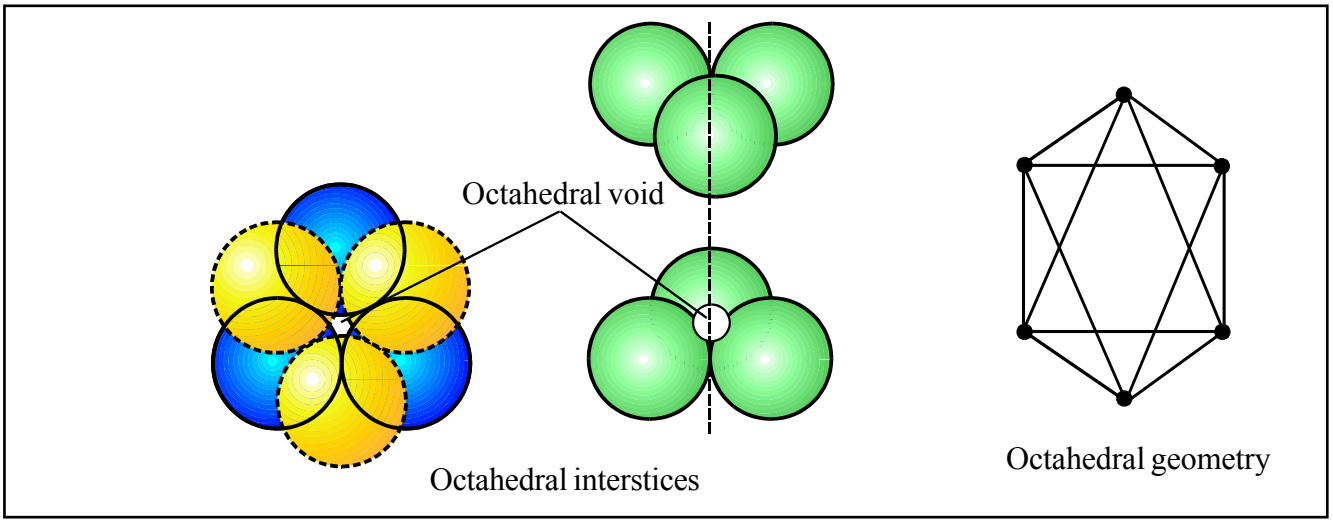
(i) **Tetrahedral voids :** We have seen that in hexagonal close packing (hcp) and cubic close packing (ccp), each sphere of second layer touches with three spheres of first layer. Thus, they leave a small space in between which is known as **tetrahedral site or interstices**. In another words, the vacant space between 4 touching spheres is called as tetrahedral void. Since a sphere touches three spheres in the below layer and three spheres in the above layer hence there are two tetrahedral sites associated with one sphere. It may by noted that a tetrahedral site does not mean that the site is tetrahedral in geometry but it means that this site is surrounded by four spheres and the centres of these four spheres lie at the apices of a regular tetrahedron.



(ii) **Octahedral voids :** Hexagonal close packing (hcp) and cubic close packing (ccp) also form another type of interstices (or site), which is called octahedral site (or interstices). In another words, the vacant space between 6 touching spheres is called as octahedral void.

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

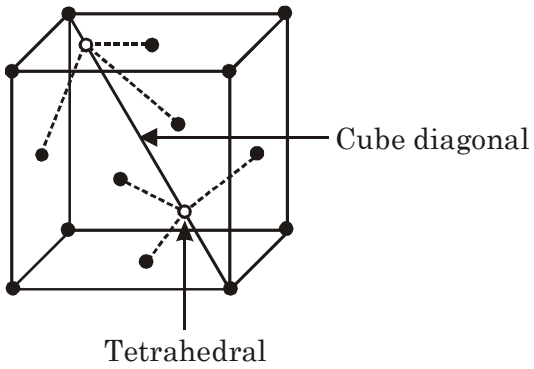
Space for Notes



The apices of these triangles point are in opposite directions. On super imposing these triangles on one another, an octahedral site is created. It may be noted that an octahedral site does not mean that the hole is octahedral in shape but it means that this site is surrounded by six nearest neighbour lattice points arranged octahedrally.

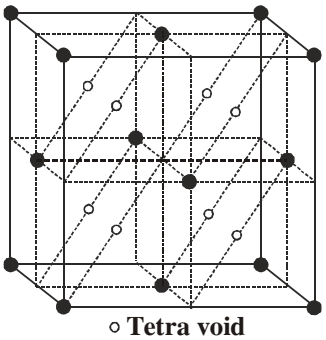
8.1 POSITIONS OF TETRAHEDRAL VOIDS IN AN FCC UNIT CELL :

In FCC, one corner and its three face centred atom of faces meeting at that corner form a tetrahedral void. In FCC, two tetrahedral voids are obtained along one cube diagonal. So in FCC 8 tetrahedral voids are present.



Space for Notes

Alternatively, the centre of tetrahedral void is located on the centre of body diagonal of each small cube of volume $\left(\frac{a^3}{8}\right)$.



Total number of particles per unit cell $= \frac{1}{2} \times 6 + 8 \times \frac{1}{8} = 4$

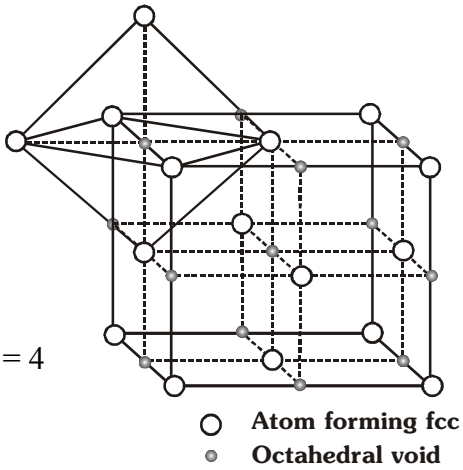
Total number of tetrahedral void = 8

$\therefore$ Effective number of tetrahedral void per particle = 2.

8.2 POSITION OF OCTAHEDRAL VOID IN FCC UNIT CELL :

Position of octahedral void is at mid-point of each edge (total 12 edges in a cube) and at the centre of cube.

Each octahedral void located at mid point of edge contributes 1/4 to the unit cell. The octahedral void situated at the centre contributes 1.



In FCC, total number of octahedral voids are

$$\underset{\text{(Cube centre)}}{(1 \times 1)} + \underset{\text{(edge)}}{(12 \times \frac{1}{4})} = 1 + 3 = 4$$

In FCC, number of particles = 4

$\therefore$ Effective number of octahedral voids per particle = 1

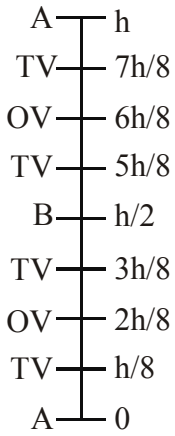
8.3 POSITION OF TETRAHEDRAL AND OCTAHEDRAL VOID IN HCP:

(i) Above & below each sphere, there is a tetrahedral void, hence number of tetrahedral void per unit cell = 12

(ii) Other than TV, all voids are OV & number of OV per unit cell = 2 × 3 = 6

Space for Notes

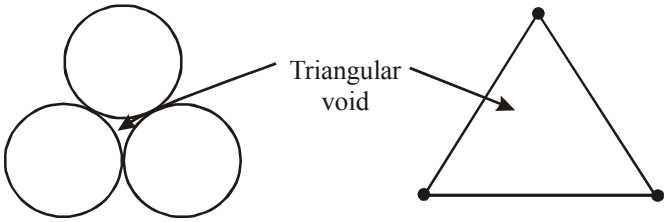
Height of voids from Base :



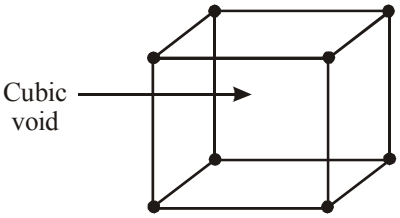
Note : In any closed packing of maximum efficiency, there are two TV & one OV per particle

8.4 Triangular and cubic voids :

(i) Triangular void : It is formed by three spheres in a plane.



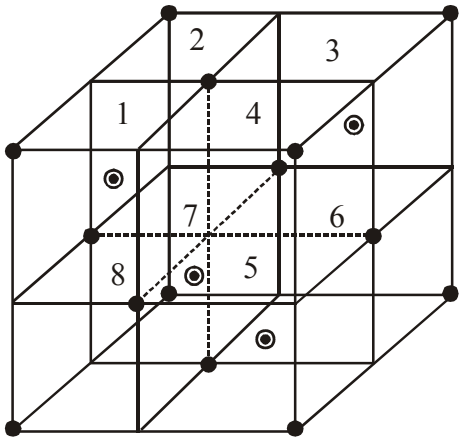
(ii) Cubic void : It is formed in simple cubic unit cell by eight spheres at the corners of cube.



Space for Notes

9. CRYSTAL OF DIAMOND

The crystal is FCC for C atom & alternate tetrahedral voids are also occupied by carbon atoms.



* $Z = \frac{1}{8} \times 8 + 6 \times \frac{1}{2} + 4 = 8$
* CN = 4
* $\frac{\sqrt{3}a}{4} = 2r = d_{C-C}$
* Number of C–C bonds/unit cell = $4 \times 4 = 16$
* Number of C–C bonds/C-atom = $\frac{16}{8} = 2$
* PE = $\frac{8 \times \frac{4}{3}\pi r^2}{\left(\frac{8r}{\sqrt{3}}\right)^3} = \frac{\sqrt{3}\pi}{16} \simeq 0.34$ or 34%

10 PACKING IN IONIC SOLID

(i) Normally anions are bigger than cations, hence ionic solid are considered as the packing of anions and cations are supposed to occupy the voids.

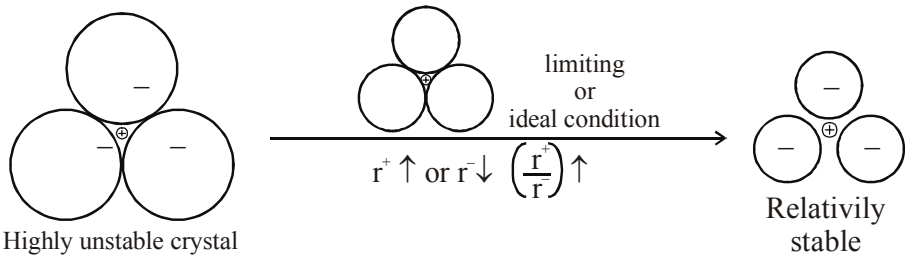
(ii) Oppositively charged particles should lie closer and smilarly charged particles should lie away from each other.

(iii) Each ion tend to maximise its coordination number (Number of oppositively charged ions around it).

Point (ii) and (iii) contradict each other because on increase the CN, the repulsion between like charges will also increases. Hence, in all the ionic solids, there must be a balance with the help of relative size of ions to ensure maximum CN and minimum repulsion between like charges.

Space for Notes

10.1 LIMITING OR IDEAL RADIUS RATION $\left(\frac{r^+}{r^-}\right)$:



The minimum $\frac{r^+}{r^-}$ values for the existence of a cation in a particular void is called **limiting radius ratio** for that void.

With the increase in radius ratio, space between anion will increase & hence the cation may tend for higher coordination number.

Voids	CN	Limiting r^+/r^-	Range of r^+/r^-
Triangular	3	0.155	0.155 – 0.225
Tetrahedral	4	0.225	0.225 – 0.414
Octahedral	6	0.414	0.414 – 0.732
Cubic	8	0.732	0.732 – 1.000

* For values lesser than 0.155, crystal will not exist.

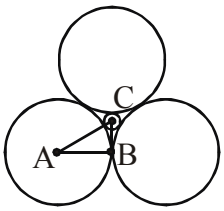
Space for Notes

Ex.3 Calculate the radius (r) of largest sphere which may be fitted in the (i) triangular voids (ii) tetrahedral voids (iii) octahedral voids (iv) cubic voids made by identical spheres of radius, 'R', without disturbing the crystal.

Sol. (i) $AB = R$

$AC = R + r$

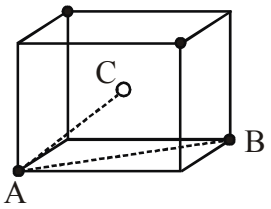
$\angle BAC = 30°$



Now, $\cos 30° = \frac{AB}{AC} \Rightarrow \frac{\sqrt{3}}{2} = \frac{R}{R+r}$

$r = \left(\frac{2}{\sqrt{3}} - 1\right)R = 0.155R$

(ii) $AB = \sqrt{2}a = 2R$

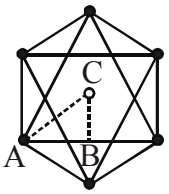


$AC = \frac{\sqrt{3}\,a}{2} = R + r$

Now, $\frac{R+r}{R} = \frac{\sqrt{3}}{\sqrt{2}}$

$\therefore \quad r = \left(\sqrt{\frac{3}{2}} - 1\right)R = 0.225R$

(iii) $AB = R$



$AC = R + r$

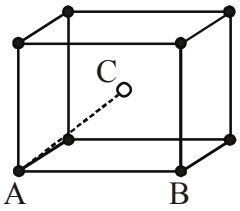
$\angle BAC = 45°$

Now, $\cos 45° = \frac{AB}{AC} \Rightarrow \frac{1}{\sqrt{2}} = \frac{R}{R+r}$

$\therefore \quad r = \left(\sqrt{2} - 1\right)R = 0.414R$

Space for Notes

(iv) $AB = a = 2R$



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

$$\text{Now, } \frac{R + r}{R} = \sqrt{3}$$

$$\therefore \quad r = \left(\sqrt{3} - 1\right)R = 0.732R$$

CLASS ILLUSTRATION - 02

10. ***A compound is formed by two elements M and N. The element N forms ccp and atoms of M occupy 1/3rd of tetrahedral voids. What is the formula of the compound?***

11. ***A solid crystallises in close packing for 'P' atoms and 25% of tetrahedral voids are occupied by 'Q' atoms. What is the simplest formula of solid ?***

12 ***A compound forms hexagonal close-packed structure. What is the total number of voids in 0.5 mole of it? How many of these are tetrahedral voids?***

13. ***An element 'M' crystallizes in ABAB....type packing. If adjacent layer A & B are*** $10\frac{\sqrt{2}}{\sqrt{3}}$ ***pm apart, then calculate radius of largest sphere which can be fitted in the void without disturbing the lattice arrangement (Given :*** $\sqrt{2} = 1.414$***)***

14. ***In compound*** M_2O_3***, if oxide ions are in close packing while 'M' occupy the voids. Then what fraction of voids (O.V. & T.V.) left unoccupied -***

15. ***An element (atomic weight = 125) crystallises in simple cubic structure. Diameter of the largest atom which can be placed without disturbing unit cell is 366 pm. If the density of element 'x' gm/cm^3 , the value of*** $\left(\frac{6x}{5}\right)$ ***is***

[Given : $\sqrt{3}$ ***= 1.732 ,*** $N_A = 6 \times 10^{23}$ ***]***

16. ***What will be packing fraction of solid in which atoms are present at corners and cubic void is occupied. The insertion of the sphere into void does not disturb simple cubic lattice.***

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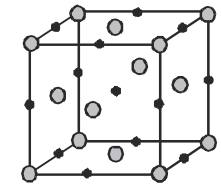
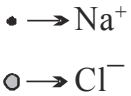
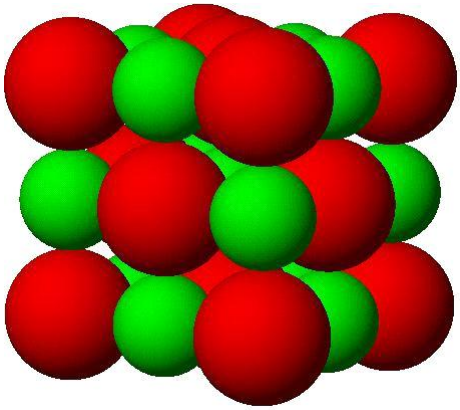
10.2 *TYPES OF IONIC STRUCTURES:*

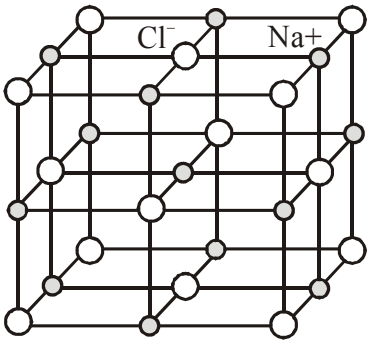
10.2.1 Rock salt structure (NaCl) :



Rock salt structure







The bigger Cl^- forms cubic close packing and small Na^+ occupy positions of all octahedral voids. The radius ratio $\frac{r^+}{r^-}$ lie in the range 0.414 – 0.732.

(i) Each Na^+ is surrounded by six Cl^- and each Cl^- is surrounded by six Na^+ ion. [6:6 coordination]

(ii) No. of Na^+ and Cl^- in each unit cell is 4.

