

**1. INTRODUCTION:**

Matter can exist in three physical states namely; solid, liquid and gas. Matter consists of tiny particles (atoms, ions or molecules). If the particles are very far off from one another, they behave like gases; nearer, they behave like liquids, and nearest, like solids. The three states of matter are thus known as the three states of aggregation from Latin word meaning "Flecking together".

The fundamental difference between the three states of aggregation lies essentially in the difference of the relative amounts of energy possessed by the particles in the three states. The relative energies in the different states of matter are governed by two universal opposing tendencies associated with the particles:

- (i) They have tendency of mutual attraction.
- (ii) They have tendency of escape from one another which is known as escaping tendency.

Whether a given system would exist as a solid, liquid or gas depends upon the relative strengths of these opposing tendencies. If the escaping tendency is greater than the attraction between them, the molecules will be carried far from each other to distances which are large as compared with their diameters, the system will exist in gaseous state. But in the liquid state the molecular attraction exceeds the escaping tendency and in the solid state the forces of attraction are so much greater than those of escaping tendency that each particle is bound into a definite place in a rigid position by the mutual attraction of molecules.

**2. THE SOLID STATE:**

The solids 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 cannot move about at random. Thus solids have definite volume, shape, slow diffusion, low vapour pressure and possess the unique property of being rigid. Such solids are known as true solids e.g. NaCl, KCl, Sugar, Ag, Cu etc. On the other hand the solid which loses shape on long standing, flows under its own weight and is easily distorted by even mild distortion forces are called pseudo solids e.g. glass, pitch etc.

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

**2.1 DIFFERENCES BETWEEN CRYSTALLINE AND AMORPHOUS SOLIDS:**

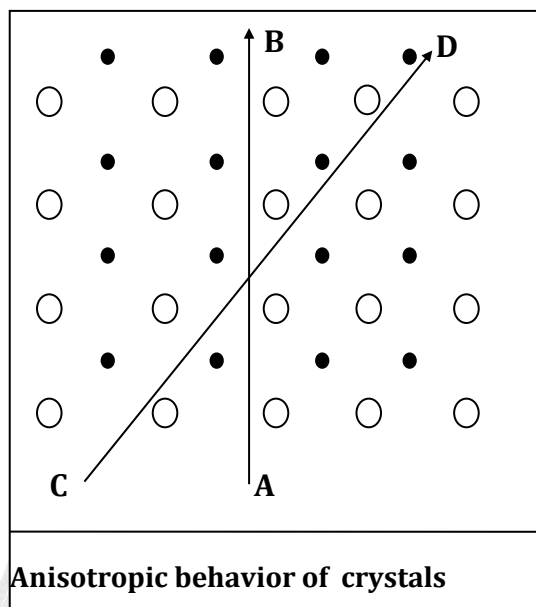
- (i) **Characteristic Geometry:** In the crystalline solids the particles (atoms, ions, or molecules) are definitely and orderly arranged thus these have characteristic geometry while amorphous solids do not have characteristic geometry.
- (ii) **Melting Points:** A crystalline solids has a sharp melting point i.e. it changes into liquid state at a definite temperature. On the contrary an amorphous solid does not have a sharp melting point. For example, when glass is heated, it softens and then starts flowing without undergoing any abrupt or sharp change from solid to liquid state. Therefore, amorphous solids are regarded as "liquids at all temperatures".
- (iii) **Cooling curve:** Amorphous solids show smooth cooling curve while crystalline solids show two breaks in cooling curve. In the case of crystalline solids two break points 'a' and 'b' are appear. These points indicate the beginning and the end of the process of crystallisation. In this time interval temperature remains constant. This is due to the fact that during crystallisation process energy is liberated which compensates for the loss of heat thus the temperature remains constant.
- (iv) **Isotropy and Anisotropy:** Amorphous solids differ from crystalline solids and resemble liquids in many respects. The properties of amorphous solids, such as electrical conductivity, thermal conductivity, mechanical strength, refractive index, coefficient of thermal expansion etc. are same in all directions.

Such solids are known as isotropic. Gases and liquids are also isotropic.

On the other hand crystalline solids show these physical properties different in different directions.

Therefore crystalline solids are called anisotropic. The anisotropy itself is a strong evidence for the existence of orderly molecular arrangement in crystals. For example, the velocity of light passing through a crystal is different in different directions. A ray of light entering in a crystal may split up into two components each following a different path and travelling with a different velocity

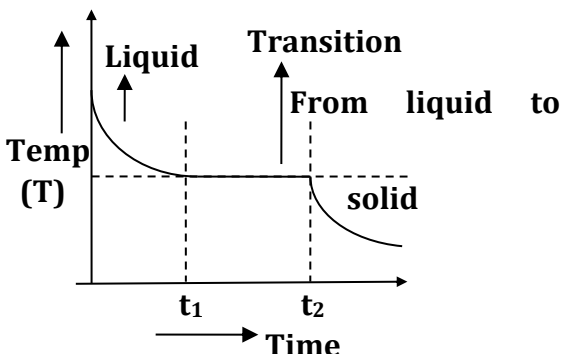
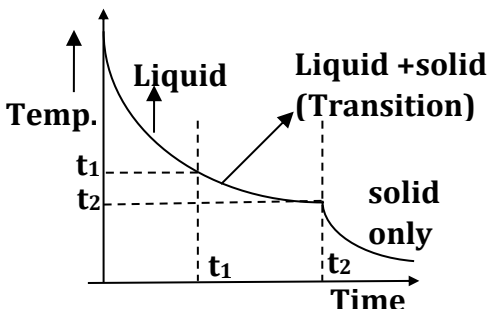
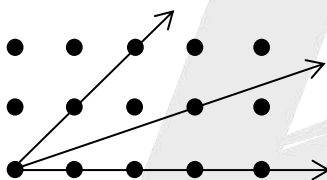
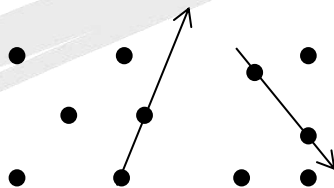
This phenomenon is called double refraction. In the figure two different kinds of atoms are shown in two dimensional arrangement. If the properties are measured along the direction CD, they will be different from those measured along the direction AB. This is due to the fact that in the direction AB each row is made up of one type of atoms while in the direction CD each row is made up of two types of atoms. It is important to note that in the case of amorphous solids, liquids and gases atoms or molecules are identical and all properties are same in all directions



(v) **Cutting:**

Crystalline solids give clean cleavage while amorphous solids give irregular cut due to conchoidal fracture on cutting with a sharp edged tool.

	Crystalline solid		Amorphous solids
1	The constituent particles (atoms, molecule, ion) follow a definite repeating arrangement.	1	No particular pattern is followed, particles are randomly arranged.
2	These have long range order.	2	They have short range order.
3	These are produced by slow cooling under controlled condition of liquid. The crystalline structure is also dependent on conditions. Same substance can have different crystalline structure in different condition. <b>Different crystalline structure of the same substance are called its polymorphic forms &amp; this is known as polymorphism.</b>	3	Rapid or suddenly cooling of the liquid generate the <b>amorphous solid</b> .