(iii) Number of formula units of NaCl per unit cell is equal to 4.

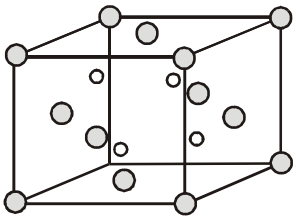
(iv) The density of NaCl crystal is given by $d = \left(\frac{4 \times M_{NaCl}}{N_A \times a^3}\right)$

(v) The edge length of NaCl unit cell is given by $(2r^+ + 2r^-) \Rightarrow \boxed{\frac{a}{2} = r^+ + r^-}$

Space for Notes

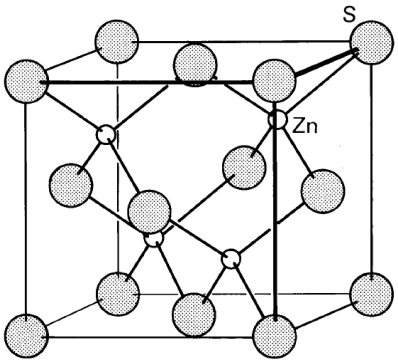
10.2.2 Zinc blende (sphalerite) structure (ZnS) :

Larger ion (S^{2-}) forming ccp arrangement and smaller ion (Zn^{2+}) filling half or alternate tetrahedral voids



$\bigcirc \rightarrow S^{2-}$

$\circ \rightarrow Zn^{2+}$



Zinc blende structure

(i) C.N. of $Zn^{2+} = 4$; C.N. of $S^{2-} = 4$ [4 : 4 coordination]

(ii) Formula units of ZnS per unit cell = 4. **(iii)** $d_{ZnS} = \frac{4 \times M_{ZnS}}{N_A \times a^3}$ **(iv)** $r_{Zn^{2+}} + r_{S^{2-}} = \frac{a\sqrt{3}}{4}$

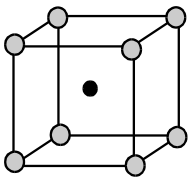
10.2.3 Cesium chloride structure (CsCl) :

Cl^- at the corners of cube and Cs^+ in the center (cubic void).

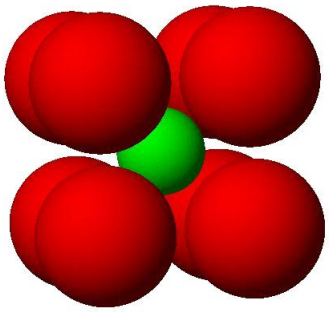
(i) C.N. of $Cs^+ = 8$; C.N. of $Cl^- = 8$ [8 : 8 coordination]

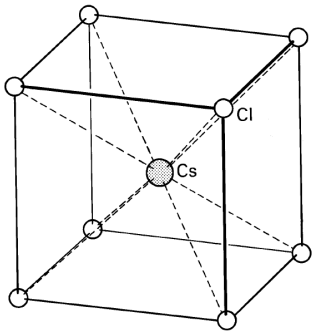
(ii) Formula units of CsCl per unit cell = 1

(iii) $d_{CsCl} = \frac{M_{CsCl}}{N_A \times a^3}$ **(iv)** $r_{Cs^+} + r_{Cl^-} = \frac{a\sqrt{3}}{2} \Rightarrow \boxed{\mathbf{r^+ + r^- = \frac{a\sqrt{3}}{2}}}$



Cesium chloride structure





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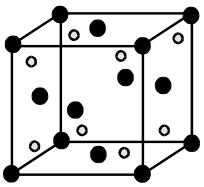
10.2.4 Fluorite structure (CaF_2) :

Ca^{2+} forming ccp arrangement and F^- filling all tetrahedral voids.

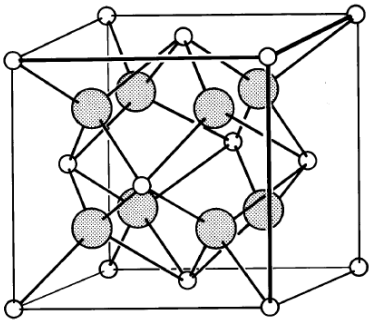
(i) C.N. of $F^- = 4$; C.N. of $Cs^+ = 8$ [8 : 4 coordination]

(ii) Formula units of CaF_2 per unit cell = 4

(iii) $d_{CaF_2} = \frac{4 \times M_{CaF_2}}{N_A \times a^3}$ **(iv)** $r_{Ca^{2+}} + r_{F^-} = \frac{a\sqrt{3}}{4}$



Fluorite structure



10.2.5 Antifluorite structure (Li_2O) :

O^{2-} ion forming ccp and Li^+ taking all tetrahedral voids.

(i) C.N. of $Li^+ = 4$

C.N. of $O^{2-} = 8$

(ii) Formula units of Li_2O ; per unit cell = 4

(iii) $d_{Li_2O} = \frac{4 \times M_{Li_2O}}{N_A \times a^3}$

(iv) $r_{Li^+} + r_{O^{2-}} = \frac{a\sqrt{3}}{4}$

10.2.6 Corundum Structure (Al_2O_3) :

O^{2-} forming hcp and Al^{3+} filling 2/3 octahedral voids.

Space for Notes

10.2.7 Rutile structure (TiO_2) **:**

O^{2-} forming hcp while Ti^{4+} ions occupy half of the octahedral voids.

10.2.8 Pervoskite structure ($CaTiO_3$) **:**

Ca^{2+} in the corner of cube, O^{2-} at the face center and Ti^{4+} at the centre of cube.

10.2.9 Spinel and inverse spinel structure ($MgAl_2O_4$) **:**

O^{2-} forming fcc, Mg^{2+} filling 1/8 of tetrahedral voids and Al^{3+} taking half of octahedral voids.

In an inverse spinel structure, O^{2-} ion form FCC lattice, A^{2+} ions occupy 1/8 of the tetrahedral voids and trivalent cation occupies 1/8 of the tetrahedral voids and 1/4 of the octahedral voids.

Ex.4 A solid A^+B^- has NaCl type close packed structure. If the anion has a radius of 250 pm, what should be the ideal radius for the cation ? Can a cation C^+ having a radius of 180 pm be slipped into the tetrahedral site of the crystal A^+B^- ? Give reason for your answer.

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

The limiting radius ratio for octahedral site = 0.414

or $\frac{A^+}{B^-} = \frac{r}{R} = 0.414$

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

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

or $r = 103.5$ ***pm***

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

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

$\therefore \quad \frac{r}{R} = 0.225$

or $r = 0.225 \quad R = 0.225 \times 250 = 56.25$ ***pm***

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

Space for Notes

CLASS ILLUSTRATION - 03

17. Solid AB has NaCl type structure. If the radius of A^+ and B^- are 0.8 Å and 1.2Å respectively and formula mass of AB is 48 g/mole, what is the density of AB solid.

Take : Avogadro's number = 6×10^{23}

18. Calculate the value of Avagadro number from the following data :

Density of NaCl = 2.165 g cm^{-3}, distance between $Na^+$and Cl^- ions in NaCl crystal = 281 pm. (1)

19 Calculate the density (in gm/cm^3) of NaCl type ionic solid (MW = 75 gm/mol) if distance between two nearest cations is $250\sqrt{2}$ pm (avogadro number = 6×10^{23})

20. KF crystallizes in the NaCl type structure. If the radius of K^+ ion is 132 pm and that of F^- ion is 135 pm, what is the shortest K–F distance? What is the edge length of the unit cell? What is the closet K^+– K^+ distance?

21. RbI crystallizes in (8 : 8) structure in which each Rb^+ is surrounded by eight iodide ions each of radius 2.17 Å. Find the length of one side of RbI unit cell , assuming anion, anion contact.

22. A cubic unit cell contains manganese ions at the corners and fluoride ions at the center of each edge.

(a) What is the empirical formula of the compound?

(b) What is the co-ordination number of the Mn ion?

(c) Calculate the edge length of the unit cell, if the radius of Mn ion is 0.65 Å and that of F^- ion is 1.36 Å.

11. IMPERFECTIONS IN SOLIDS

Although crystalline solids have short range as well as long range order in the arrangement of their constitutent particles, yet crystals are not perfect. Usually a solid consists of an aggregate of large number of small crystals. These small crystals have defects in them. This happens when crystallisation process occurs at fast or moderate rate. Single crystals are formed when the process of crystallisation occurs at extremely slow rate. Even these crystals are not free of defects.

Space for Notes

The defects are basically irregularities in the arrangement of constituent particles. Broadly speaking, the defects are of two types, namely, **point defects** and **line defects**. Point defects are the irrgularties or deviations from ideal arrangement around a point or an atom in a crystalline substance, whereas the line defects are the irregularities or deviations from ideal arrangement in entire rows of lattice points. These irregularities are called crystal defects. We shall confine our discussion to point defects only.

11.1 Types of Point Defects

Point defect can be classified into three types:

(i) Stoichiometric defects

(ii) Non-stoichiometric defects

(iii) Impurity added defect

(i) Stoichiometric Defect

These are the point defect that do not disturb the stoichiometry of the solid. They are also called ***intrinsic*** or **thermodynamic defects**. Basically these are of two types; vacancy defects and interstitial defect.

(a) Vacancy Defect :

When some of the lattice sites are vacant, the crystal is said to have vacancy defect. This results in decrease in density of the substance. This defect can also develop when a substance is heated.

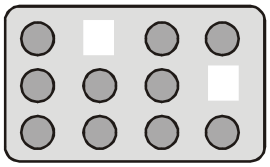


Fig. : Vacancy defects

(b) Interstitial Defect : When some constituent particles (atoms or molecules) occupy an interstitial site. the crystal is said to have interstitial defect. This defect increases the density of the substance.

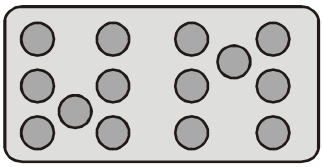


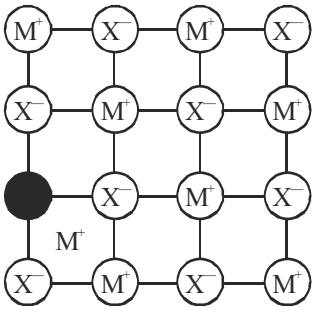
Fig. : Interstitial defects

Space for Notes

Vacancy and interstitial defects as explained above can be shown by non-ionic solids. Ionic solids must always maintain electrical neutrality. Rather than simple vacancy or interstitial defects, they show these defects as **Frenkel and Schottky defects**.

(c) Frenkel Defect : This defect is shown by ionic solids.

The smaller ion (usually cation) is delocalised from its normal site to an interstitial site . It creates a vacancy defect at its original site and an interstitial defect at its new location.



Frenkel Defect

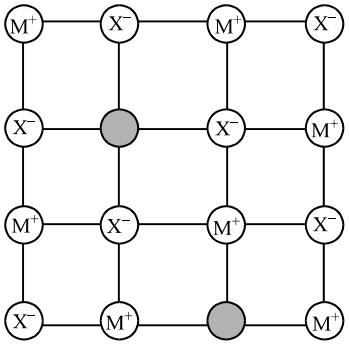
Frenkel defect is also called **dislocation defect**. It does not change the density of the solid.

Frenkel defect is shown by ionic substance in which there is a large difference in the size of ions, for example, ZnS, AgCl, AgBr and AgI due to small size of Zn^{2+} and Ag^{+} ions.

Influences : Makes solid crystals good conductor. In Frenkel defect , ions in interstitial sites increases the dielectric constant.

(d) Schottky Defect : It is basically a vacancy defect in ionic solids. In order to maintain electrical neutrality, the number of missing cations and anions are equal (in stoichiometric ratio)

Like simple vacancy defect, Schottky defect also decreases the density of the substance. Number of such defects in ionic solids is quite significant. For example, in NaCl there are approximately,



Schottky Defect

10^6 Schottky pairs per cm^3 at room temperature. In 1 cm^3 there are about 10^{22} ions. Thus, there is one Schottky defect per 10^{16} ions. Schottky defect is shown by ionic substances in which the cation and anion are of almost similar sizes. For example, NaCl, KCl, CsCl and AgBr. It may be noted that AgBr shows both, Frenkel as well as Schottky defects.

Space for Notes

Influence : The presence of large number of schottky defects in crystal results in significant decrease in its density.

(ii) Non-Stoichiometric Defects

The defects discussed so far do not disturbs the stoichiometry of the crystalline substance. However, a large number of non-stoichiometric inorganic solids are known which contain the constituent elements in non-stoichiometric ratio due to defects in their crystal structures. These defects are of two types:

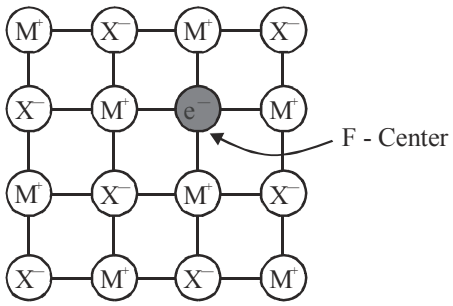
(a) Metal excess defect.

(b) Metal deficiency defect.

(a) Metal Excess Defect

(I) Metal excess defect due to anionic vacancies :

Alkali halides like NaCl and KCl show his type of defect. When crystals of NaCl are heated in an atmosphere of sodium vapour, the sodium atoms are deposited on the surface of the crystal. The Cl^- ions diffuse to the surface of the crystal and combine with Na atoms to give NaCl. This happens by loss of electron by sodium atoms to form Na^+ ions.



Metal excess defects due to anion vacancies

The released electrons diffuse into the crystal and occupy anionic sites . As a result the crystal now has an excess of sodium. The anionic sites occupied by unpaired electrons are called ***F-centres*** (from the German word ***Farbenzenter*** for colour centre).

They impart yellow colour to the crystals of NaCl. The colour results by excitation of these electrons when they absorb energy from the visible light falling on the crystals. Similarly, excess of lithium makes LiCl crystals pink and excess of potassium makes KCl crystals violet (or lilac).

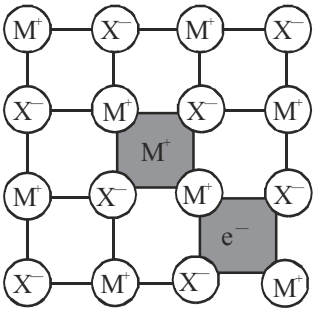
Space for Notes

(II) ***Metal excess defect due to the presence of extra cations at interstitial sites :***

Zinc oxide is white in colour at room temperature. On heating it loses oxygen and turns yellow.

$$ZnO \xrightarrow{\text{heating}} Zn^{2+} + \frac{1}{2}O_2 + 2e^-$$

Now there is excess of zinc in the crystal and its formula becomes $Zn_{1+x}O$. The excess Zn^{2+} ions move to interstitial sites and the electrons to neighbouring interstitual sites.



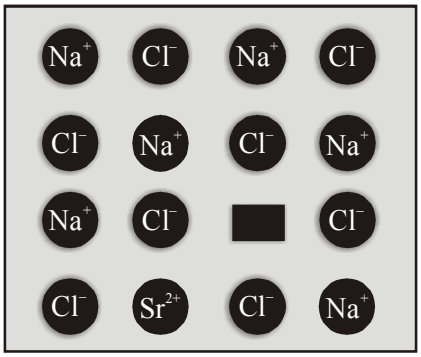
Metal excess defects
due to interstitial cation

(b) Metal Deficiency Defect

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

(iii) **Impurity Defects**

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



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

Space for Notes

Note: (i) As temperature increases, no. of defects increases exponentially.

(ii) For defect formation : $\Delta H > 0$, $\Delta S > 0$

$\therefore$ More spontaneous at higher temperatures.

(iii) No matter how many imperfections are present in a crystal, it is always electrically neutral (no net charge).

12. ELECTRICAL PROPERTIES

Solids exhibit an amazing range of electrical conductivities, extending over 27 orders of magnitude ranging from 10^{-20} to 10^{7} ohm^{-1} m^{-1}. Solids can be classified into three types on the basis of their conductivities.

(i) Conductors : The solids with conductivities ranging between 10^{4} to 10^{7} ohm^{-1}m^{-1} are called conductors. Metals having conductivities in the order of 10^{7} ohm^{-1}m^{-1} are good conductors.

(ii) Insulators : These are the solids with very low conductivities ranging between 10^{-20} to 10^{-10} ohm^{-1}m^{-1}.

(iii) Semiconductors : These are the solids with conductivities in the intermediate range from 10^{-6} to 10^{4} Ohm^{-1}m^{-1}.

12.1 : Conduction of Electricity in Metals

A conductor may conduct electricity through movement of electrons or ions. Metallic conductors belong to the former category and electrolytes to the latter.