4	<p>These have fixed or Sharp melting point and enthalpy of fusion</p> <p>Cooling curve :</p>  <p>The graph shows Temperature (T) on the y-axis and Time on the x-axis. The curve starts in the 'Liquid' region, then drops sharply at time <math>t_1</math> to a constant temperature plateau labeled 'Transition From liquid to solid'. It remains at this temperature until time <math>t_2</math>, after which it drops again into the 'solid' region.</p>	4	<p>These have a range of temperature in which they melts as. Their melting point and enthalpy of fusion is not fixed.</p>  <p>The graph shows Temperature (T) on the y-axis and Time on the x-axis. The curve starts in the 'Liquid' region, then gradually drops through a 'Liquid + solid (Transition)' region between times <math>t_1</math> and <math>t_2</math>, and finally drops into the 'solid only' region after <math>t_2</math>.</p>
5	<p><b>These are anisotropic :</b> Physical properties will have different values in different direction.</p>  <p>The diagram shows a regular grid of particles. Three arrows originate from a single point, pointing in different directions, representing different physical properties in different directions.</p> <p>Ex. : Ag, Fe, Cu, NaCl, <math>H_2O</math> (s), Diamond, Quartz, Sucrose (Sugar)</p>	5	<p><b>These are isotropic</b></p> <p>All different physical properties are same in all different direction.</p> <p><b>Reason :</b> Due to random arrangement of particles.</p>  <p>The diagram shows a random arrangement of particles. Two arrows originate from different points, pointing in different directions, representing the same physical properties in all directions.</p> <p>Ex. Glass, plastic, Amorphous silica, Rubber, Starch</p>

## 2.2 TYPES OF THE CRYSTALLINE SOLIDS:

Crystals are divided into four important types on the basis of chemical bonding of the constituent atoms.

The important characteristics of the various types of crystals are given in the following table:

## Various type of Crystalline Solids

Types of Solid	Constituent Particles	Bonding/ Attractive forces	Examples	Physical Nature	Electrical Conductivity	Melting Point
<b>(1)</b> Molecular Solids	Molecules	Dispersion or London forces	Ar, CCl <sub>4</sub> , H <sub>2</sub> , I <sub>2</sub> , O <sub>2</sub> , HCl, SO <sub>2</sub> , H <sub>2</sub> O, (ice)	Soft	Insulator	Very low
(i) Non Polar				Soft	Insulator	Low
(ii) Polar		Dipole-dipole		Hard	Insulator	Low
(iii) Hydrogen bonded	Ions	Hydrogen bonding	NaCl, MgO, ZnS, CaF <sub>2</sub>	Hard and brittle	Insulator in Solid state but	High
<b>(2)</b> Ionic Solids		Columbic or electrostatic			conductors in molten state and in aqueous solutions	Fairly high
	Positive ions in a sea of delocalised electrons		Fe, Cu, Ag, Mg	Hard but malleable and ductile	Conductors in solid state as well as in molten state	Very high
<b>(3)</b> Metallic Solids		Metallic bonding	SiO <sub>2</sub> (quartz)			
	Atoms		SiC, C (diamond)	Hard		
			AlN, C <sub>(graphite)</sub>	Soft	Insulators	
<b>(4)</b> Covalent Or network Solids		Covalent bonding			Conductor (exception)	

**Ex.1** Identify molecular solid, covalent solid, ionic solid:

P<sub>4</sub>(s), S<sub>8</sub> (s), SiC (s), Al<sub>2</sub>O<sub>3</sub>(s), He (s), Al<sub>2</sub>Cl<sub>6</sub>(s).

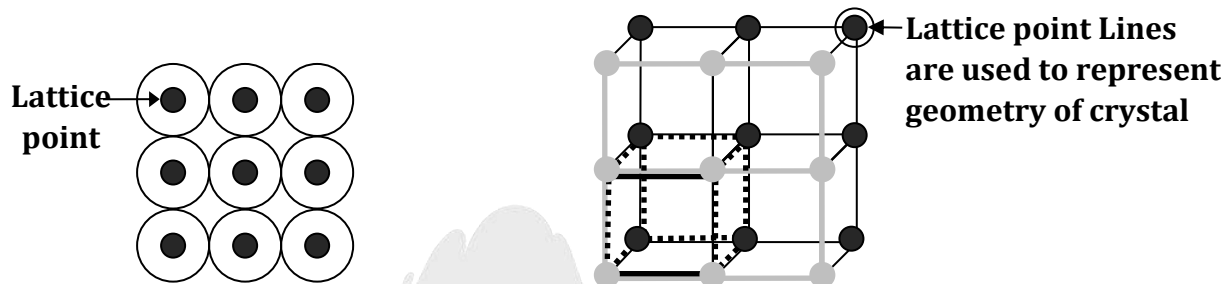
**Sol.** Molecular solid  $\rightarrow$   $P_4(s)$ ,  $S_8(s)$ ,  $He(s)$ ,  $Al_2Cl_6(s)$

Covalent solid  $\rightarrow$   $SiC$

Ionic solid  $\rightarrow$   $Al_2O_3(s)$ .

### 2.3 SPACE LATTICE (CRYSTALLINE LATTICE) :

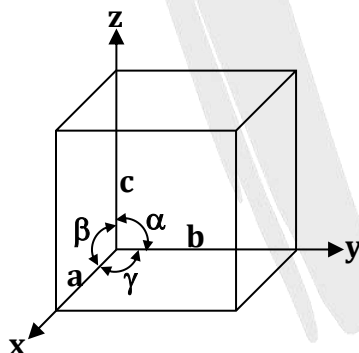
The three dimensional arrangement of constituent particles in a crystal, where each particle depicted as a point is called lattice.