Metals conduct electricity in solid as well as molten state. The conductivity of metals depend upon the number of valence electrons available per atom. The atomic orbitals of metal atoms from molecular orbitals which are so close in energy to each other as to form a band. If this band is partially filled or it overlaps with a higher energy unoccupied conduction band, then electrons can flow easily under an applied electric field and the metal shows conductivity.

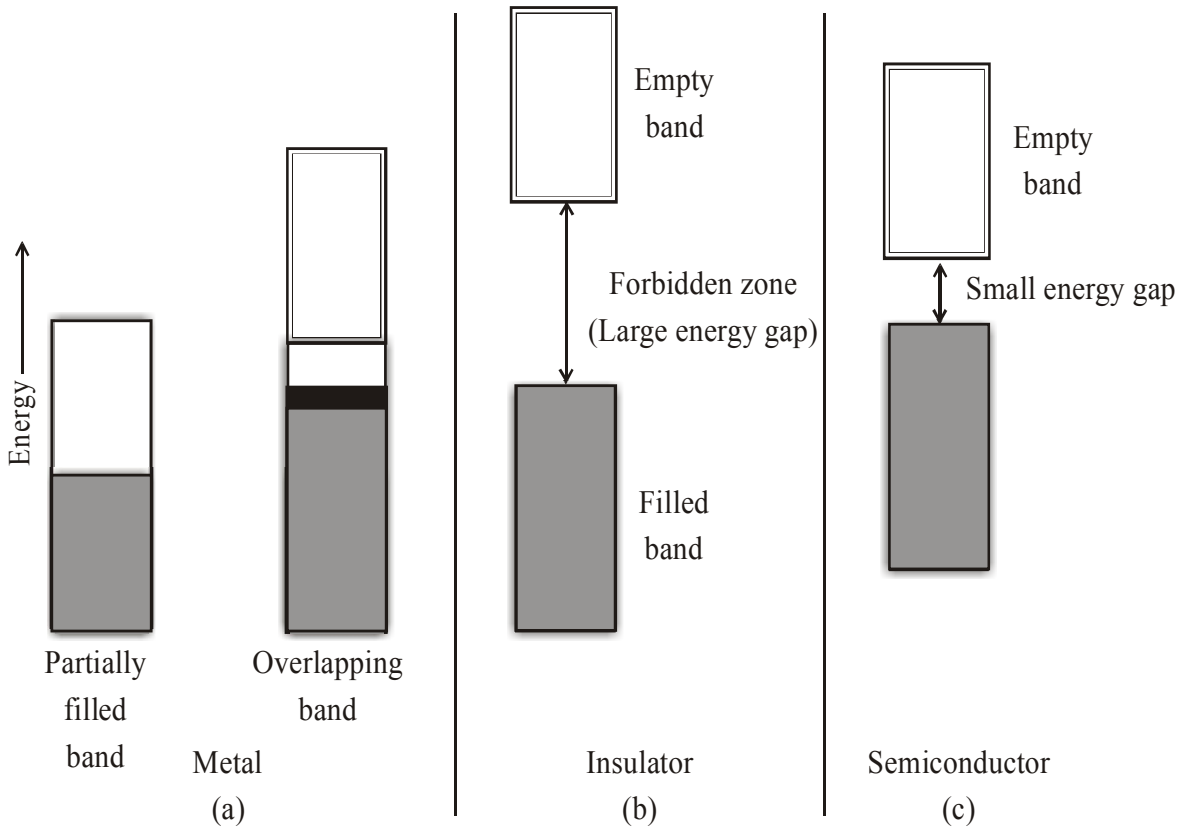
12.2 : Insulator :

If the gap between filled valence band and the next higher unoccupied band (conduction band) is large, electron cannot jump to it and such a substance has very small conductivity and it behaves as an insulator.

Space for Notes

12.3 : Conduction of Electricity in Semi-conductor

In case of semiconductors, the gap between the valence band and conduction band is small. Therefore, some electrons may jump to conduction band and show some conductivity. Electrical conductivity of semconductors increases with rise in temperature, since more electrons can jump to the conduction band. Substances like silicon and germanium show this type of behaviour and are called **intrinsic semiconductors**.



Distinction among (a) metals (b) insulators and (c) semiconductors.
In each case, an unshaded area represents a conduction band.

Space for Notes

The conducitivity of these interinsic semiconductors is too low to be of practical use. Their conductivity is increased by adding an appropriate amount of suitable impurity. This process is called **doping**. Doping can be done with an impurity which is electron rich or electron deficient as compared to the intrinsic semiconductor silicon or germanium. Such impurities introduce ***electrical defect*** in them.

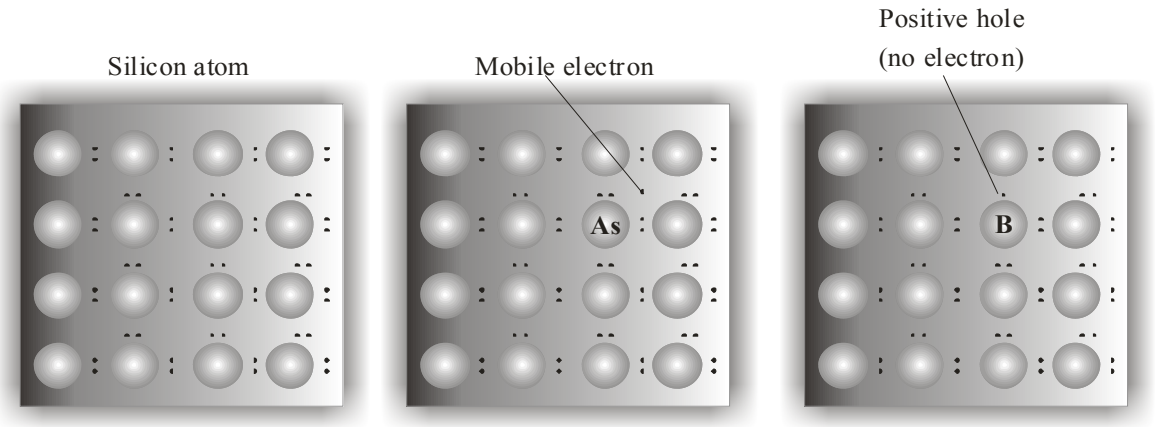
(a) Electron – rich impurities

Silicon and germanium belong to group 14 of the periodic table and have four valence electrons each. In their crystals each atom forms four covalent bonds with its neighbours . When doped with a group 15 element like P or As, which contains five valence electrons, they occupy some of the lattice sites in silicon or germanium crystal. Four out of five electrons are used in the formation of four covalent bonds with the four neighbouring silicon atoms. The fifth electron is extra and becomes delocalised. These delocalised electrons increase the conductivity of doped silicon (or germanium). Here the increase in conductivity is due to the negatively charged electron, hence silicon doped with electron-rich impurity is called ***n-type semiconductor***.

(b) Electron – deficit impurities

Silicon or germanium can also be doped with a group 13 element like B, Al or Ga which contains only three valence electrons. The place where the fourth valence electron is missing is called ***electron hole or electron vacancy*** . An electron from a neighbouring atom can come and fill the electron hole, but in doing so it would leave an electron hole at its original position. If it happens, it would appear as if the electron hole has moved in the direction opposite to that of the electron that filled it. Under the influence of electric field, electrons would move towards the positively charged plate through electronic holes, but it would appear as if electron holes are positively charged and are moving towards negatively charged plate. This type of semi conductors are called ***p-type semiconductors***.

Space for Notes



Creation of n-type and p-type semi conductors by doping groups 13 and 15 elements

(c) Applications of n-type and p-type semiconductors

Various combinations of *n*-type and *p*-type semiconductors are used for making electronic components. Diode is a combination of *n*-type and *p*-type semiconductor and is used as a rectifier. Transistors are made by sandwiching a layer of one type of semiconductor between two layers of the other type of semiconductor. *npn* and *pnp* type of transistors are used to detect or amplify radio or audio signals. The solar cell is an efficient photo-diode used for conversion of ligh energy into electrical energy.

Germinium and Silicon are group 14 elements and therefore, have a characteristic valence of four and form four bonds as in diamond. A large variety of solid state materials have been prepared by combination of group 13 and 15 or 12 and 16 to simulate average valence of four as in Ge or Si. Typical compounds of groups 13-15 are InSb, AIP and GaAs. Gallium arsenide (GaAs) semiconductor have very fast response and have revolutionised the design of semiconductor devices. ZnS, CdS, CdSe and HgTe are examples of groups 12-16 compounds. In these compounds, the bonds are not perfectly covalent and the ionic character depends on the electronegativities of the two elements.

It is interesting to learn that transition metal oxides show marked differences in electrical properties. TiO, CrO_2 and ReO_3 behave like metals. Rhenium oxide, ReO_3 is like metallic copper in its conductivity and appearance. Certain other oxides like VO, VO_2, VO_3 and TiO_3 show metallic or insulating properties depending on temperature.

Space for Notes

13. MAGNETIC PROPERTIES :

Every substance has some magnetic properties associated with it. The origin of these properties lies in the electrons. Each electron in an atom behaves like a tiny magnet. Its magnetic moment originates from two types of motions (i) its orbital motion around the nucleus and (ii) its spin around its own axis . Electron being a charged particle and undergoing these motions can be considered as a small loop of current which possesses a magnetic moment. Thus, each electron has a permanent spin and an orbital magnetic moment associated with it. Magnitude of this magnetic moment is very small and is measured in the unit called Bohr magneton, μ_B. It is equal to 9.27×10^{-24}A m^2.

On the basis of their magnetic properties, substances can be classified into five categories: (i) paramagnetic (ii) diamagnetic (iii) ferromagnetic (iv) antiferromagnetic and (v) ferrimagnetic.

(i) **Paramagnetism :** Paramagnetic substances are weakly attracted by a magnetic field. They are magnetised in a magnetic field in the same direction. They lose their magnetism in the absence of magnetic field. Paramagnetism is due to presence of one or more unpaired electrons which are attracted by the magnetic field. O_2, Cu^{2+}, Fe^{3+}, Cr^{3+} are some examples of such substances.

(ii) **Diamagnetism :** Diamagnetic substances are weakly repelled by a magnetic field. H_2O, NaCl and C_6H_6 are some examples of such substances. They are weakly magnetised in a magnetic field in opposite direction. Diamagnetism is shown by those substances in which all the electrons are paired and there are no unpaired electrons. Pairing of electrons cancels their magnetic moments and they lose their magnetic character.

(iii) **Ferromagnetism :** A few substances like iron, cobalt, nickel, gadolinium and CrO_2 are attracted very strongly by a magnetic field. Such substances are called ferromagnetic substances. Besides strong attractions, these substances can be permanently magnetised. In solid state, the metal ions of ferromagnetic substances are grouped together into small regions called ***domains***. Thus, each domain acts as a tiny magnet. In an unmagnetised piece of a ferromagnetic substance the domains are randomly oriented and their magnetic moments get cancelled. When the substance is placed in a magnetic field all the domains get oriented in the direction of the magnetic field and a strong magnetic effect is produced. This ordering of domains persist even when the magnetic field is removed and the ferromagnetic substance becomes a permanent magnet.

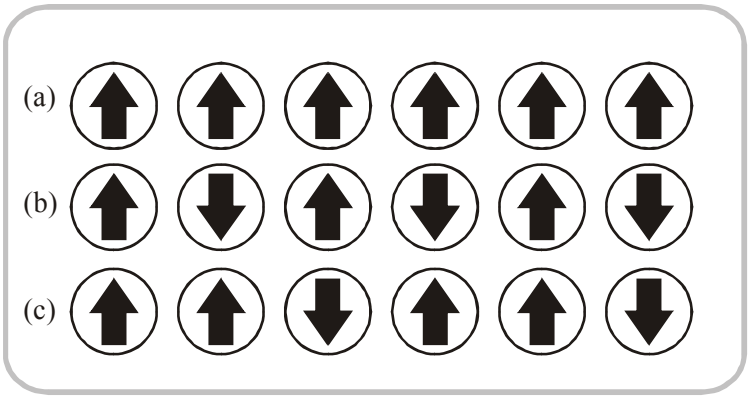
Space for Notes

(iv) **Antiferromagnetism :**

Substances like MnO showing antiferromagnetism have domain structure similar to ferromagnetic substance, but their domains are oppositely oriented and cancel out each other's magnetic moment

(v) **Ferrimagnetism :**

Ferrimagnetism is observed when the magnetic moments of the domains in the substance are aligned in parallel and anti-parallel directions in unequal numbers. They are weakly attracted by magnetic field as compared to ferromagnetic substances. Fe_3O_4 (magnetite) and ferrites like $MgFe_2O_4$ and $ZnFe_2O_4$ are examples of such substances. These substances also lose ferrimagnetism on heating and become paramagnetic.



Schematic alignment of magnetic moments in (a) ferromagnetic
(b) antiferromagnetic and (c) ferrimagnetic

Space for Notes

CLASS ILLUSTRATION - 04

23. *A crystal of NaCl, which has sodium ions and chloride ions missing from the lattice point, is said to exhibit*

(A) Surface defect (B) Lattice defect (C) Frenkel defect (D) Schottky defect

24. *A piece of copper and another of Ge are cooled from room temperature to 80 K. The resistance of:*

(A) each of them increases

(B) Cu increases and that of Ge decreases

(C) Cu decreases and that of Ge increases

(D) each of them decreases

25. *The composition of a sample of wustite is $Fe_{0.93}O_{1.0}$. What percentage of iron is present in the form of Fe(III)?*

26 *An element X (atomic weight = 24 gm/mole) forms a face centred cubic lattice. If the edge length of the lattice is 4×10^{-8} cm and the observed density is 2.40×10^3 kg/m^3 , calculate the percentage occupancy of lattice points by X element. (Given : $N_A = 6 \times 10^{23}$)*

27. *AgCl has the same structure as that of NaCl. The edge length of unit cell of AgCl is found to be 523.5 pm and the density of AgCl is 6.0 g cm^{-3}. Find the percentage of sites that are unoccupied.*

[Ag = 108 , $(5.235)^3 = 143.5$]

28. *The pyknometric density of sodium chloride crystal is 2.165×10^3 kg m^{-3} while its X–ray density is 2.178×10^3 kg m^{-3}.The fraction of unoccupied sites in sodium chloride crystal is :*

[Hint : Fraction of unoccupied sites

$= \dfrac{\text{X} - \text{ray density} - \text{pyknometric density}}{\text{X} - \text{ray density}}$ *]*

Space for Notes

ANSWER KEY

CLASS ILLUSTRATION - 01

1. Ans. X_2Y_3
2. ***Ans. 2.81 × 10^{-23} cm^3***
3. ***Ans.*** $r = 1.136$ Å
4. ***Ans.*** $\ell = 4.0 \times 10^{-8}$ *cm*
5. ***Ans. 4***
6. ***Ans.(a) 4.5 Å, (b) 5.2 Å, (c) 8, (d) 6, (e) 0.929 g/cm^3***
7. ***Ans.41.67 g cm^{-3}***
8. ***Ans.Ans.8***
9. ***Ans.5 × 10^{24}***

CLASS ILLUSTRATION - 02

10. ***Ans.*** N_3M_2.
11. ***Ans.*** P_2Q
12. ***Ans.*** *1 mol.*
13. ***Ans.(2.07 pm)***
14. ***Ans.*** $\left(\frac{7}{9}\right)$
15. ***Ans.(2)***
16. ***Ans.0.72***

CLASS ILLUSTRATION - 03

17. ***Ans.(5 gm/cm^3)***
18. ***Ans.6.09 × 10^{23}***
19. ***Ans (4)***
20. ***Ans.267 pm, 534 pm, 377.6 pm***
21. ***Ans.4.34 Å***
22. ***Ans.(a) MnF_3, (b) 6, (c) 4.02Å***

CLASS ILLUSTRATION - 04

23. ***Ans.(D)***
24. ***Ans.(C)***
25. ***Ans.15.05 %***
26. ***96% Ans.***
27. ***Ans.10***
28. ***Ans.5.96 × 10^{-3}***

Space for Notes

PREVIOUS YEARS SOLVED QUESTION

1. A metal cryatallises into two cubic phases, FCC and BCC whose unit cell lengths are 3.5 and 3.0 Å respectively. Calculate the ratio of densities of FCC and BCC. **[JEE-1999]**

Ans. **1.259**

Sol. $\rho_{Fcc} = \dfrac{4\times M}{N_A\times\left(3.5\times10^{-10}\right)^3}$

$\rho_{Bcc} = \dfrac{2\times M}{N_A\times\left(3\times10^{-10}\right)^3}$

$\dfrac{\rho_{Fcc}}{\rho_{Bcc}} = \dfrac{4}{2}\times\left(\dfrac{3}{3.5}\right)^3$

$= 1.259$

2. The coordination number of a metal crystallising in a hcp structure is **[JEE-2000]**

(A) 12 (B) 4 (C) 8 (D) 6

Ans. **(A)**

Sol. Theory Based

3. In any ionic solid [MX] with schottky defects , the number of positive and negative ions are same. **[T/F]** **[JEE-2000]**

Ans. **True**

Sol. Theory Based

4. In a solid "AB" having NaCl structure "A" atoms occupy the corners of the cubic unit cell. If all the face-centred atoms along one of the axes are removed, then the resultant stoichiometry of the solid is

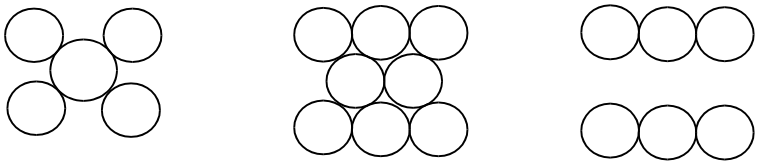
(A) AB_2 (B) A_2B (C) A_4B_3 (D) A_3B_4 **[JEE-2000]**

Sol. $\left.\begin{aligned} Z_A &= 8\times\frac{1}{8}+4\times\frac{1}{2}=3\\ Z_B &= 1+12\times\frac{1}{4}=4\end{aligned}\right] \Rightarrow A_3B_4$

Space for Notes

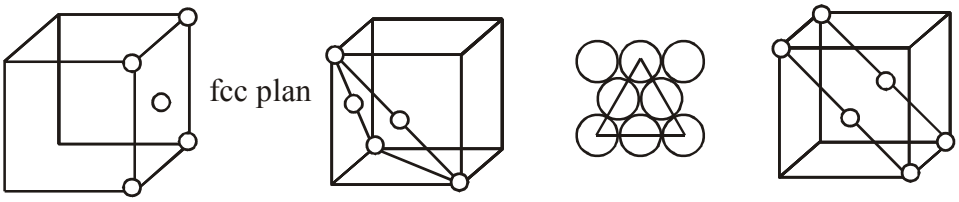
5. The figures given below show the location of atoms in three crystallographic planes in FCC lattice. Draw the unit cell for the corresponding structure and identify these planes in your diagram.