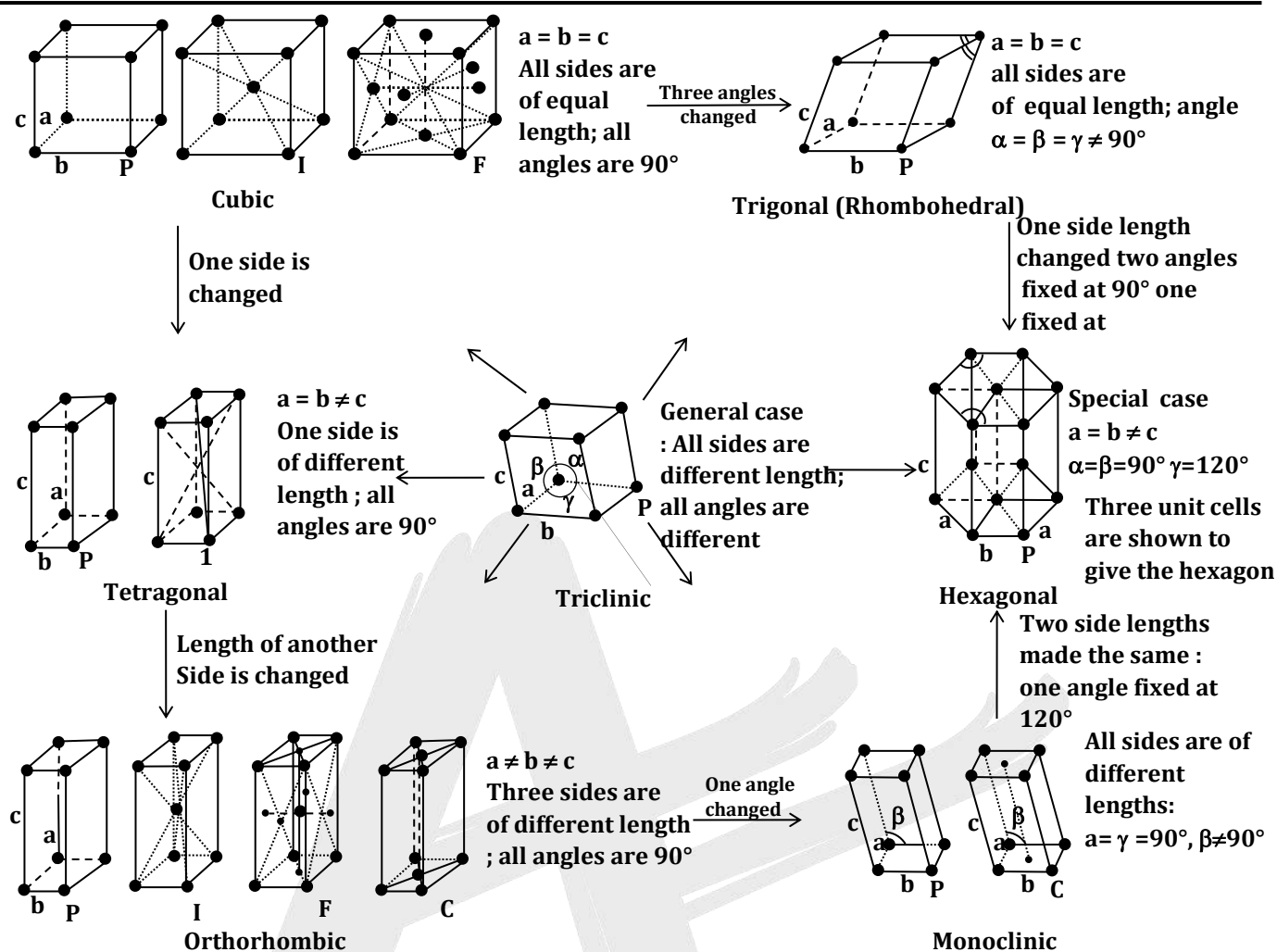
### 2.4 UNIT CELL :

"The parallelepiped which can be used as repetitive unit to build up the whole lattice is called a unit cell."

For eg. brick in wall. A unit cell is the smallest picture of the whole crystal. A unit cell is characterized by the edge lengths  $a$ ,  $b$  and  $c$  along the three edges of the unit cell and the angles  $\alpha$ ,  $\beta$  and  $\gamma$  between the pair of edges  $bc$ ,  $ca$  and  $ab$  respectively. These unit cell are also known as Bravais lattices.



### 2.5 BRAVAIS LATTICES (UNIT CELL) : There are 14 Bravais lattices



## 2.6 THE SEVEN CRYSTAL SYSTEMS

On the basis of the classification of symmetry, the lattices 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 Centered Unit Cells

Crystal system	Possible Variations	Axial distance or edge lengths	Axial angles	Examples
Cubic	Primitive Body centered Face centred	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	NaCl, Zinc blende, Cu
Tetragonal	Primitive Body centered.	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	White tin, $\text{SnO}_2$ , $\text{TiO}_2$ , $\text{CaSO}_4$



Orthorhombic	Primitive Body centered. Face centered, End centered	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Rhombic sulphur, $\text{KNO}_3$ , $\text{BaSO}_4$
Hexagonal	Primitive	$a = b \neq c$	$\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	Graphite, $\text{ZnO}$ , $\text{CdS}$
Rhombohedral or Trigonal	Primitive	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	Calcite ( $\text{CaCO}_3$ ), $\text{HgS}$ (Cinnabar)
Monoclinic	Primitive End centred	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ$ $\beta \neq 90^\circ$	Monoclinic suphur, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
Triclinic	Primitive	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	$\text{K}_2\text{CrO}_7$ , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , $\text{H}_3\text{O}$

**Ex.2** Define the following terms in relation of crystalline solids:

(i) Unit cell

(ii) Coordination number

Give one example in each case.

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

e.g., primitive unit cells: simple cubic centered unit cells : bcc, fcc, hcp

(ii) The number of spheres which are touching a given sphere is called the coordination number. e.g.,

In simple cubic arrangement coordination number is: 6. In bcc arrangement coordination number is: 8.

In hcp or fcc arrangement coordination number is: 12.

**Ex.3** Tetragonal crystal system has the following unit cell dimensions:

(A)  $a = b = c$  and  $\alpha = \beta = \gamma = 90^\circ$

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

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

(D)  $a = b \neq c$  and  $\alpha = \beta = 90^\circ$ ,  $\gamma = 120^\circ$

**Ans.** (B)

## 2.7 CO-ORDINATION NUMBER:

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



## 2.8 PACKING EFFICIENCY OR PACKING DENSITY (P.E.) :

Packing efficiency is defined as the ratio of volume occupied by the atoms to the total volume of the crystalline substance ie packing efficiency is equal to-

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

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

$$\text{P.E.} = \frac{n \times (4/3)\pi r^3}{V}$$

Where n = number of atoms present in unit cell

## 2.9 GEOMETRY OF A CUBE

Number of corners = 8

Number of faces = 6

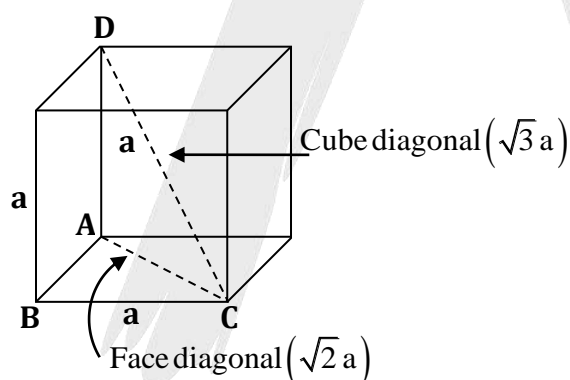
Number of edges = 12

Number of cube centre = 1

Number of cube diagonals = 4

Number of face diagonals = 12

## 2.10 LENGTH OF FACE DIAGONAL AND CUBE DIAGONAL :



Distance between

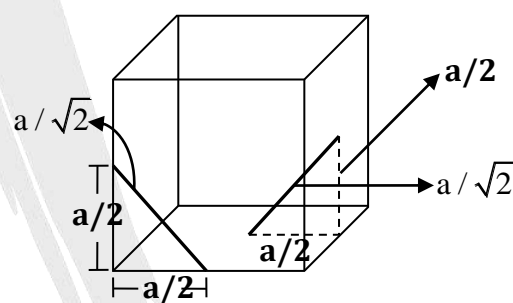
$$2 \text{ adjacent face centers} = \frac{a}{\sqrt{2}}$$

Consider the triangle ABC, with the help of Pythagoras theorem

$$AC = \sqrt{AB^2 + BC^2} = \sqrt{a^2 + a^2} = \sqrt{2}a \text{ (length of face diagonal.)}$$

Consider the triangle DAC, with the help of Pythagoras theorem

$$\begin{aligned} DC &= \sqrt{DA^2 + AC^2} \\ &= \sqrt{a^2 + (\sqrt{2}a)^2} \end{aligned}$$



Distance between

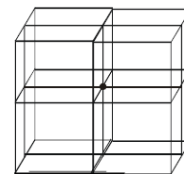
$$2 \text{ adjacent edge centre} = \frac{a}{\sqrt{2}}$$

$$= \sqrt{3}a \text{ (length of cube diagonal)}$$

### 2.11 CONTRIBUTION OF AN ATOM AT DIFFERENT SITES OF CUBE :

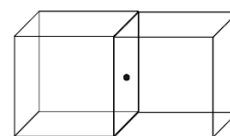
- A corner of a cube is common in 8 cubes.

So  $\frac{1}{8}$  th part of an atom present at this corner contribution in a cube.



- A face of a cube is common in 2 cubes.

So  $\frac{1}{2}$  th part of an atom presents at the face contribution in a cube.



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

So  $\frac{1}{4}$  th part of the atom presents at the edge contribution in a cube



**Ex.4** In a face centered cubic arrangement of A and B atoms where A atoms are at the corner of the unit cell and B atoms at the face centers. One of the A atom is missing from one corner in unit cell. The simplest formula of the compound is

- (A)  $A_7B_3$                       (B)  $AB_3$                       (C)  $A_7B_{24}$                       (D)  $A_2B_3$

**Ans.** (C)

**Sol.**  $A = 7 \times \frac{1}{8} = \frac{7}{8}$  ;  $B = 6 \times \frac{1}{2} = 3$

Formula =  $A_{7/8} B_3$  or  $A_7B_{24}$

**Ex.5** A compound has cubical unit cell in which X atom are present at 6 corner, Y atom are at remaining corner & only at those face centers which are not opposite to each other & Z atoms are present at remaining face center & body center then Formula of compound is

- (A)  $X_3 Y_7 Z_{12}$                       (B)  $X_4 Y_7 Z_{10}$                       (C)  $X_3 Y_7 Z_{10}$                       (D)  $X_2 Y_9 Z_{10}$

**Ans.** (C)

**Sol.** (i)  $X = \frac{1}{8} \times 6 = \frac{3}{4}$ ,

$$Y = \left(\frac{1}{8} \times 2\right) + \left(\frac{1}{2} \times 3\right) = \frac{7}{4}$$

$$Z = \left(\frac{1}{2} \times 3\right) + 1 + 1 = \frac{5}{2} = \frac{10}{4}$$

For formula :  $X_{\frac{3}{4}} Y_{\frac{7}{4}} Z_{\frac{10}{4}} = X_3 Y_7 Z_{10}$

DO YOURSELF-1

- The lattice parameters of a given crystal are  $a = 5.62\text{\AA}$ ,  $b = 7.41\text{\AA}$  and  $c = 9.48\text{\AA}$ . The three coordinate axes are mutually perpendicular to each other. The crystal is :  
(A) tetragonal (B) orthorhombic (C) monoclinic (D) trigonal.
- In a lattice of **X** and **Y** atoms, if **X** atoms are present at corners and **Y** atoms at the body centre & one **X** atom is removed from a corner from each unit cell, then the formula of the compound will be :  
(A)  $X_7Y$  (B)  $X_8Y_7$  (C)  $X_7Y_8$  (D)  $X_7Y_7$
- A compound alloy of gold and copper crystallises in a cubic lattice in which the gold atoms occupy the lattice points at the corner of a cube and the copper atoms occupy the centres of each of the cube faces. Hence compound alloy has formula:  
(A) **AuCu** (B) **Au<sub>3</sub>Cu** (C) **Au<sub>2</sub>Cu** (D) **AuCu<sub>3</sub>**
- A compound is formed by elements A and B. This crystallises in the cubic structure where the **A** atoms are at the corners of the cube and **B** atoms are at the body centres. The simplest formula of the compound is :  
(A) **A<sub>8</sub>B<sub>4</sub>** (B) **AB<sub>6</sub>** (C) **AB** (D) **A<sub>6</sub>B**
- Column-I and Column-II contains four entries each. Entries of Column-I are to be matched with some entries of Column-II. One or more than one entries of Column-I may have the matching with the same entries of Column-II.

Column-I

(Bravais Lattice(s))

- Primitive, face centered, body centered, end centered
- Primitive, face centered, body centered
- Primitive, body centered
- Primitive only

Column-II

[Crystal system]

- Cubic
- Orthorhombic
- Hexagonal
- Tetragonal

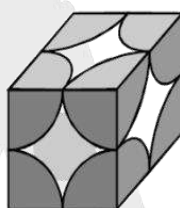
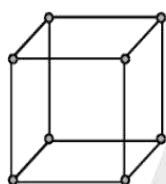
- The lattice parameters of a given crystals are  $a = 8.42\text{\AA}$ ,  $b = 8.42\text{\AA}$  and  $c = 9.80\text{\AA}$ . There coordinate axes are mutually perpendicular to each other. The crystal is:  
(A) Tetragonal (B) Ortho rhombic (C) Monoclinic (D) Trigonal
- The crystal dimensions  $a = b \neq c$ ;  $\alpha = \beta = 90^\circ$ ,  $\gamma = 120^\circ$  represents :  
(A) Tetragonal (B) Hexagonal system  
(C) Monoclinic (D) Orthorhombic system
- Which of the following unit cells has least symmetry ?  
(A) Tetragonal (B) Monoclinic (C) Triclinic (D) Cubic
- Among the unit cells given below, which has highest symmetry ?  
(A) Hexagonal (B) Orthorhombic (C) Cubic (D) Monoclinic