[JEE-2000]



Ans.

Sol.



6. A substance A_xB_y crystallises in a FCC lattice in which atoms "A" occupy each corner of the cube and atoms "B" occupy the centres of each face of the cube. Identify the correct composition of the substance A_xB_y.

(A) AB_3 (B) A_4B_3

(C) A_3B (D) composition cannot be specified **[JEE-2002]**

Ans. **(A)**

Sol. AB_3

7. Marbles of diameter 10 mm each are to be arranged on a flat surface so that their centres lie within the area enclosed by four lines of length each 40 mm. Sketch the arrangement that will give the maximum number of marbles per unit area, that can be enclosed in this manner and deduce the expression to calculate it.

[JEE 2003]

Ans. 18

Sol. $\frac{n \times \pi r^2}{a^2} = \frac{\pi}{2\sqrt{3}}$

$\frac{n \times \pi 5^2}{40 \times 40} = \frac{\pi}{2\sqrt{3}}$

$n = 18.475$

$n \approx 18$

Space for Notes

8. (i) AB crystallizes in a rock salt structure with A : B = 1 : 1. The shortest distance between A and B is $Y^{1/3}$ nm. The formula mass of AB is 6.023 Y amu where Y is any arbitrary constant. Find the density in kg m^{-3}.

(ii) If measured density is 20 kg m^{-3}. Identify the type of point defect. **[JEE–2004]**

Sol. (i) shortest distance b/w A & B = $Y^{1/3}$ nm

$$a = 2Y^{1/3}$$

$$\rho = \frac{4 \times 6.023Y \times 10^{-3}}{6.023 \times 10^{23} \times \left[2Y^{1/3} \times 10^{-9}\right]^3}$$

$$\rho = \frac{4 \times 10^{-3}}{8 \times 10^{-4}}$$

$$= 5 \text{ kgm}^{-3}$$

(ii) copy statement for answer Key

9. Which of the following FCC structure contains cations in alternate tetrahedral voids?

(A) NaCl (B) ZnS (C) Na_2O (D) CaF_2 **[JEE 2005]**

Ans. **(B)**

10. An element crystallises in FCC lattice having edge length 400 pm. Calculate the maximum diameter which can be placed in interstital sites without disturbing the structure. **[JEE 2005]**

Ans. **117.1 pm**

Sol. $\sqrt{2}\, a = 4r$

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

for octahedral void

$r^1 = .414 \times 141.4$

$d = 2r^1$

$= 117.07$

Space for Notes

11. The edge length of unit cell of a metal having atomic weight 75 g/mol is 5 Å which crystallizes in cubic lattice. If the density is 2 g/cc then find the radius of metal atom. ($N_A = 6 \times 10^{23}$). Give the answer in pm. **[JEE 2006]**

Ans. **216.5 pm**

Sol. a = 5Å

M = 75 gram/mol

d = 2 gram/cm

r

$$2 = \frac{Z \times 75}{\left(6.02 \times 10^{+23}\right)\left(5 \times 10^{-8}\right)^3}$$

Z = 2 (Bcc)

$\sqrt{3}$ a = 4r

$$r = \frac{\sqrt{3}a}{4} = 2.165Å$$

12. Match the crystal system / unit cells mentioned in Column I with their characteristic features mentioned in Column II. Indicate your answer by darkening the appropriate bubbles of the 4 × 4 matrix given in the OMR.

	Column I	**Column II**
(A)	simple cubic and face-centred cubic	(P) have these cell parameters a = b = c and $\alpha = \beta = \gamma$
(B)	cubic and rhombohedral	(Q) are two crystal systems
(C)	cubic and tetragonal	(R) have only two crystallographic angles of 90°
(D)	hexagonal and monoclinic	(S) belong to same crystal system.

[JEE 2007]

Ans. **(A) P, S ; (B) -P,Q ; (C) - Q ; (D) - Q,R**

Space for Notes

Paragraph for Question No. 13 to 15

In hexagonal systems of crystals, a frequently encountered arrangement of atoms is described as a hexagonal prism. Here, the top and bottom of the cell are regular hexagons and three atoms are sandwiched in between them. A space-filling model of this structure, called hexagonal close-packed (HCP), is constituted of a sphere on a flat surface surrounded in the same plane by six identical spheres as closely as possible. Three spheres are then placed over the first layer so that they touch each other and represent the second layer. Each one of these three spheres touches three spheres of the bottom layer. Finally, the second layer is covered with a third layer that is identical to the bottom layer in relative position. Assume radius of every sphere to be 'r'.

13. The number of atoms in this HCP unit cells is **[JEE 2008]**

(A) 4 (B) 6 (C) 12 (D) 17

Ans. **(B)**

Sol. $12 \times \frac{1}{6} + 2 \times \frac{1}{2} + 3 \times 1 = 6$ atoms

14. The volume of this HCP unit cell is **[JEE 2008]**

(A) $24\sqrt{2}\,r^3$ (B) $16\sqrt{2}\,r^3$ (C) $12\sqrt{2}\,r^3$ (D) $\frac{64}{3\sqrt{3}}\,r^3$

Ans. **(A)**

Sol. $V = \frac{6\sqrt{3}a^3}{4} \times C$

$a = 2r$

$C = \frac{4\sqrt{2}r}{\sqrt{3}}$

$V = 24\sqrt{2}r^3$

15. The empty space in this HCP unit cell is **[JEE 2008]**

(A) 74% (B) 47.6 % (C) 32% (D) 26%

Ans. **(D)**

Space for Notes

16. The correct statement(s) regarding defects in solid is (are) **[JEE 2009]**

(A) Frenkel defect is usually favoured by a very small difference in the sizes of cation and anion.

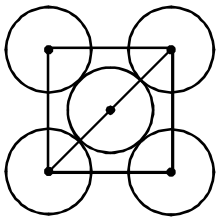
(B) Frenkel defect is a dislocation defect

(C) Trapping of an electron in the lattice leads to the formation of F-center.

(D) Schottky defects have no effect on the physical properties of solids.

Ans. (B,C)

17. The packing effeciency of the two-dimensional square unit cell shown below is **[JEE-2010]**



(A) 39.27% (B) 68.02% (C) 74.05% (D) 78.54%

Ans. (D)

Sol. $PF = \dfrac{2\pi r^2}{\left(\dfrac{4r}{\sqrt{2}}\right)^2} = .785$

% PF = 78.5%

Space for Notes

EXERCISE # S-I

METALLIC CRYSTALS

Cubic crystals

1. A closed packed structure of uniform spheres has the edge length of 600 pm. Calculate the radius of sphere, if it exist in $(\sqrt{2}=1.4, \sqrt{3}=1.7)$

(a) simple cubic lattice (b) BCC lattice (c) FCC lattice

2. Xenon crystallises in the face-centred cubic lattice and the edge length of the unit cell is $438\sqrt{2}$ pm. What is the nearest neighbour distance and what is the radius of xenon atom?

3. The effective radius of the iron atom is $\sqrt{2}$ Å. It has FCC structure. Calculate its density (Fe = 56 amu , $N_A = 6 \times 10^{23}$)

4. Calculate the ratio of densities if same element undergoes fcc as well as simple cubic packing. Assume same atomic radius in both crystals.

5. Potassium has body-centred cubic structure with the nearest neighbour distance $260\sqrt{3}$ pm . Its density would be ($\frac{1}{(5.2)^2} = 0.036$, $N_A = 6 \times 10^{23}$, K = 39)

6. A cubic solid is made up of two elements 'A' and 'B'. Atoms 'B' are at the corners of the cube and 'A' at the body centre. What is the simplest formula of compound ?

7. An element 'X' crystallizes in bcc. Find volume of unit cell in $(Å)^3$, if atomic radius is $\sqrt{3}$ Å.

8. A lattice has simple cube unit cell then number of faces which meets at a corner of a cube in this lattice is.

9. How many next nearest neighbours does potassium have in bcc lattice ?

PACKING IN SOLIDS

10. A cubic solid is made by atoms 'A' forming close pack arrangement, 'B' occupying one-fourth of tetrahedral void and C occupying half of the octahedral voids. What is the formula of compound ?

11. If number of nearest neighbours, next nearest (2^{nd} nearest) neighbour and next to next nearest (3^{rd} nearest) neighbours are x, y and z respectively for body centred cubic unit cell, then calculate value of $\frac{xy}{z}$ is.

12. In FCC unit cell, what fraction of edge is not covered by atoms ?

13. For ABC ABC ABC .... packing, distance between two succesive tetrahedral void is X and distance between two successive octahedral void is y in an unit cell, then $\frac{y\sqrt{2}}{X}$ is

IONIC CRYSTALS

14. 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.

15. The two ions A^+ and B^- have radii 88 pm and 200 pm respectively. In the closed packed crystal of compound AB, predict the co-ordination number of A^+.

16. Spinel is a important class of oxides consisting of two types of metal ions with the oxide ions arranged in CCP pattern. The normal spinel has one-eight of the tetrahedral holes occupied by one type of metal ion and one half of the octahedral hole occupied by another type of metal ion. Such a spinel is formed by Zn^{2+}, Al^{3+} and O^{2-}, with Zn^{2+} in the tetrahedral holes. Give the formula of spinel.

17. CsCl has bcc unit cell with edge length 400 pm. Calculate the interionic distance in CsCl.

18. The density of KBr is 2.38 g cm^{-3} . The length of the edge of the unit cell is 700 pm. Find the number of fomula unit of KBr present in the single unit cell.

($N_A = 6 \times 10^{23}$ mol^{-1} , At. mass : K = 39, Br = 80)

19. A crystal of lead(II) sulphide has NaCl structure. In this crystal the shortest distance between Pb^{+2} ion and S^{2-} ion is 300 pm. What is the length of the edge of the unit cell in lead sulphide? Also calculate the unit cell volume.

20. If the length of the body diagonal for CsCl which crystallises into a cubic structure with Cl^- ions at the corners and Cs^+ ions at the centre of the unit cell, is 7 Å and the radius of the Cs^+ ion is 1.69 Å, what is the radius of Cl^- ion?

PROBLEMS RELATED WITH DEFECTS IN SOLID

21. If NaCl is dopped with 10^{-3} mol % $SrCl_2$, what is the number of cation vacancies per mole of NaCl? ($N_A = 6 \times 10^{23}$)

22. A non stoichiometric compound Fe_7S_8 consist of iron in both Fe^{+2} and Fe^{+3} form and sulphur is present as sulphide ions. Calculate cation vacancies as a percentage of Fe^{+2} initially present in the ideal crystal.

23. The density of ZnS crystal (Zinc blende structure) having 10% Frenkel defect is

[$r_{Zn^{2+}} = 40\sqrt{3}$pm, $r_{S^{2-}} = 110\sqrt{3}$pm , Zn = 65.2, S = 32]

EXERCISE # S-II

1. The density of diamond from the fact that it has face centred cubic structure with two atoms per lattice point and unit cell edge length of 3.6 Å, is 'x' gm / cm^3, then the value of (1.458x) is ($N_A = 6 \times 10^{23}$)

2. What is the percent by mass of titanium in rutile, a mineral that contain titanium and oxygen, if structure can be described as a closest packed array of oxide ions, with titanium in one half of the octahedral holes. What is the oxidation number of titanium? (Ti = 48)

3. The mineral hawleyite, one form of CdS, crystallizes in one of the cubic lattices, with edge length 5.87Å. The density of hawleyite is 4.63 g cm^{-3}. (Cd = 112)

(i) In which cubic lattice does hawleyite crystallize?

(ii) Find the Schottky defect in g cm^{-3}.

4. KCl crystallizes in the same type of lattice as does NaCl. Given that $\frac{r_{Na^+}}{r_{Cl^-}}=0.5$ and $\frac{r_{Na^+}}{r_{K^+}}=0.7$ Calculate:

(a) The ratio of the sides of unit cell for KCl to that for NaCl and

(b) The ratio of densities of NaCl to that for KCl.

$\left(\left(\frac{8}{7}\right)^3 = 1.5, \frac{74.5}{58.5} = 1.25\right)$

EXERCISE # O-I

***SINGLE CORRECT* :**

1. Which of the following are the correct axial distances and axial angles for rhombohedral system ?
(A) $a = b = c$, $\alpha = \beta = \gamma \neq 90^0$ (B) $a = b \neq c$, $\alpha = \beta = \gamma = 90^0$
(C) $a \neq b = c$, $\alpha = \beta = \gamma = 90^0$ (D) $a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90^0$

2. $a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90^0$ represents
(A) tetragonal system (B) orthorhombic system
(C) monoclinic system (D) triclinic system

3. Diamond belongs to the crystal system :
(A) Cubic (B) triclinic (C) tetragonal (D) hexagonal

4. A match box exhibits -
(A) Cubic geometry (B) Monoclinic geometry
(C) Tetragonal geometry (D) Orthorhombic geometry

5. Which of the following solids substances will have same refractive index when measured in different directions?
(A) NaCl (B) Monoclinic sulphur
(C) Rubber (D) Graphite

6. An ionic compound has a unit cell consisting of A ions at the corners of a cube and B ions on the centres of the faces of the cube. The empirical formula of this compound would be-**[AIEEE-05]**
(A) A_2B (B) AB (C) A_3B (D) AB_3

7. In the body-centred cubic unit cell & face centred cubic unit cell, the radius of atom in terms of edge lengh(a) of the unit cell is respectively:
(A) $\frac{a}{2}, \frac{a}{2\sqrt{2}}$ (B) $\frac{a}{2\sqrt{2}}, \frac{\sqrt{3}a}{4}$ (C) $\frac{\sqrt{3}a}{4}, \frac{a}{2\sqrt{2}}$ (D) $\frac{\sqrt{3}a}{2}, \frac{a}{2\sqrt{2}}$

8. Crystal system in which maximum number of Bravais lattices are possible is
(A) Cubic (B) Triclinic (C) Orthorhombic (D) Rhombohedral

9. Number of atoms at second nearest position from a given atom in a BCC structure is
(A) 8 (B) 6 (C) 12 (D) 4

10. Percentage area of each face covered by atoms in a FCC unit cell is -
(A) 60.4% (B) 68% (C) 74% (D) 78.5%

11. Correct sequence of the coordination number in SC, FCC & BCC is-
(A) 6, 8, 12 (B) 6, 12, 8 (C) 8, 12, 6 (D) 8, 6, 12

12. The no. of atoms per unit cell in B.C.C. & F.C.C. is respectively : **[AIEEE-02]**
(A) 8, 10 (B) 2, 4 (C) 1, 2 (D) 1, 3

13. Total volume of atoms present in a face-centred cubic unit cell of a metal is (r is atomic radius) : **[AIEEE-06]**
(A) $\frac{24}{3}\pi r^3$ (B) $\frac{12}{3}\pi r^3$ (C) $\frac{16}{3}\pi r^3$ (D) $\frac{20}{3}\pi r^3$

14. Percentages of free space in cubic close packed structure and in body centred packed structure are respectively :- **[AIEEE-10]**

(A) 48% and 26% (B) 30% and 26% (C) 26% and 32% (D) 32% and 48%

15. If 'Z' is the number of atoms in the unit cell that represents the closest packing sequence ---A B C A B C ---, the number of tetrahedral voids in the unit cell is equal to

(A) Z (B) 2Z (C) Z/2 (D) Z/4

16. The interstitial hole is called tetrahedral because

(A) It is formed by four spheres.