### 3. TYPE OF CUBIC UNIT CELL (BRAVAIS LATTICE) :

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

#### 3.1 Simple/Primitive/Basic Unit cell :

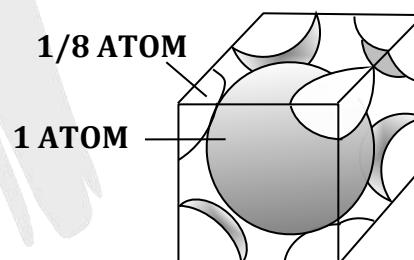
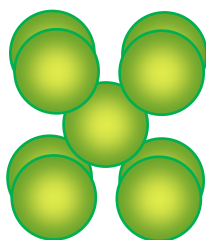
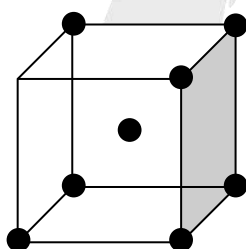
A unit cell having lattice point only at corners called as primitive or simple unit cell. i.e. in this case there is one atom at each of the eight corners of the unit cell considering an atom at one corner as the centre, it will be found that this atom is surrounded by six equidistant neighbours (atoms)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



#### 3.2 Body centred cubic (bcc) cell : A unit cell having lattice point at the body centre in addition to the lattice point at every corner is called as body centered unit cell.

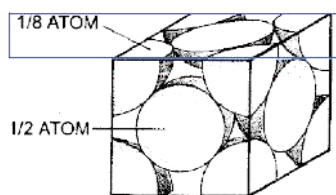
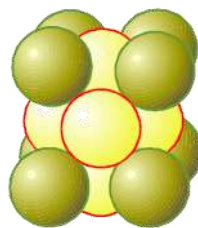
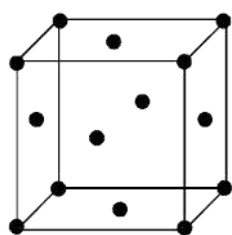
Here the central atom is surrounded by eight equidistant atoms and hence the coordination number is eight.

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



#### 3.3 Face centred cubic (fcc) cell: A unit cell having lattice point at every face centre in addition to the lattice point at every corner called as face centred unit cell. i.e. in this case there are eight atoms at the eight corners of the unit cell and six atoms at the centre of six faces. Considering an atom 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 atoms will be  $\frac{a}{\sqrt{2}}$ .



4. NUMBER OF ATOMS PER UNIT CELL IN CUBIC CLOSE PACKED STRUCTURE OF ATOMS

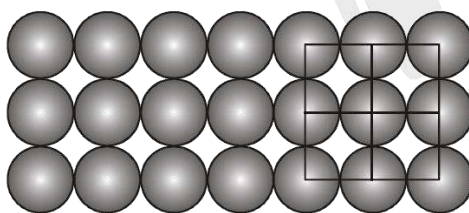
Unit cell	Number of atom at			No. of atoms per unit cell	Volume occupied by particles (%)
	Corners	Centres	Faces		
Simple cube	$8 \times \frac{1}{8} = 1$	0	0	1	52.4
Body Centered cube (BCC)	$8 \times \frac{1}{8} = 1$	1	0	2	68
Face centered (FCC)	$8 \times \frac{1}{8} = 1$	0	$6 \times \frac{1}{2} = 3$	4	74

5. CLOSE PACKING OF IDENTICAL SOLID SPHERES:

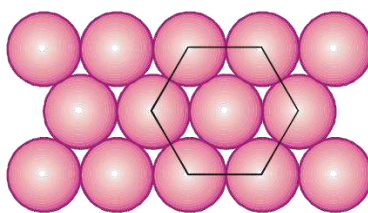
5.1 Two dimensional close packing:

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

In square close packing co-ordination number is 4

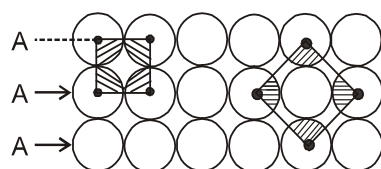


- (ii) Another type of arrangement of atoms is shown below. This type of packing is called hexagonal close packing. In such packing one sphere touches six other spheres. In this case 60.4% of the volume is occupied. The remaining 39.6% of the volume is empty and is called void volume. Therefore this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



**(i) Square arrangement (poor arrangement)**

Array are arranged such that sphere of one array are exactly above the sphere of another array



A-A-A type packing

Square packing in two dimension.

Two type of unit cell : = [primitive & non-primitive]

(i) Effective no. of atom (Z) = [1 atom & 2 atoms.]

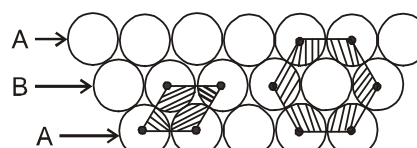
(ii) Edge length (a = b) = 2R.

(iii) Packing efficiency (Area wise) =  $\frac{1 \times \pi R^2}{4R^2} = \frac{\pi}{4} = 78.5\%$

(iv) Co-ordination no. (CN) = 4.

**Hexagonal Arrangement (Better arrangement)**

One dimensional array are arranged such that sphere of one array occupy the depression of other array.



AB-AB type packing

Hexagonal close packing in two dimension.

Two type of unit cell : = [primitive & non-primitive]

(i) Effective no. of atom (Z) = [1 atom & 3 atoms.]

(ii) Edge length (a = b) = 2R.

(iii) Packing efficiency (Area wise) =  $\frac{3(\pi R^2)}{6 \times \frac{\sqrt{3}}{4} (2R)^2} = 90.6\%$

(iv) Co-ordination no. (CN) = 6.

**5.2 Three Dimensional close packing:**

When 2-D close packed layers are kept on each other 3-D close packing will be generated.

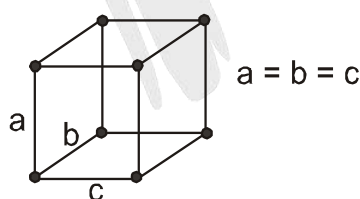
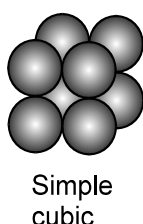
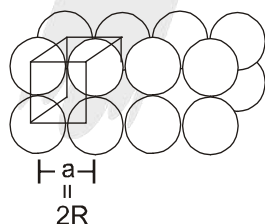
**(A) Square packed sheets:** Following two arrangements are possible

**5.2.1 Simple cubic :**

atoms / spheres of one sheet are exactly above spheres of other sheet.

→ A A A A ..... pattern repeat.

→ Simple cube can be taken as unit cell of this particular lattice :



**(i) Relation between a & R.**

Corner atoms are touching each other so, **a = 2R.**

**(ii) Effective no. of atom (Z) (per unit cell).**

$$Z = 8 [\text{corner}] \times \frac{1}{8} = 1 \text{ atom.}$$

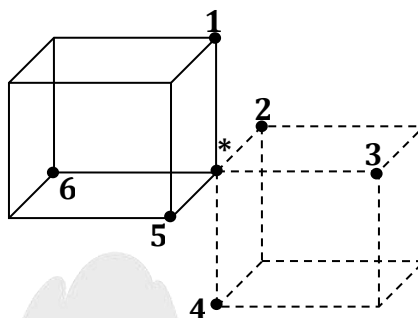
**(iii) Packing efficiency:**  $\frac{1 \times \frac{4}{3} \pi R^3}{(2R)^3} = \frac{\pi}{6} = 52.33\%.$

(iv)  $\text{Density} = \frac{\text{Mass of unit cell}}{\text{volume of unit cell}} = \left( \frac{Z \times M}{N_A \times a^3} \right)$

(v) **Co-ordination number:**

Number of nearest neighbours or (no. of sphere which are touching any particular sphere).

CN = 6.



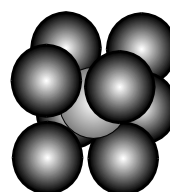
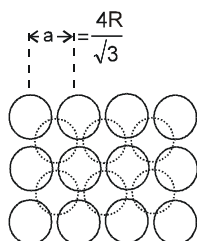
(The \* marked atom touches atom number 1, 5, 6 in its own unit cell and 2, 3, 4 in other unit cells hence total number of nearest atom = 6)

Type of neighbours	Distance	No. of neighbours
Nearest	a	6
Second nearest	$a\sqrt{2}$	12
Third nearest	$a\sqrt{3}$	8

**5.2.2 Body centred cubic (b.c.c.):** A unit cell having lattice point at the body centre in addition to the lattice point at every corner is called as body centered unit cell.

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

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



(i) **Relation between a & R: ( $a \neq 2R$ )**

Spheres are not touching along edge. They are touching along the body diagonal.

So  $\frac{a\sqrt{3}}{2} = 2R$ .



(ii) Effective no. of atom (Z) =  $8 \times [\text{corner}] \times \frac{1}{8} + 1 = 2$

(iii) Packing fraction

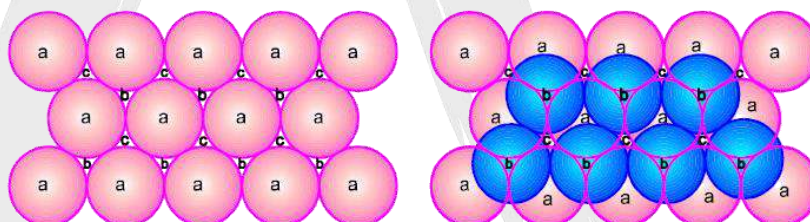
$$= \frac{2 \times \frac{4}{3} \pi R^3}{\left(\frac{4R}{\sqrt{3}}\right)^3} = \frac{\pi\sqrt{3}}{8} = 68\%.$$

(iv) Coordination No. = 8. (Body centered atom have only 8 nearest neighbouring atoms so CN = 8)

Type of neighbours	Distance	No. of neighbours
Nearest	$\frac{a\sqrt{3}}{2}$	8
Second nearest	a	6
Third nearest	$a\sqrt{2}$	12

(B) Arrangement of hexagonal closed packed sheets:

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.



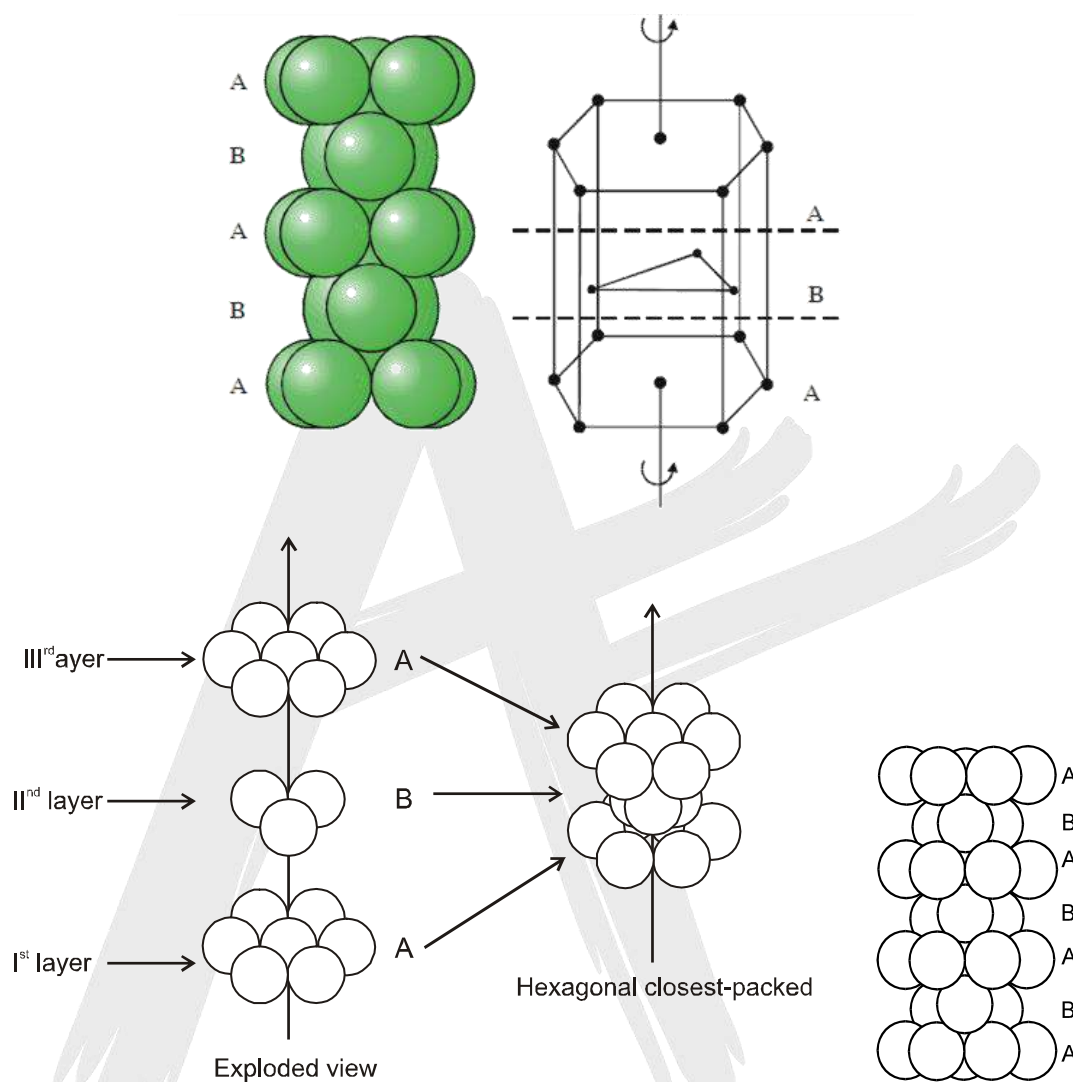
Now we extend the arrangement of spheres in three dimensions by placing second close packed layer (hexagonal close packing) (B) on the first layer (A). The spheres of second layer may placed either on space denoted by 'b' or 'c'. It may be noted that it is not possible to place spheres on both types 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 two ways :

### 5.2.3 Hexagonal close packing (HCP) AB-AB-AB- - -Type.

Spheres of III<sup>rd</sup> layer occupy those voids of II layer under which there are sphere of I<sup>st</sup> layer. So third layer is exactly identical to I<sup>st</sup> layer.