(B) Partly same and partly different.

(C) It is formed by four spheres the centres of which form a regular tetrahedron.

(D) None of the above three.

17. The size of an octahedral void formed in a closest packed lattice as compared to tetrahedral void is

(A) Equal (B) Smaller (C) Larger (D) Not definite

18. If the anions (A) form hexagonal closest packing and cations (C) occupy only 2/3 octahedral voids in it, then the general formula of the compound is

(A) CA (B) CA_2 (C) C_2A_3 (D) C_3A_2

19. In a compound, atoms of element Y form ccp lattice and those of element X occupy $2/3^{rd}$ of tetrahedral voids. The formula of the compound will be - **[AIEEE-08]**

(A) X_4Y_3 (B) X_2Y_3 (C) X_2Y (D) X_3Y_4

20. In fcc unit cell smallest distance between octahedral void & tetrahedral void is -
(a = edge length of unit cell)

(A) $\frac{a}{\sqrt{2}}$ (B) $\frac{\sqrt{3}a}{2}$ (C) a (D) $\frac{\sqrt{3}a}{4}$

21. What is not true regarding hexagonal close packing (hcp)

(A) packing fraction is 0.74

(B) coordination number is 12

(C) ABC ABC.....type packing

(D) Containing both tetrahedral and octahedral voids

22. In which of the following arrangement distance between two nearest neighbours is maximum, considering identical sized atoms in all arrangements ?

(A) Simple cubic (B) bcc (C) fcc (D) equal in all

23. How many unit cell are there in 1 gram cubic crystal of NaCl ?

(A) $\frac{4\times N_A}{58.5}$ (B) $\frac{N_A}{58.5}$ (C) $\frac{N_A}{58.5\times 4}$ (D) $\frac{N_A}{58.5\times 8}$

24. How many unit cells are present in a cube-shaped ideal crystal of NaCl of mass 1.00g ?

(A) 1.28×10^{21} unit cells (B) 1.71×10^{21} unit cells **[AIEEE-03]**

(C) 2.57×10^{21} unit cells (D) 5.14×10^{21} unit cells

25. The edge length of a face centred cubic cell of an ionic substance is 508 pm. If the radius of the cation is 110 pm, the radius of the anion is :- **[AIEEE-10]**

(A) 144 pm (B) 288 pm (C) 398 pm (D) 618 pm

26. The coordination number of cation and anion in Fluorite CaF_2 and CsCl are respectively

(A) 8:4 and 6:3 (B) 6:3 and 4:4 (C) 8:4 and 8:8 (D) 4:2 and 2:4

27. A compound XY crystallizes in 8 : 8 lattice with unit cell edge lenght of 480 pm. If the radius of Y^- is 225 pm, then the radius of X^+ is

(A) 127.5 pm (B) 190.68 pm (C) 225 pm

(D) 255 pm

28. The mass of a unit cell of CsCl corresponds to

(A) 1 Cs^+ and 1 Cl^- (B) 1 Cs^+ and 6 Cl^- (C) 4 Cs^+ and 4 Cl^- (D) 8 Cs^+ and 1 Cl^-

29. An ionic compound AB has ZnS type structure. If the radius A^+ is 22.5 pm, then the ideal radius of B^- would be

(A) 54.35 pm (B) 100 pm (C) 145.16 pm (D) none of these

30. Edge length of M^+X^- (NaCl structure) is 7.2 Å. Assuming $M^+ - X^-$ contact along the cell edge, radius of X^- ion is ($r_{M^+} = 1.6Å$) :

(A) 2.0 Å (B) 5.6 Å (C) 2.8 Å (D) 38 Å

31. NH_4Cl crystallizes in CsCl type lattice with a unit cell edge length of 387 pm. The distance between the oppositively charged ions in the lattice is

(A) 335.1 pm (B) 83.77 pm (C) 274.46 pm (D) 137.23 pm

32. $r_{Na^+} = 95$ pm and $r_{Cl^-} = 181$ pm in NaCl (rock salt) structure. What is the shortest distance between Na^+ ions?

(A) 778.3 pm (B) 276 pm (C) 195.7 pm (D) 390.3 pm

33. AB crystallises itself as NaCl crystal. If $r_+ = \frac{2}{\sqrt{6}}$ and $r_- = \sqrt{6}$, the edge length of cube is

(A) $2\sqrt{3}$ (B) $\frac{4}{\sqrt{3}}$ (C) $\frac{8}{\sqrt{6}}$ (D) $\frac{16}{\sqrt{6}}$

34. Which of the following is the most likely to show schottky defect ?

(A) CaF_2 (B) ZnS (C) AgCl (D) CsCl

35. In the Schottky defect, in AB type ionic solids

(A) cations are missing from the lattice sites and occupy the interstitial sites

(B) equal number of cations and anions are missing

(C) anions are missing and electrons are present in their place

(D) equal number of extra cations and electrons are present in the interstitial sites

36. Choose the correct option.

(A) Two adjacent face centre atom doesn't touch each other in fcc unit cell because they are not nearest atom of face each other in fcc lattice

(B) Number of nearest Na^+ ions of another Na^+ in Na_2O crystal will be 24.

(C) Minimum distance between two cubical voids in simple cube unit cell lattice will be 'a' where 'a' is length of edge of unit cell

(D) By defects in solids, density of solids either remains constant or decreases but it can never increase.

37. The measured density of AgI is 6.94 g/cm^{-3} and the theoretical density is 5.67 g/cm^{-3}. These data indicate that solid AgI has -

(A) Schottky defect (B) Frenkel defect

(C) Interstitial impurities defect (D) Both (A) and (B)

38. Which of the following statement is **CORRECT** ?

(A) A metal can show only non- stoichiometric defects

(B) Schottky defect reduces the density of a solid due to significant increase in volume.

(C) Impurity defect always change the density.

(D) Solids having F-centres may have metal excess defect due to missing anions.

39. What type of crystal defect is indicated in the diagram below ? **[AIEEE-04]**

Na^+	Cl^-	Na^+	Cl^-	Na^+	Cl^-
Cl^-		Cl^-	Na^+		Na^+
Na^+	Cl^-		Cl^-	Na^+	Cl^-
Cl^-	Na	$^+Cl^-$	Na^+		Na^+

(A) Frenkel defect (B) Schottky defect

(C) Interstitial defect (D) Frenkel and Schottky defects

40. Lattice energy of an ionic compound depends upon - **[AIEEE-05]**

(A) Size of the ion only (B) Charge on the ion only

(C) Charge on the ion and size of the ion (D) Packing of ions only

EXERCISE # O-II

***SINGLE CORRECT* :**

1. The only incorrect statement for the packing of identical spheres in two dimension is :

(A) For square close packing , coordination number is 4.

(B) For hexagonal close packing, coordination number is 6.

(C) There is only one void per atom in both, square and hexagonal close packing.

(D) Hexagonal close packing is more efficiently packed than square close packing.

2. Which of the following statements is correct in the rock-salt structure of an ionic compounds?

(A) coordination number of cation is four whereas that of anion is six.

(B) coordination number of cation is six whereas that of anion is four.

(C) coordination number of each cation and anion is four.

(D) coordination number of each cation and anion is six.

3. Which one of the following schemes of ordering closest packed sheets of equal sized spheres do not generate close packed lattice.

(A) ABCABC (B) ABACABAC (C) ABBAABBA (D) ABCBCABCBC

4 . Copper metal crystallizes in FCC lattice. Edge length of unit cell is 362 pm. The radius of largest atom that can fit into the voids of copper lattice without disturbing it is

(A) 53 pm (B) 45 pm (C) 93 pm (D) 93 pm

5. Packing fraction in 2-D hexagonal arrangement of identical sphere is

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

6. The density of CaF_2 (fluorite structure) is 3.18 g/cm^3. The length of the side of the unit cell is (Ca = 40, F = 19)

(A) 253 pm (B) 344 pm (C) 546 pm (D) 273 pm

7. Choose the correct option.

(A) Two adjacent face centre atom doesn't touch each other in fcc unit cell because they are not nearest atom of face each other in fcc lattice

(B) Number of nearest Na^+ ions of another Na^+ in Na_2O crystal will be 24.

(C) Minimum distance between two cubical voids in simple cube unit cell lattice will be 'a' where 'a' is length of edge of unit cell

(D) By defects in solids, density of solids either remains constant or decreases but it can never increase.

MORE THAN ONE MAY BE CORRECT :

8. Lead metal has a density of 11.34 g/cm^3 and crystallizes in a face–centred lattice. Choose the correct alternatives (Pb = 208 , $N_A = 6 \times 10^{23}$)

(A) the volume of one unit cell is 1.22×10^{-22} cm^3.

(B) the volume of one unit cell is 1.22×10^{-19} cm^3.

(C) the atomic radius of lead is 175 pm.

(D) the atomic radius of lead is 155.1 pm.

9. Select the correct statement (s) :

(A) CsCl mainly shows Schottky defect (B) ZnS mainly shows Frenkel defect

(C) NaCl unit cell contain $4Na^+$ and $4Cl^-$ (D) Truncated octahedron have 24 corners.

10. Select the correct statement(s) –

(A) The ionic crystal of AgBr has Schottky defect.

(B) The unit cell having crystal parameters, $a = b \neq c$, $\alpha = \beta = 90°$, $\gamma = 120°$ is hexagonal

(C) Ionic compounds having Frenkel defect has high r^+/r^- ratio.

(D) The co-ordination number of Na^+ ion in NaCl is 6

ASSERTION / REASON :

11. **Statement-1**: In diamond , carbon atoms occupy alternate tetrahedral voids in the FCC lattice formed by the carbon atoms.

Statement-2 : In diamond, packing fraction is more than 74%.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

12. **Statement-1 :** Due to Frenkel defect, there is no effect on the density of the crystalline solid.

Statement-2 : In Frenkel defect, no cation or anion leaves the crystal.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

13. **Statement-1 :** Conductivity of silicon increased by doping it with group 15 element.

Statement-2 : Doping means introduction of small amount of impurities like P or As into pure silicon crytstal.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

***TABLE TYPE* COMPREHENSION :**

Column-I	Column-II	Column-III
(A) NaCl (Rock salt) structure	(i) Cation - FCC Anion - Tetrahedral void	(I) All tetrahedral voids are occupied
(B) CsCl structure	(ii) Anion - FCC Cation - Tetrahedral voids	(II) All octahedral voids are occupied
(C) ZnS (zinc blende) structure	(iii) Anion - SC Cation - Cubic voids	(III) 50 % of tetrahedral voids are occupied
(D) CaF_2 (fluorite) structure	(iv) Anion - FCC Cation - Octahedral void	(IV) All octahedral voids are empty

14. Which of the following is correct match ?

(A) A, i, I (B) A, ii, IV (C) A, iv, II (D) A, iv, IV

15. Which of the following is incorrect match ?

(A) B, iii, I (B) C, ii, III (C) D, i, I (D) D, i, IV

16. Which of the following is correct match ?

(A) D, ii, I (B) B, iv, IV (C) D, iii, I (D) C, ii, IV

MATCH THE COLUMN :

17. Match the column

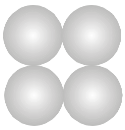
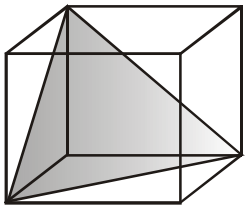
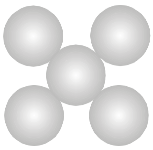
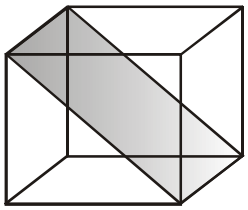
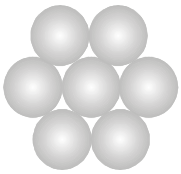
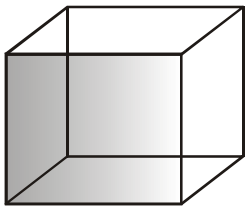
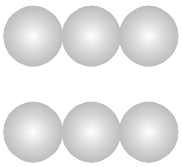
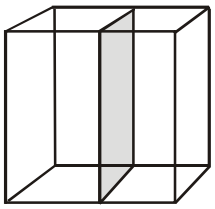
	Column I		Column II
(A)	Tetragonal and Hexagonal	(P)	are two crystal systems
(B)	Cubic and Rhombohedral	(Q)	$a = b \neq c$
(C)	Monoclinic and Triclinic	(R)	$a \neq b \neq c$
(D)	Cubic and Hexagonal	(S)	$a = b = c$

18. Match the column:

	Column I		Column II
(A)	Rock salt structure	(P)	Co-ordination number of cation is 4
(B)	Zinc Blend structure	(Q)	$\frac{\sqrt{3}a}{4} = r_+ + r_-$
(C)	Flourite structure	(R)	Co-ordination number of cation and anion are same
		(S)	Distance between two nearest anion is $\frac{a}{\sqrt{2}}$

***MATCHING LIST TYPE* :**

19. Match the column

Column I (Arrangement of the atoms/ions)	**Column II** (Planes in fcc lattice)
(P) 	(1) 
(Q) 	(2) 
(R) 	(3) 
(S) 	(4) 

Code :

	P	Q	R	S
(A)	4	3	1	2
(B)	4	3	2	1
(C)	3	2	1	4
(D)	1	2	4	3

EXERCISE # J-MAIN

1. Copper crystallises in fcc with a unit cell edge length of 361pm. What is the radius of copper atom? **[AIEEE-2011]**

(1) 181pm (2) 128pm (3) 157pm (4) 108pm

2. The radius of a calcium ion is 94 pm and of the oxide ion is 146 pm. The possible crystal structure of calcium oxide will be :- **[Jee-Main (online)-12]**

(1) Octahedral (2) Tetrahedral (3) Pyramidal (4) Trigonal

3. Ammonium chloride crystallizes in a body centred cubic lattice with edge length of unit cell of 390 pm. If the size of chloride ion is180 pm, the size of ammonium ion would be: **[Jee-Main (online)-12]**

(1) 158 pm (2) 174 pm (3) 142 pm (4) 126 pm

4. A solid has 'bcc' structure. If the distance of nearest approach between two atoms is 1.73 Å, the edge length of the cell is :- **[Jee-Main (online)-12]**

(1) 314.20 pm (2) 216 pm (3) 200 pm (4) 1.41 pm

5. Among the following the incorrect statement is :- **[Jee-Main (online)-12]**

(1) Density of crystals remains unaffected due to Frenkel defect

(2) In BCC unit cell the void space is 32%

(3) Electrical conductivity of semiconductors and metals increases with increase in temperature

(4) Density of crystals decreases due to Schottky defect

6 Lithium forms body centred cubic structure. The length of the side of its unit cell is 351 pm. Atomic radius of the lithium will be :- **[Jee-Main (offline)-12]**

(1) 152 pm (2) 75 pm (3) 300 pm (4) 240 pm

7. In a face centred cubic lattice, atoms of A form the corner points and atoms of B form the face centred points. If two atoms of A are missing from the corner points, the formula of the ionic compound is **[Jee-Main (online)-13]**

(1) AB_2 (2) AB_3 (3) AB_4 (4) A_2B_5

8. Which one of the following statements about packing in solids is **incorrect** ?

(1) Void space in ccp mode of packing is 26% **[Jee-Main (online)-13]**

(2) Coordination number in hcp mode of packing is 12

(3) Void space in hcp mode of packing is 32%

(4) Coordination number in bcc mode of packing is 8

9. An element having an atomic radius of 0.14 nm crystallizes in an fcc unit cell. What is the length of a side of the cell ? **[Jee-Main (online)-13]**

(1) 0.96 nm (2) 0.4 nm (3) 0.24 nm (4) 0.56 nm

10. Experimentally it was found that a metal oxide has formula $M_{0.98}O$. Metal M, is present as M^{2+} and M^{3+} in its oxide. Fraction of the metal which exists as M^{3+} would be :- **[Jee-Main (offline)-13]**

(1) 7.01% (2) 4.08% (3) 6.05% (4) 5.08

11. The total number of octahedral void(s) per atom present in a cubic close packed structure is :- **[Jee-Main (online)-14]**

(1) 1 (2) 2 (3) 3 (4) 4

12. In a monoclinic unit cell, the relation of sides and angles are respectively [**Jee-Main (online)-14]**

(1) $a \neq b \neq c$ and $\alpha \neq \beta \neq \gamma \neq 90^\circ$ (2) $a \neq b \neq c$ and $\beta = \gamma = 90^\circ \neq \alpha$

(3) $a = b \neq c$ and $\alpha = \beta = \gamma = 90^\circ$ (4) $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90^\circ$

13. The appearance of colour in solid alkali metal halides is generally due to :

[Jee-Main (online)-14]

(1) Frenkel defect (2) F-centres (3) Schottky defect (4) Interstitial position

14. In a face centred cubic lattice atoms A are at the corner points and atoms B at the face centred points. If atom B is missing from one of the face centred points, the formula of the ionic compound is :

[AIEEE-2011, Jee-Main (online)-14]

(1) AB_2 (2) A_2B_3 (3) A_5B_2 (4) A_2B_5

15. CsCl crystallises in body centred cubic lattice. if 'a' is its edge length then which of the following expression is correct : **[Jee-Main (offline)-14]**

(1) $r_{Cs^+} + r_{Cl^-} = \frac{\sqrt{3}}{2}a$ (2) $r_{Cs^+} + r_{Cl^-} = \sqrt{3}a$ (3) $r_{Cs^+} + r_{Cl^-} = 3a$ (4) $r_{Cs^+} + r_{Cl^-} = \frac{3a}{2}$

16. Sodium metal crystallizes in a body centred cubic lattice with a unit cell edge of 4.29Å. The radius of sodium atom is approximately :- **[Jee-Main (offline)-15]**

(1) 5.72Å (2) 0.93Å (3) 1.86Å (4) 3.022Å

17. Which of the following compounds is metallic and ferromagnetic ? **[Jee-Main (offline)-16]**

(1) MnO_2 (2) TiO_2 (3) CrO_2 (4) VO_2

18. A metal crystallises in a face centred cubic structure. If the edge length of its unit cell is 'a', the closest approach between two atoms in metallic crystal will be :- **[Jee-Main (offline)-17]**

(1) 2a (2) $2\sqrt{2}\,a$

(3) $\sqrt{2}\,a$ (4) $\frac{a}{\sqrt{2}}$

19. Which type of effect 'defect' has the presence of cations in the interstitial sites -

(1) Vacancy defect (2) Frenkel defect **[Jee-Main (offline)-18]**

(3) Metal deficiency defect (4) Schottky defect

20. All of the following share the same crystal structure except :- **[Jee-Main (online)-18]**

(1) RbCl (2) CsCl

(3) LiCl (4) NaCl

21. Which of the following arrangements shows the schematic alignment of magnetic moments of antiferromagnetic substance ? **[Jee-Main (online)-18]**

(1)  (2) 

(3)  (4) 

22. An element crystallises in a face-centred cubic (fcc) unit cell with cell edge a. The distance between the centres of two nearest octahedral voids in the crystal lattice is **[Jee-Main (online)-2020]**

(1) a (2) $\sqrt{2}a$ (3) $\frac{a}{\sqrt{2}}$ (4) $\frac{a}{2}$

23. A diatomic molecule X_2 has a body-centred cubic (bcc) structure with a cell edge of 300 pm. The density of the molecule is 6.17 g cm^{-3}. The number of molecules present in 200 g of X_2 is

(Avogadro constant (N_A) = 6×10^{23} mol^{-1}) **[Jee-Main (online)-2020]**

(1) 8 N_A (2) 40 N_A (3) 4 N_A (4) 2 N_A

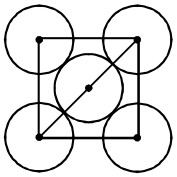
24. A crystal is made up of metal ions 'M_1' ana 'M_2' and oxide ions. Oxide ions form a ccp lattice structure. The cation 'M_1' occupies 50% of octahedral voids and the cation 'M_2' occupies 12.5% of tetrahedral voids of oxide lattice. The oxidation numbers of 'M_1' and 'M_2' are, respectively :

[Jee-Main (online)-2020]

(1) +2, +4 (2) +3, +1 (3) +1, +3 (4) +4, +2

EXERCISE # J-ADVANCED

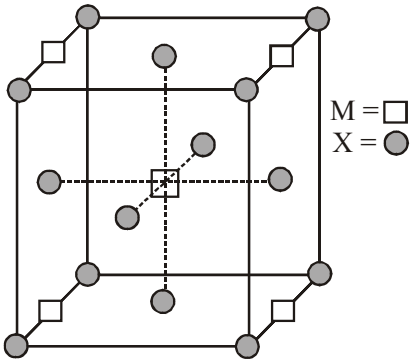
1. The packing effeciency of the two-dimensional square unit cell shown below is **[JEE-2010]**



(A) 39.27% (B) 68.02% (C) 74.05% (D) 78.54%

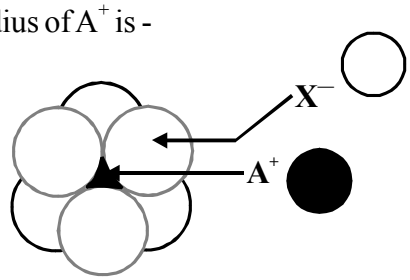
2. The number of hexagonal faces that present in a truncated octahedron is. **[JEE-2011]**

3. A compound M_pX_q has cubic close packing (ccp) arrangement of X. Its unit cell structure is shown below. The empirical formula of the compound is : **[JEE-2012]**



(A) MX (B) MX_2 (C) M_2X (D) M_5X_{14}

4. The arrangement of X^- ions around A^+ ion in solid AX is given in the figure (not drawn to scale). If the radius of X^- is 250 pm, the radius of A^+ is - **[JEE-2013]**



(A) 104 pm (B) 125 pm (C) 183 pm (D) 57 pm

5. If the unit cell of a mineral has cubic close packed (ccp) array of oxygen atoms with m fraction of octahedral holes occupied by aluminium ions and n fraction of tetrahedral holes occupied by magnesium ions m and n respectively, are - **[JEE-2015]**

(A) $\frac{1}{2},\frac{1}{8}$ (B) $1,\frac{1}{4}$ (C) $\frac{1}{2},\frac{1}{2}$ (D) $\frac{1}{4},\frac{1}{8}$

6. The **CORRECT** statement(s) for cubic close packed (ccp) three dimensional structure is (are)

(A) The number of the nearest neighbours of an atom present in the topmost layer is 12

(B) The efficiency of atom packing is 74% **[JEE-2016]**

(C) The number of octahedral and tetrahedral voids per atom are 1 and 2, respectively

(D) The unit cell edge length is $2\sqrt{2}$ times the radius of the atom

7. A crystalline solid of a pure substance has a face-centred cubic structure with a cell edge of 400 pm. If the density of the substance in the crystal is 8g cm^{-3}, then the number of atoms present in 256g of the crystal is $N \times 10^{24}$. The value of N is **[JEE-2017]**

8. Consider an ionic solid MX with NaCl structure. Construct a new structure (Z) whose unit cell is constructed from the unit cell of MX following the sequential instructions given below. Neglect the charge balance. **[JEE-2018]**

(i) Remove all the anions (X) except the central one

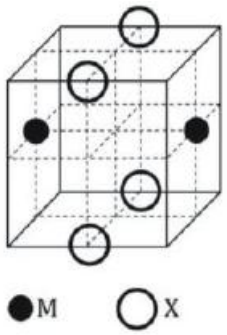
(ii) Replace all the face centered cations (M) by anions (X)

(iii) Remove all the corner cations (M)

(iv) Replace the central anion (X) with cation (M)

The value of $\left(\frac{\text{number of anions}}{\text{number of cations}}\right)$ in Z is____.

9. The cubic unit cell structure of a compound containing cation M and anion X is shown below. When compared to the anion, the cation has smaller ionic radius. Choose the correct statement(s). **[JEE-2020]**



(A) The empirical formula of the compound is MX.

(B) The cation M and anion X have different coordination geometries.

(C) The ratio of M-X bond length to the cubic unit cell edge length is 0.866.

(D) The ratio of the ionic radii of cation M to anion X is 0.414.

ANSWER KEY

EXERCISE # S-I

1. Ans. (a) 300 pm, (b) 255 pm, (c) 210 pm
2. Ans. 438 pm, 219 pm
3. Ans. 5.83 g cm^{-3}
4. Ans. ($\sqrt{2}:1$)
5. Ans. (0.9 gm/cm^{-3})
6. Ans. (A,B)
7. Ans. (64)
8. Ans. (12)
9. Ans. (6)
10. Ans. A_2BC
11. Ans. (4)
12. Ans. (0.293)
13. Ans. (2) $\frac{\frac{a}{\sqrt{2}}\times\sqrt{2}}{a/2}=2$
14. Ans. 4, 6, 8
15. Ans.(6)
16. Ans. $ZnAl_2O_4$
17. Ans.346.4 pm
18. Ans. 4
19. Ans.a =600 pm, V=2.16 × 10^{-22} cm^3
20. Ans. 1.81Å
21. Ans.6.0 × 10^{18}
22. Ans. 12.5%
23. Ans. 3.0 gm/cm^3

EXERCISE # S-II

1. Ans. (5)
2. Ans. 60%, +4
3. Ans. (i) FCC (ii) 0.116 g/cc
4. Ans. (a) 1.143, (b) 1.2

EXERCISE # O-I

1.	Ans.(A)	**2.**	Ans.(D)	**3.**	Ans.(A)
4.	Ans.(D)	**5.**	Ans.(C)	**6.**	Ans.(D)
7.	Ans.(C)	**8.**	Ans.(C)	**9.**	Ans (B)
10.	Ans (D)	**11.**	Ans (B)	**12.**	Ans.(B)
13.	Ans.(C)	**14.**	Ans.(C)	**15.**	Ans.(B)
16.	Ans.(C)	**17.**	Ans.(C)	**18.**	Ans.(C)
19.	Ans.(A)	**20**	Ans (D)	**21.**	Ans (C)
22.	Ans (D)	**23.**	Ans.(C)	**24.**	Ans.(C)
25.	Ans.(A)	**26.**	Ans.(C)	**27.**	Ans.(B)
28.	Ans.(A)	**29.**	Ans.(B)	**30.**	Ans.(A)
31.	Ans.(A)	**32.**	Ans.(D)	**33.**	Ans.(D)
34.	Ans.(D)	**35.**	Ans.(B)	**36.**	Ans(C)
37.	Ans.(C)	**38.**	Ans.(D)	**39.**	Ans.(B)
40.	Ans.(C)				

EXERCISE # O-II

1.	Ans.(C)	2.	Ans.(D)	3.	Ans.(C)
4.	Ans.(A)	5.	Ans.(B)	6.	Ans.(C)
7.	Ans.(C)	8.	Ans.(A,C)	9.	Ans.(A,B,C,D)
10.	Ans.(A,B,D)	11.	Ans.(C)	12	Ans.(A)
13.	Ans.(A)	14.	Ans.(C)	15.	Ans.(A)

16. Ans.(D)

17. Ans.(A) $\rightarrow$ P, Q ; (B) $\rightarrow$ P,S ; (C) $\rightarrow$ P,R ; (D) $\rightarrow$ P

18. Ans.(A) $\rightarrow$ R,S ; (B) $\rightarrow$ P,Q,R,S ; (C) $\rightarrow$ Q

19. Ans.Ans.(A)

EXERCISE # J-MAIN

1.	Ans.(2)	2	Ans.(1)	3.	Ans.(1)
4.	Ans.(3)	5.	Ans.(3)	6	Ans.(1)
7.	Ans.(3)	8.	Ans.(3)	9.	Ans.(2)
10.	Ans.(2)	11.	Ans.(1)	12.	Ans.(2)
13.	Ans.(2)	13.	Ans.(4)	15.	Ans.(1)
16.	Ans.(3)	17.	Ans.(3)	18	Ans. (4)
19.	Ans.(2)	20.	Ans.(2)	21.	Ans.(4)
22.	Ans.(3)	23.	Ans.(3)	24.	Ans.(1)

EXERCISE # J-ADVANCED

1.	Ans.(D)	2.	Ans.(8)	3.	Ans.(B)
4.	Ans.(A)	5.	Ans. (A)	6.	Ans.(B,C,D)
7.	Ans.(2)	8.	Ans.(3)	9.	Ans.(A,C)

Important Notes

EXERCISE # S-I

METALLIC CRYSTALS

Cubic crystals

1. A closed packed structure of uniform spheres has the edge length of 600 pm. Calculate the radius of sphere, if it exist in ($\sqrt{2} = 1.4, \sqrt{3} = 1.7$)

(a) simple cubic lattice (b) BCC lattice (c) FCC lattice

SS0001

2. Xenon crystallises in the face-centred cubic lattice and the edge length of the unit cell is $438\sqrt{2}$ pm. What is the nearest neighbour distance and what is the radius of xenon atom?

SS0002

3. The effective radius of the iron atom is $\sqrt{2}$ Å. It has FCC structure. Calculate its density (Fe = 56 amu , $N_A = 6 \times 10^{23}$)

SS0003

4. Calculate the ratio of densities if same element undergoes fcc as well as simple cubic packing. Assume same atomic radius in both crystals.

SS0004

5. Potassium has body-centred cubic structure with the nearest neighbour distance $260\sqrt{3}$ pm . Its density would be ($\frac{1}{(5.2)^2} = 0.036$, $N_A = 6 \times 10^{23}$, K = 39)

SS0005

6. A cubic solid is made up of two elements 'A' and 'B'. Atoms 'B' are at the corners of the cube and 'A' at the body centre. What is the simplest formula of compound ?

SS0006

7. An element 'X' crystallizes in bcc. Find volume of unit cell in $(Å)^3$, if atomic radius is $\sqrt{3}$ Å.

SS0007

8. A lattice has simple cube unit cell then number of faces which meets at a corner of a cube in this lattice is.

SS0008

9. How many next nearest neighbours does potassium have in bcc lattice ?

SS0009

PACKING IN SOLIDS

10. A cubic solid is made by atoms 'A' forming close pack arrangement, 'B' occupying one-fourth of tetrahedral void and C occupying half of the octahedral voids. What is the formula of compound ?

SS0011

11. If number of nearest neighbours, next nearest (2^{nd} nearest) neighbour and next to next nearest (3^{rd} nearest) neighbours are x, y and z respectively for body centred cubic unit cell, then calculate value of $\frac{xy}{z}$ is.

SS0012

12. In FCC unit cell, what fraction of edge is not covered by atoms ?

SS0013

13. For C ABC ABC .... packing, distance between two succesive tetrahedral void is X and distance between two successive octahedral void is y in an unit cell, then $\frac{y\sqrt{2}}{X}$ is

SS0015

IONIC CRYSTALS

14. 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.

SS0021

15. The two ions A^{+} and B^{-} have radii 88 pm and 200 pm respectively. In the closed packed crystal of compound AB, predict the co-ordination number of A^{+}.

SS0022

16. Spinel is a important class of oxides consisting of two types of metal ions with the oxide ions arranged in CCP pattern. The normal spinel has one-eight of the tetrahedral holes occupied by one type of metal ion and one half of the octahedral hole occupied by another type of metal ion. Such a spinel is formed by Zn^{2+}, Al^{3+} and O^{2-}, with Zn^{2+} in the tetrahedral holes. Give the formula of spinel.

SS0023

17. CsCl has bcc unit cell with edge length 400 pm. Calculate the interionic distance in CsCl.

SS0025

18. The density of KBr is 2.38 g cm^{-3} . The length of the edge of the unit cell is 700 pm. Find the number of fomula unit of KBr present in the single unit cell.
($N_A = 6 \times 10^{23}$ mol^{-1} , At. mass : K = 39, Br = 80)

SS0026

19. A crystal of lead(II) sulphide has NaCl structure. In this crystal the shortest distance between Pb^{+2} ion and S^{2-} ion is 300 pm. What is the length of the edge of the unit cell in lead sulphide? Also calculate the unit cell volume.

SS0027

20. If the length of the body diagonal for CsCl which crystallises into a cubic structure with Cl^{-} ions at the corners and Cs^{+} ions at the centre of the unit cell, is 7 Å and the radius of the Cs^{+} ion is 1.69 Å, what is the radius of Cl^{-} ion?

SS0028

PROBLEMS RELATED WITH DEFECTS IN SOLID

21. If NaCl is dopped with 10^{-3} mol % $SrCl_2$, what is the number of cation vacancies per mole of NaCl?
($N_A = 6 \times 10^{23}$)

SS0032

22. A non stoichiometric compound Fe_7S_8 consist of iron in both Fe^{+2} and Fe^{+3} form and sulphur is present as sulphide ions. Calculate cation vacancies as a percentage of Fe^{+2} initially present in the ideal crystal.

SS0034

23. The density of ZnS crystal (Zinc blende structure) having 10% Frenkel defect is
[$r_{Zn^{2+}} = 40\sqrt{3}$pm, $r_{S^{2-}} = 110\sqrt{3}$pm , Zn = 65.2, S = 32]

SS0035

EXERCISE # S-II

1. The density of diamond from the fact that it has face centred cubic structure with two atoms per lattice point and unit cell edge length of 3.6 Å, is 'x' gm / cm^3, then the value of (1.458x) is ($N_A = 6 \times 10^{23}$)

SS0037

2. What is the percent by mass of titanium in rutile, a mineral that contain titanium and oxygen, if structure can be described as a closest packed array of oxide ions, with titanium in one half of the octahedral holes. What is the oxidation number of titanium? (Ti = 48)

SS0039

3. The mineral hawleyite, one form of CdS, crystallizes in one of the cubic lattices, with edge length 5.87Å. The density of hawleyite is 4.63 g cm^{-3}. (Cd = 112)

(i) In which cubic lattice does hawleyite crystallize?