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 identical to the first layer. If this arrangement is continued indefinitely in the same order this is represented as ABABAB ....

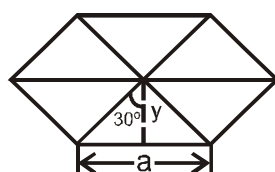
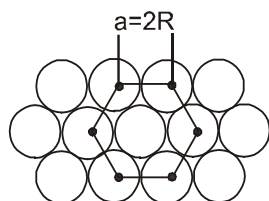
This type of arrangement represents hexagonal close packing (hcp) symmetry (or structure),



Unit cell :  $a = 2R$ ;  $\gamma = 120^\circ$

(i) Relation between  $a$ ,  $b$ ,  $c$  and  $R$  :

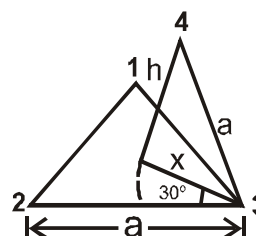
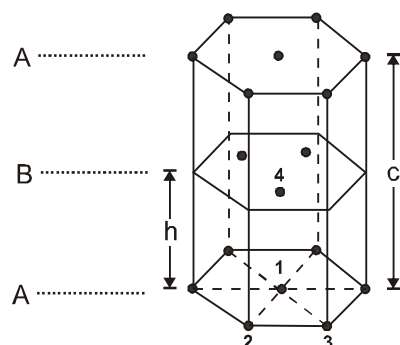
$$a = b = 2R$$



$$\tan 30^\circ = \frac{(a/2)}{y} \quad \text{So} \quad y = \frac{a \times \sqrt{3}}{2 \times 1} = \frac{\sqrt{3}}{2} a.$$

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

calculation of c.



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

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

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

$$h = \sqrt{\frac{2}{3}} a \quad (h = \text{distance between two consecutive layers A - B})$$

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

c = height of hexagonal unit cell (Least distance between two same layers A - A or I<sup>st</sup> and III<sup>rd</sup>).

so volume of hexagon = area of base  $\times$  height

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

(ii) Effective no. of atoms (Z) =  $3 + (2 \times \frac{1}{2}) + (12 \times \frac{1}{6}) = 3 + 1 + 2 = 6$ .

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

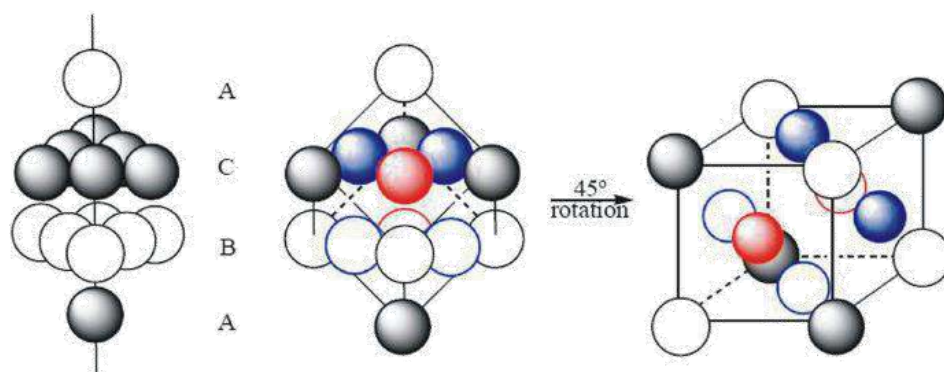
(iv) Coordination number (CN) = 12

(Each sphere touch 6 sphere in its layer 3 above and 3 below)

#### 5.2.4 Cubic close packing (CCP) or ABCABCA...

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 continuous in the same order this is represented as ABC ABC ABC.... This type of arrangement represent cubic close packed (ccp) structure.

- III<sup>rd</sup> layer will be different from I<sup>st</sup> layer as well as II<sup>nd</sup> layer.



- ABC – ABC type of arrangement.
- It is also known as cubical close packing, unit cell chosen is face centered unit cell (FCC).

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

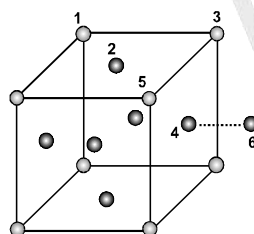
$$a \neq 2R \Rightarrow \sqrt{2}a = 4R \quad (\text{sphere are touching along the face diagonal})$$

(ii) Effective no. of atoms per unit cell (Z) =  $\frac{1}{8} \times 8 + \frac{1}{2} \times 6 = 4$

(iii) Packing fraction :  $P.F = \frac{4 \times \frac{4}{3} \pi R^3}{4 \times 4 \times 4 R^3} \times \sqrt{2} \times 2 = 0.74 (74\%)$

(iv) Coordination number, (CN) = 12

Type of neighbour	Distance	No. of neighbours
(i) Nearest	$\frac{a}{\sqrt{2}}$ (1 & 2)	12
(ii) (next) <sup>1</sup>	a (1 & 3)	6



Reference Figure

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.

**Ex.6** How many 'nearest' and 'next nearest' neighbors respectively does potassium have in b.c.c. lattice?

(A) 8, 8

(B) 8, 6

(C) 6, 8

(D) 8, 2

**Ans.** (B)**Ex.7** Sodium metal crystallises in body centred cubic lattice with cell edge = 4.29 Å. What is radius of sodium atom?**Sol.** In 'BCC' structure

$$\text{body diagonal} = 4 \times r_{\text{Na}} = \sqrt{3} \times a$$

$$\therefore 4 \times r_{\text{Na}} = \sqrt{3} \times 4.29$$

$$r_{\text{Na}} = \frac{\sqrt{3}}{4} \times 4.29 = 1.86 \text{ Å}$$

**Ex.8** Potassium crystallizes in body centered cubic lattice with a unit cell length  $a = 5.2 \text{ Å}$ 

(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 have?

(E) What is calculated density of crystalline K.

**Sol.** (A) 4.5 Å, (B) 5.2, (C) 8, (D) 6 (E) 0.92 g/mL

$$(A) 2r = \frac{\sqrt{3}a}{2} = \frac{\sqrt{3} \times 5.2}{2} = 4.5 \text{ Å} \quad (B) \text{ distance} = a = 5.2 \text{ Å}$$

(C) 8 (D) 6

$$(E) d = \frac{2 \times 39}{(5.2 \times 10^{-8})^3 \times 6.02 \times 10^{23}} = 0.92 \text{ g/mL}$$

**Ex.9** A compound has cubical unit cell in which X atom are present at 6 corner, Y atom are at remaining corner & only at those face centers which are not opposite to each other & Z atoms are present at remaining face center & body center, if edge length of unit cell is 2 Å, then density of solid is : (Given : Atomic mass of X = 40 amu, Y = 60 amu, Z = 80 amu.)