(ii) Find the Schottky defect in g cm^{-3}.

SS0043

4. KCl crystallizes in the same type of lattice as does NaCl. Given that $\frac{r_{Na^+}}{r_{Cl^-}}=0.5$ and $\frac{r_{Na^+}}{r_{K^+}}=0.7$ Calculate:

(a) The ratio of the sides of unit cell for KCl to that for NaCl and

(b) The ratio of densities of NaCl to that for KCl.

$\left(\left(\frac{8}{7}\right)^3 = 1.5, \frac{74.5}{58.5} = 1.25\right)$

SS0044

EXERCISE # O-I

***SINGLE CORRECT* :**

1. Which of the following are the correct axial distances and axial angles for rhombohedral system ?

(A) $a = b = c$, $\alpha = \beta = \gamma \neq 90^0$ (B) $a = b \neq c$, $\alpha = \beta = \gamma = 90^0$

(C) $a \neq b = c$, $\alpha = \beta = \gamma = 90^0$ (D) $a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90^0$

SS0050

2. $a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90^0$ represents

(A) tetragonal system (B) orthorhombic system

(C) monoclinic system (D) triclinic system

SS0051

3. Diamond belongs to the crystal system :

(A) Cubic (B) triclinic (C) tetragonal (D) hexagonal

SS0052

4. A match box exhibits -

(A) Cubic geometry (B) Monoclinic geometry

(C) Tetragonal geometry (D) Orthorhombic geometry

SS0053

5. Which of the following solids substances will have same refractive index when measured in different directions?

(A) NaCl (B) Monoclinic sulphur

(C) Rubber (D) Graphite

SS0054

6. An ionic compound has a unit cell consisting of A ions at the corners of a cube and B ions on the centres of the faces of the cube. The empirical formula of this compound would be- **[AIEEE-05]**

(A) A_2B (B) AB (C) A_3B (D) AB_3

SS0142

7. In the body-centred cubic unit cell & face centred cubic unit cell, the radius of atom in terms of edge lengh(a) of the unit cell is respectively:

(A) $\frac{a}{2}, \frac{a}{2\sqrt{2}}$ (B) $\frac{a}{2\sqrt{2}}, \frac{\sqrt{3}a}{4}$ (C) $\frac{\sqrt{3}a}{4}, \frac{a}{2\sqrt{2}}$ (D) $\frac{\sqrt{3}a}{2}, \frac{a}{2\sqrt{2}}$

SS0055

8. Crystal system in which maximum number of Bravais lattices are possible is

(A) Cubic (B) Triclinic (C) Orthorhombic (D) Rhombohedral

SS0056

9. Number of atoms at second nearest position from a given atom in a BCC structure is

(A) 8 (B) 6 (C) 12 (D) 4

SS0057

10. Percentage area of each face covered by atoms in a FCC unit cell is -

(A) 60.4% (B) 68% (C) 74% (D) 78.5%

SS0058

11. Correct sequence of the coordination number in SC, FCC & BCC is-
(A) 6, 8, 12 (B) 6, 12, 8 (C) 8, 12, 6 (D) 8, 6, 12

SS0059

12. The no. of atoms per unit cell in B.C.C. & F.C.C. is respectively : **[AIEEE-02]**
(A) 8, 10 (B) 2, 4 (C) 1, 2 (D) 1, 3

SS0143

13. Total volume of atoms present in a face-centred cubic unit cell of a metal is (r is atomic radius) :

[AIEEE-06]

(A) $\frac{24}{3}\pi r^3$ (B) $\frac{12}{3}\pi r^3$ (C) $\frac{16}{3}\pi r^3$ (D) $\frac{20}{3}\pi r^3$

SS0144

14. Percentages of free space in cubic close packed structure and in body centred packed structure are respectively :- **[AIEEE-10]**
(A) 48% and 26% (B) 30% and 26% (C) 26% and 32% (D) 32% and 48%

SS0145

15. If 'Z' is the number of atoms in the unit cell that represents the closest packing sequence ---A B C A B C ---, the number of tetrahedral voids in the unit cell is equal to
(A) Z (B) 2Z (C) Z/2 (D) Z/4

SS0060

16. The interstitial hole is called tetrahedral because
(A) It is formed by four spheres.
(B) Partly same and partly different.
(C) It is formed by four spheres the centres of which form a regular tetrahedron.
(D) None of the above three.

SS0061

17. The size of an octahedral void formed in a closest packed lattice as compared to tetrahedral void is
(A) Equal (B) Smaller (C) Larger (D) Not definite

SS0062

18. If the anions (A) form hexagonal closest packing and cations (C) occupy only 2/3 octahedral voids in it, then the general formula of the compound is
(A) CA (B) CA_2 (C) C_2A_3 (D) C_3A_2

SS0063

19. In a compound, atoms of element Y form ccp lattice and those of element X occupy 2/3rd of tetrahedral voids. The formula of the compound will be - **[AIEEE-08]**
(A) X_4Y_3 (B) X_2Y_3 (C) X_2Y (D) X_3Y_4

SS0146

20. In fcc unit cell smallest distance between octahedral void & tetrahedral void is -
(a = edge length of unit cell)

(A) $\frac{a}{\sqrt{2}}$ (B) $\frac{\sqrt{3}a}{2}$ (C) a (D) $\frac{\sqrt{3}a}{4}$

SS0067

21. What is not true regarding hexagonal close packing (hcp)
(A) packing fraction is 0.74
(B) coordination number is 12
(C) ABC ABC.....type packing
(D) Containing both tetrahedral and octahedral voids

SS0068

22. In which of the following arrangement distance between two nearest neighbours is maximum, considering identical sized atoms in all arrangements ?

(A) Simple cubic (B) bcc (C) fcc (D) equal in all

SS0069

23. How many unit cell are there in 1 gram cubic crystal of NaCl ?

(A) $\frac{4\times N_A}{58.5}$ (B) $\frac{N_A}{58.5}$ (C) $\frac{N_A}{58.5\times 4}$ (D) $\frac{N_A}{58.5\times 8}$

SS0070

24. How many unit cells are present in a cube-shaped ideal crystal of NaCl of mass 1.00g ?
(A) 1.28×10^{21} unit cells (B) 1.71×10^{21} unit cells **[AIEEE-03]**
(C) 2.57×10^{21} unit cells (D) 5.14×10^{21} unit cells

SS0147

25. The edge length of a face centred cubic cell of an ionic substance is 508 pm. If the radius of the cation is 110 pm, the radius of the anion is :- **[AIEEE-10]**

(A) 144 pm (B) 288 pm (C) 398 pm (D) 618 pm

SS0148

26. The coordination number of cation and anion in Fluorite CaF_2 and CsCl are respectively
(A) 8:4 and 6:3 (B) 6:3 and 4:4 (C) 8:4 and 8:8 (D) 4:2 and 2:4

SS0072

27. A compound XY crystallizes in 8 : 8 lattice with unit cell edge lenght of 480 pm. If the radius of Y^- is 225 pm, then the radius of X^+ is
(A) 127.5 pm (B) 190.68 pm (C) 225 pm (D) 255 pm

SS0073

28. The mass of a unit cell of CsCl corresponds to
(A) 1 Cs^+ and 1 Cl^- (B) 1 Cs^+ and 6 Cl^- (C) 4 Cs^+ and 4 Cl^- (D) 8 Cs^+ and 1 Cl^-

SS0074

29. An ionic compound AB has ZnS type structure. If the radius A^+ is 22.5 pm, then the ideal radius of B^- would be
(A) 54.35 pm (B) 100 pm (C) 145.16 pm (D) none of these

SS0149

30. Edge length of M^+X^- (NaCl structure) is 7.2 Å. Assuming $M^+ - X^-$ contact along the cell edge, radius of X^- ion is ($r_{M^+} = 1.6Å$) :

(A) 2.0 Å (B) 5.6 Å (C) 2.8 Å (D) 38 Å

SS0150

31. NH_4Cl crystallizes in CsCl type lattice with a unit cell edge length of 387 pm. The distance between the oppositively charged ions in the lattice is

(A) 335.1 pm (B) 83.77 pm (C) 274.46 pm (D) 137.23 pm

SS0077

32. $r_{Na^+} = 95$ pm and $r_{Cl^-} = 181$ pm in NaCl (rock salt) structure. What is the shortest distance between Na^+ ions?

(A) 778.3 pm (B) 276 pm (C) 195.7 pm (D) 390.3 pm

SS0078

33. AB crystallises itself as NaCl crystal. If $r_+ = \frac{2}{\sqrt{6}}$ and $r_- = \sqrt{6}$, the edge length of cube is

(A) $2\sqrt{3}$ (B) $\frac{4}{\sqrt{3}}$ (C) $\frac{8}{\sqrt{6}}$ (D) $\frac{16}{\sqrt{6}}$

SS0079

34. Which of the following is the most likely to show schottky defect ?

(A) CaF_2 (B) ZnS (C) AgCl (D) CsCl

SS0080

35. In the Schottky defect, in AB type ionic solids

(A) cations are missing from the lattice sites and occupy the interstitial sites

(B) equal number of cations and anions are missing

(C) anions are missing and electrons are present in their place

(D) equal number of extra cations and electrons are present in the interstitial sites

SS0081

36. Choose the correct option.

(A) Two adjacent face centre atom doesn't touch each other in fcc unit cell because they are not nearest atom of face each other in fcc lattice

(B) Number of nearest Na^+ ions of another Na^+ in Na_2O crystal will be 24.

(C) Minimum distance between two cubical voids in simple cube unit cell lattice will be 'a' where 'a' is length of edge of unit cell

(D) By defects in solids, density of solids either remains constant or decreases but it can never increase.

SS0082

37. The measured density of AgI is 6.94 g/cm^{-3} and the theoretical density is 5.67 g/cm^{-3}. These data indicate that solid AgI has -

(A) Schottky defect (B) Frenkel defect

(C) Interstitial impurities defect (D) Both (A) and (B)

SS0083

38. Which of the following statement is **CORRECT** ?

(A) A metal can show only non- stoichiometric defects

(B) Schottky defect reduces the density of a solid due to significant increase in volume.

(C) Impurity defect always change the density.

(D) Solids having F-centres may have metal excess defect due to missing anions.

SS0084

39. What type of crystal defect is indicated in the diagram below ? **[AIEEE-04]**

Na^+ Cl^- Na^+ Cl^- Na^+ Cl^-

Cl^- Cl^- Na^+ Na^+

Na^+ Cl^- Cl^- Na^+ Cl^-

Cl^- Na $^+Cl^-$ Na^+ Na^+

(A) Frenkel defect (B) Schottky defect

(C) Interstitial defect (D) Frenkel and Schottky defects

SS0151

40. Lattice energy of an ionic compound depends upon - **[AIEEE-05]**

(A) Size of the ion only (B) Charge on the ion only

(C) Charge on the ion and size of the ion (D) Packing of ions only

SS0152

EXERCISE # O-II

***SINGLE CORRECT* :**

1. The only incorrect statement for the packing of identical spheres in two dimension is :

(A) For square close packing , coordination number is 4.

(B) For hexagonal close packing, coordination number is 6.

(C) There is only one void per atom in both, square and hexagonal close packing.

(D) Hexagonal close packing is more efficiently packed than square close packing.

SS0085

2. Which of the following statements is correct in the rock-salt structure of an ionic compounds?

(A) coordination number of cation is four whereas that of anion is six.

(B) coordination number of cation is six whereas that of anion is four.

(C) coordination number of each cation and anion is four.

(D) coordination number of each cation and anion is six.

SS0087

3. Which one of the following schemes of ordering closest packed sheets of equal sized spheres do not generate close packed lattice.

(A) ABCABC (B) ABACABAC (C) ABBAABBA (D) ABCBCABCBC

SS0064

4. Copper metal crystallizes in FCC lattice. Edge length of unit cell is 362 pm. The radius of largest atom that can fit into the voids of copper lattice without disturbing it is

(A) 53 pm (B) 45 pm (C) 93 pm (D) 93 pm

SS0065

5. Packing fraction in 2-D hexagonal arrangement of identical sphere is

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

SS0066

6. The density of CaF_2 (fluorite structure) is 3.18 g/cm^3. The length of the side of the unit cell is (Ca = 40, F = 19)

(A) 253 pm (B) 344 pm (C) 546 pm (D) 273 pm

SS0071

7. Choose the correct option.

(A) Two adjacent face centre atom doesn't touch each other in fcc unit cell because they are not nearest atom of face each other in fcc lattice

(B) Number of nearest Na^+ ions of another Na^+ in Na_2O crystal will be 24.

(C) Minimum distance between two cubical voids in simple cube unit cell lattice will be 'a' where 'a' is length of edge of unit cell

(D) By defects in solids, density of solids either remains constant or decreases but it can never increase.

SS00082

MORE THAN ONE MAY BE CORRECT :

8. Lead metal has a density of 11.34 g/cm^3 and crystallizes in a face–centred lattice. Choose the correct alternatives (Pb = 208 , $N_A = 6 \times 10^{23}$)

(A) the volume of one unit cell is 1.22×10^{-22} cm^3.

(B) the volume of one unit cell is 1.22×10^{-19} cm^3.

(C) the atomic radius of lead is 175 pm.

(D) the atomic radius of lead is 155.1 pm.

SS0090

9. Select the correct statement (s) :

(A) CsCl mainly shows Schottky defect (B) ZnS mainly shows Frenkel defect

(C) NaCl unit cell contain $4Na^+$ and $4Cl^-$ (D) Truncated octahedron have 24 corners.

SS0092

10. Select the correct statement(s) –

(A) The ionic crystal of AgBr has Schottky defect.

(B) The unit cell having crystal parameters, $a = b \neq c$, $\alpha = \beta = 90°$, $\gamma = 120°$ is hexagonal

(C) Ionic compounds having Frenkel defect has high r^+/r^- ratio.

(D) The co-ordination number of Na^+ ion in NaCl is 6

SS0093

ASSERTION / REASON :

11. **Statement-1**: In diamond , carbon atoms occupy alternate tetrahedral voids in the FCC lattice formed by the carbon atoms.

Statement-2 : In diamond, packing fraction is more than 74%.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

SS0097

12. **Statement-1 :** Due to Frenkel defect, there is no effect on the density of the crystalline solid.

Statement-2 : In Frenkel defect, no cation or anion leaves the crystal.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

SS0098

13. **Statement-1 :** Conductivity of silicon increased by doping it with group 15 element.

Statement-2 : Doping means introduction of small amount of impurities like P or As into pure silicon crytstal.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

SS0099

***TABLE TYPE* COMPREHENSION :**

Column-I	Column-II	Column-III
(A) NaCl (Rock salt) structure	(i) Cation - FCC Anion - Tetrahedral void	(I) All tetrahedral voids are occupied
(B) CsCl structure	(ii) Anion - FCC Cation - Tetrahedral voids	(II) All octahedral voids are occupied
(C) ZnS (zinc blende) structure	(iii) Anion - SC Cation - Cubic voids	(III) 50 % of tetrahedral voids are occupied
(D) CaF_2 (fluorite) structure	(iv) Anion - FCC Cation - Octahedral void	(IV) All octahedral voids are empty

14. Which of the following is correct match ?

(A) A, i, I (B) A, ii, IV (C) A, iv, II (D) A, iv, IV

SS0106

15. Which of the following is incorrect match ?

(A) B, iii, I (B) C, ii, III (C) D, i, I (D) D, i, IV

SS0107

16. Which of the following is correct match ?

(A) D, ii, I (B) B, iv, IV (C) D, iii, I (D) C, ii, IV

SS0108

MATCH THE COLUMN :

17. Match the column

	Column I		**Column II**
(A)	Tetragonal and Hexagonal	(P)	are two crystal systems
(B)	Cubic and Rhombohedral	(Q)	$a = b \neq c$
(C)	Monoclinic and Triclinic	(R)	$a \neq b \neq c$
(D)	Cubic and Hexagonal	(S)	$a = b = c$

SS0109

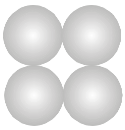
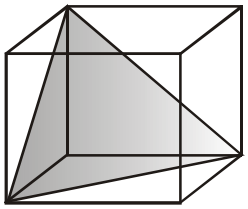
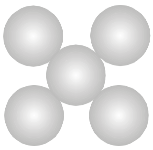
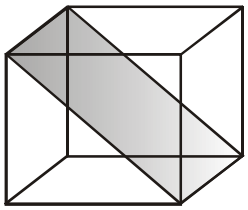
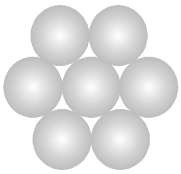
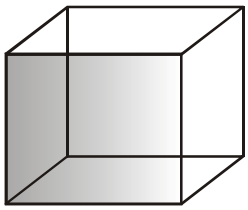
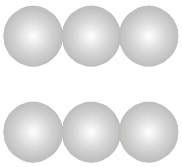
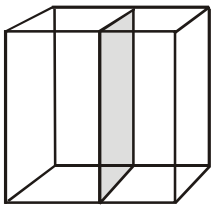
18. Match the column:

	Column I		**Column II**
(A)	Rock salt structure	(P)	Co-ordination number of cation is 4
(B)	Zinc Blend structure	(Q)	$\frac{\sqrt{3}a}{4} = r_+ + r_-$
(C)	Flourite structure	(R)	Co-ordination number of cation and anion are same
		(S)	Distance between two nearest anion is $\frac{a}{\sqrt{2}}$

SS0110

***MATCHING LIST TYPE* :**

19. Match the column

Column I (Arrangement of the atoms/ions)	**Column II** (Planes in fcc lattice)
(P) 	(1) 
(Q) 	(2) 
(R) 	(3) 
(S) 	(4) 

Code :

	P	Q	R	S
(A)	4	3	1	2
(B)	4	3	2	1
(C)	3	2	1	4
(D)	1	2	4	3

SS0111

EXERCISE # J-MAIN

1. Copper crystallises in fcc with a unit cell edge length of 361pm. What is the radius of copper atom?
[AIEEE-2011]

(1) 181pm (2) 128pm (3) 157pm (4) 108pm

SS0153

2. The radius of a calcium ion is 94 pm and of the oxide ion is 146 pm. The possible crystal structure of calcium oxide will be :- **[Jee-Main (online)-12]**

(1) Octahedral (2) Tetrahedral (3) Pyramidal (4) Trigonal

SS0154

3. Ammonium chloride crystallizes in a body centred cubic lattice with edge length of unit cell of 390 pm. If the size of chloride ion is180 pm, the size of ammonium ion would be:
[Jee-Main (online)-12]

(1) 158 pm (2) 174 pm (3) 142 pm (4) 126 pm

SS0155

4. A solid has 'bcc' structure. If the distance of nearest approach between two atoms is 1.73 Å, the edge length of the cell is :- **[Jee-Main (online)-12]**

(1) 314.20 pm (2) 216 pm (3) 200 pm (4) 1.41 pm

SS0156

5. Among the following the incorrect statement is :- **[Jee-Main (online)-12]**

(1) Density of crystals remains unaffected due to Frenkel defect

(2) In BCC unit cell the void space is 32%

(3) Electrical conductivity of semiconductors and metals increases with increase in temperature

(4) Density of crystals decreases due to Schottky defect

SS0157

6 Lithium forms body centred cubic structure. The length of the side of its unit cell is 351 pm. Atomic radius of the lithium will be :- **[Jee-Main (offline)-12]**

(1) 152 pm (2) 75 pm (3) 300 pm (4) 240 pm

SS0119

7. In a face centred cubic lattice, atoms of A form the corner points and atoms of B form the face centred points. If two atoms of A are missing from the corner points, the formula of the ionic compound is **[Jee-Main (online)-13]**

(1) AB_2 (2) AB_3 (3) AB_4 (4) A_2B_5

SS0120

8. Which one of the following statements about packing in solids is **incorrect** ?

(1) Void space in ccp mode of packing is 26% **[Jee-Main (online)-13]**

(2) Coordination number in hcp mode of packing is 12

(3) Void space in hcp mode of packing is 32%

(4) Coordination number in bcc mode of packing is 8

SS0121

9. An element having an atomic radius of 0.14 nm crystallizes in an fcc unit cell. What is the length of a side of the cell ? **[Jee-Main (online)-13]**

(1) 0.96 nm (2) 0.4 nm (3) 0.24 nm (4) 0.56 nm

SS0122

10. Experimentally it was found that a metal oxide has formula $M_{0.98}O$. Metal M, is present as M^{2+} and M^{3+} in its oxide. Fraction of the metal which exists as M^{3+} would be :- **[Jee-Main (offline)-13]**

(1) 7.01% (2) 4.08% (3) 6.05% (4) 5.08

SS0123

11. The total number of octahedral void(s) per atom present in a cubic close packed structure is :- **[Jee-Main (online)-14]**

(1) 1 (2) 2 (3) 3 (4) 4

SS0124

12. In a monoclinic unit cell, the relation of sides and angles are respectively **[Jee-Main (online)-14]**

(1) $a \neq b \neq c$ and $\alpha \neq \beta \neq \gamma \neq 90^\circ$ (2) $a \neq b \neq c$ and $\beta = \gamma = 90^\circ \neq \alpha$

(3) $a = b \neq c$ and $\alpha = \beta = \gamma = 90^\circ$ (4) $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90^\circ$

SS0125

13. The appearance of colour in solid alkali metal halides is generally due to : **[Jee-Main (online)-14]**

(1) Frenkel defect (2) F-centres (3) Schottky defect (4) Interstitial position

SS0126

14. In a face centred cubic lattice atoms A are at the corner points and atoms B at the face centred points. If atom B is missing from one of the face centred points, the formula of the ionic compound is : **[AIEEE-2011, Jee-Main (online)-14]**

(1) AB_2 (2) A_2B_3 (3) A_5B_2 (4) A_2B_5

SS0127

15. CsCl crystallises in body centred cubic lattice. if 'a' is its edge length then which of the following expression is correct : **[Jee-Main (offline)-14]**

(1) $r_{Cs^+} + r_{Cl^-} = \frac{\sqrt{3}}{2}a$ (2) $r_{Cs^+} + r_{Cl^-} = \sqrt{3}a$ (3) $r_{Cs^+} + r_{Cl^-} = 3a$ (4) $r_{Cs^+} + r_{Cl^-} = \frac{3a}{2}$

SS0128

16. Sodium metal crystallizes in a body centred cubic lattice with a unit cell edge of 4.29Å. The radius of sodium atom is approximately :- **[Jee-Main (offline)-15]**

(1) 5.72Å (2) 0.93Å (3) 1.86Å (4) 3.022Å

SS0129

17. Which of the following compounds is metallic and ferromagnetic ? **[Jee-Main (offline)-16]**

(1) MnO_2 (2) TiO_2 (3) CrO_2 (4) VO_2

SS0130

18. A metal crystallises in a face centred cubic structure. If the edge length of its unit cell is 'a', the closest approach between two atoms in metallic crystal will be :- **[Jee-Main (offline)-17]**

(1) 2a (2) $2\sqrt{2}\,a$ (3) $\sqrt{2}\,a$ (4) $\frac{a}{\sqrt{2}}$

SS0131

19. Which type of effect 'defect' has the presence of cations in the interstitial sites -

(1) Vacancy defect (2) Frenkel defect **[Jee-Main (offline)-18]**

(3) Metal deficiency defect (4) Schottky defect

SS0132

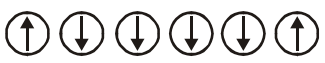
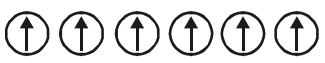
20. All of the following share the same crystal structure except :- **[Jee-Main (online)-18]**

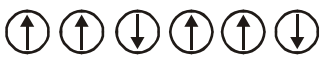
(1) RbCl (2) CsCl

(3) LiCl (4) NaCl

SS0133

21. Which of the following arrangements shows the schematic alignment of magnetic moments of antiferromagnetic substance ? **[Jee-Main (online)-18]**

(1)  (2) 

(3)  (4) 

SS0134

22. An element crystallises in a face-centred cubic (fcc) unit cell with cell edge a. The distance between the centres of two nearest octahedral voids in the crystal lattice is **[Jee-Main (online)-2020]**

(1) a (2) $\sqrt{2}a$ (3) $\frac{a}{\sqrt{2}}$ (4) $\frac{a}{2}$

SS0158

23. A diatomic molecule X_2 has a body-centred cubic (bcc) structure with a cell edge of 300 pm. The density of the molecule is 6.17 g cm^{-3}. The number of molecules present in 200 g of X_2 is

(Avogadro constant (N_A) = 6×10^{23} mol^{-1}) **[Jee-Main (online)-2020]**

(1) 8 N_A (2) 40 N_A (3) 4 N_A (4) 2 N_A

SS0159

24. A crystal is made up of metal ions 'M_1' ana 'M_2' and oxide ions. Oxide ions form a ccp lattice structure. The cation 'M_1' occupies 50% of octahedral voids and the cation 'M_2' occupies 12.5% of tetrahedral voids of oxide lattice. The oxidation numbers of 'M_1' and 'M_2' are, respectively :

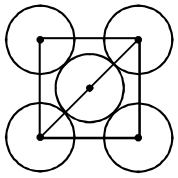
[Jee-Main (online)-2020]

(1) +2, +4 (2) +3, +1 (3) +1, +3 (4) +4, +2

SS0160

EXERCISE # J-ADVANCED

1. The packing effeciency of the two-dimensional square unit cell shown below is **[JEE-2010]**



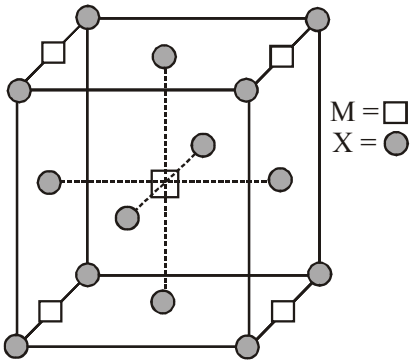
(A) 39.27% (B) 68.02% (C) 74.05% (D) 78.54%

SS0161

2. The number of hexagonal faces that present in a truncated octahedron is. **[JEE-2011]**

SS0135

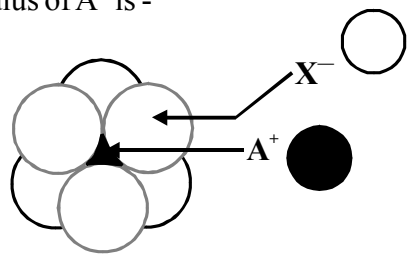
3. A compound M_pX_q has cubic close packing (ccp) arrangement of X. Its unit cell structure is shown below. The empirical formula of the compound is : **[JEE-2012]**



(A) MX (B) MX_2 (C) M_2X (D) M_5X_{14}

SS0136

4. The arrangement of X^- ions around A^+ ion in solid AX is given in the figure (not drawn to scale). If the radius of X^- is 250 pm, the radius of A^+ is - **[JEE-2013]**



(A) 104 pm (B) 125 pm (C) 183 pm (D) 57 pm

SS0137

5. If the unit cell of a mineral has cubic close packed (ccp) array of oxygen atoms with m fraction of octahedral holes occupied by aluminium ions and n fraction of tetrahedral holes occupied by magnesium ions m and n respectively, are - **[JEE-2015]**

(A) $\frac{1}{2},\frac{1}{8}$ (B) $1,\frac{1}{4}$ (C) $\frac{1}{2},\frac{1}{2}$ (D) $\frac{1}{4},\frac{1}{8}$

SS0138

6. The **CORRECT** statement(s) for cubic close packed (ccp) three dimensional structure is (are)

(A) The number of the nearest neighbours of an atom present in the topmost layer is 12

(B) The efficiency of atom packing is 74% **[JEE-2016]**

(C) The number of octahedral and tetrahedral voids per atom are 1 and 2, respectively

(D) The unit cell edge length is $2\sqrt{2}$ times the radius of the atom

SS0139

7. A crystalline solid of a pure substance has a face-centred cubic structure with a cell edge of 400 pm. If the density of the substance in the crystal is 8g cm^{-3}, then the number of atoms present in 256g of the crystal is $N \times 10^{24}$. The value of N is **[JEE-2017]**

SS0140

8. Consider an ionic solid MX with NaCl structure. Construct a new structure (Z) whose unit cell is constructed from the unit cell of MX following the sequential instructions given below. Neglect the charge balance. **[JEE-2018]**

(i) Remove all the anions (X) except the central one

(ii) Replace all the face centered cations (M) by anions (X)

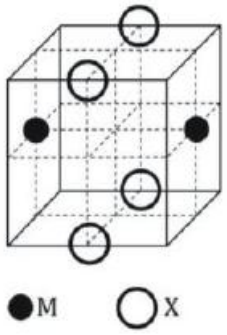
(iii) Remove all the corner cations (M)

(iv) Replace the central anion (X) with cation (M)

The value of $\left(\frac{\text{number of anions}}{\text{number of cations}}\right)$ in Z is____.

SS0141

9. The cubic unit cell structure of a compound containing cation M and anion X is shown below. When compared to the anion, the cation has smaller ionic radius. Choose the correct statement(s). **[JEE-2020]**



(A) The empirical formula of the compound is MX.

(B) The cation M and anion X have different coordination geometries.

(C) The ratio of M-X bond length to the cubic unit cell edge length is 0.866.

(D) The ratio of the ionic radii of cation M to anion X is 0.414.

SS0162

ANSWER KEY

EXERCISE # S-I

1. Ans. (a) 300 pm, (b) 255 pm, (c) 210 pm
2. Ans. 438 pm, 219 pm
3. Ans. 5.83 g cm^{-3}
4. Ans. ($\sqrt{2}:1$)
5. Ans. (0.9 gm/cm^{-3})
6. Ans. (A,B)
7. Ans. (64)
8. Ans. (12)
9. Ans. (6)
10. Ans. A_2BC
11. Ans. (4)
12. Ans. (0.293)
13. Ans. (2) $\frac{\frac{a}{\sqrt{2}}\times\sqrt{2}}{a/2}=2$
14. Ans. 4, 6, 8
15. Ans.(6)
16. Ans. $ZnAl_2O_4$
17. Ans.346.4 pm
18. Ans. 4
19. Ans.a =600 pm, V=2.16×10^{-22} cm^3
20. Ans. 1.81Å
21. Ans.6.0×10^{18}
22. Ans. 12.5%
23. Ans. 3.0 gm/cm^3

EXERCISE # S-II

1. Ans. (5)
2. Ans. 60%, +4
3. Ans. (i) FCC (ii) 0.116 g/cc
4. Ans. (a) 1.143, (b) 1.2

EXERCISE # O-I

1. Ans.(A)
2. Ans.(D)
3. Ans.(A)
4. Ans.(D)
5. Ans.(C)
6. Ans.(D)
7. Ans.(C)
8. Ans.(C)
9. Ans (B)
10. Ans (D)
11. Ans (B)
12. Ans.(B)
13. Ans.(C)
14. Ans.(C)
15. Ans.(B)
16. Ans.(C)
17. Ans.(C)
18. Ans.(C)
19. Ans.(A)
20 Ans (D)
21. Ans (C)
22. Ans (D)
23. Ans.(C)
24. Ans.(C)
25. Ans.(A)
26. Ans.(C)
27. Ans.(B)
28. Ans.(A)
29. Ans.(B)
30. Ans.(A)
31. Ans.(A)
32. Ans.(D)
33. Ans.(D)
34. Ans.(D)
35. Ans.(B)
36. Ans(C)
37. Ans.(C)
38. Ans.(D)
39. Ans.(B)
40. Ans.(C)

EXERCISE # O-II

1.	Ans.(C)	2.	Ans.(D)	3.	Ans.(C)
4.	Ans.(A)	5.	Ans.(B)	6.	Ans.(C)
7.	Ans.(C)	8.	Ans.(A,C)	9.	Ans.(A,B,C,D)
10.	Ans.(A,B,D)	11.	Ans.(C)	12	Ans.(A)
13.	Ans.(A)	14.	Ans.(C)	15.	Ans.(A)

16. Ans.(D)

17. Ans.(A) $\rightarrow$ P, Q ; (B) $\rightarrow$ P,S ; (C) $\rightarrow$ P,R ; (D) $\rightarrow$ P

18. Ans.(A) $\rightarrow$ R,S ; (B) $\rightarrow$ P,Q,R,S ; (C) $\rightarrow$ Q

19. Ans.Ans.(A)

EXERCISE # J-MAIN

1.	Ans.(2)	2	Ans.(1)	3.	Ans.(1)
4.	Ans.(3)	5.	Ans.(3)	6	Ans.(1)
7.	Ans.(3)	8.	Ans.(3)	9.	Ans.(2)
10.	Ans.(2)	11.	Ans.(1)	12.	Ans.(2)
13.	Ans.(2)	13.	Ans.(4)	15.	Ans.(1)
16.	Ans.(3)	17.	Ans.(3)	18	Ans. (4)
19.	Ans.(2)	20.	Ans.(2)	21.	Ans.(4)
22.	Ans.(3)	23.	Ans.(3)	24.	Ans.(1)

EXERCISE # J-ADVANCED

1.	Ans.(D)	2.	Ans.(8)	3.	Ans.(B)
4.	Ans.(A)	5.	Ans. (A)	6.	Ans.(B,C,D)
7.	Ans.(2)	8.	Ans.(3)	9.	Ans.(A,C)

Important Notes