(A) 10.8 g/mL

(B) 96 g/mL

(C) 69.8 g/mL

(D) 9.6 g/mL

**Ans.** (C)

$$\text{Sol. (i)} \quad X = \frac{1}{8} \times 6 = \frac{3}{4},$$

$$Y = \frac{1}{8} \times 2 + \frac{1}{2} \times 3 = \frac{7}{4}$$

$$Z = \frac{1}{2} \times 3 + 1 + 1 = \frac{5}{2} = \frac{10}{4}$$

Formula of unit cell:  $X_{\frac{3}{4}}Y_{\frac{7}{4}}Z_{\frac{10}{4}}$

(ii)  $1 \text{ amu} = 1.67 \times 10^{-24} \text{ gram} = \frac{1}{6.02 \times 10^{23}} \text{ g}$

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}} = \frac{\frac{3}{4} \times 40 + \frac{7}{4} \times 60 + \frac{10}{4} \times 80}{(2 \times 10^{-8})^3} \text{ amu/cc}$$

$$= \frac{335 \times 1.67 \times 10^{-24}}{8 \times 10^{-24}} = 69.8 \text{ gram/cc.}$$

**Ex.10** An element (atomic mass = 60) having face centred cubic structure has a cell edge of 400 pm.  
What is its density? [ $N_A = 6.023 \times 10^{23}$ ]

**Sol.** **Given:**  $M = 60 \text{ g mol}^{-1}$ ,  $Z = 4$ ,  $a = 400 \text{ pm} = 400 \times 10^{-10} \text{ cm}$ ,  $N_A = 6.023 \times 10^{23}$

$$d = \frac{4 \times 60}{6.023 \times 10^{23} \times (400 \times 10^{-10})^3}$$

$$= 6.23 \text{ g cm}^{-3}$$

**Ex.11** A metal crystallises in bcc. Find the % fraction of edge length not covered

- (A) 10.4%                      (B) 13.4%                      (C) 86.6%                      (D) 11.4%

**Ans.** (B)

**Sol.** In bcc  $r = \frac{\sqrt{3}a}{4}$

also, edge length of unit cell =  $a$

radius of atom =  $r$

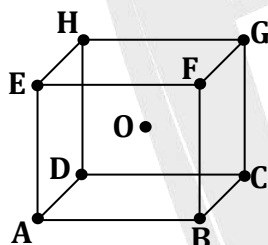
$\therefore$  Edge length not covered by atom =  $a - 2r$

or  $a - \frac{\sqrt{3}}{2}a = \left[ \frac{2 - \sqrt{3}}{2} \right] a$

$\therefore$  Percentage fraction not covered =  $\frac{a \left[ \frac{2 - \sqrt{3}}{2} \right]}{a} \times 100 = 0.134 \times 100 = 13.4\%$

DO YOURSELF-2

1. A metal crystallizes in two cubic phases i.e., FCC and BCC whose unit cell lengths are  $3.5\text{\AA}$  and  $3.0\text{\AA}$  respectively. The ratio of their densities is :  
 (A) 3.12 (B) 2.04 (C) 1.26 (D) 0.72
2. In a ccp structure, the:  
 (A) first and third layers are repeated  
 (B) first and fourth layers are repeated  
 (C) second and fourth layers are repeated  
 (D) first, third and sixth layers are repeated.
3. An fcc lattice has lattice parameter  $a = 400\text{ pm}$ . Calculate the molar volume of the lattice including all the empty space:  
 (A) 10.8 mL (B) 96 mL (C) 8.6 mL (D) 9.6 mL
4. The shortest distance between I<sup>st</sup> and V<sup>th</sup> layer of HCP arrangement is :  
 (A)  $8r\sqrt{\frac{2}{3}}$  (B)  $4r\sqrt{\frac{2}{3}}$  (C)  $16r\sqrt{\frac{2}{3}}$  (D)  $8r\frac{\sqrt{2}}{3}$
5. A body centred cubic arrangement is show :

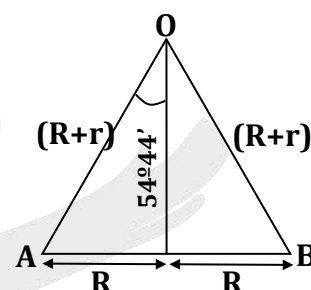
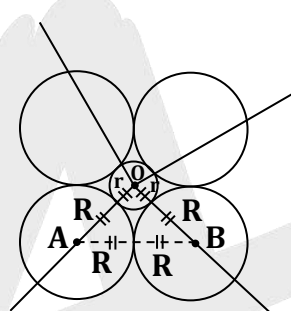
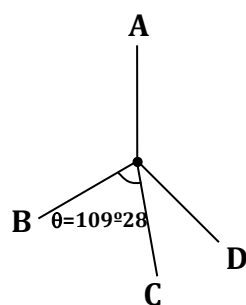
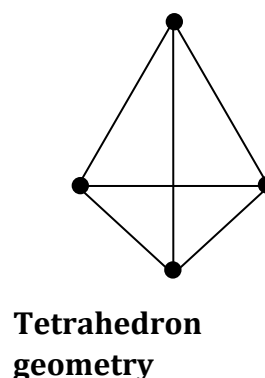
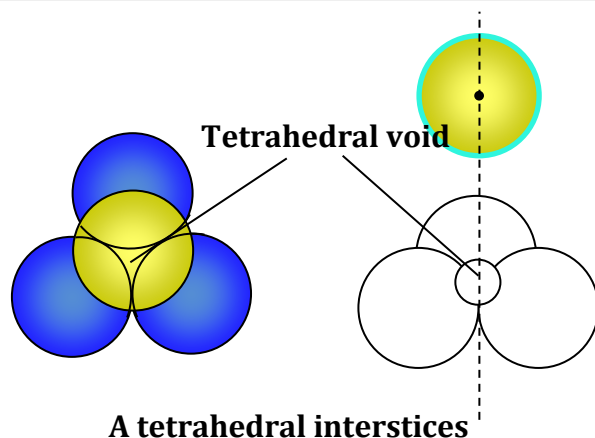


O is the body centre ; A, B, C, D, ....., H are the corners. What is the magnitude of the angle AOB?

- (A)  $120^\circ$  (B)  $109^\circ 28'$  (C)  $104^\circ 31'$  (D)  $70^\circ 32'$
6. The radius of metal atom can be expressed in terms of the length of a unit cell is :  
 (A) it is  $a/2$  for simple cubic lattice  
 (B) it is  $a\sqrt{3}/4$  for b.c.c. lattice  
 (C) it is  $a/2\sqrt{2}$  for F.C.C. lattice  
 (D) All of the above.



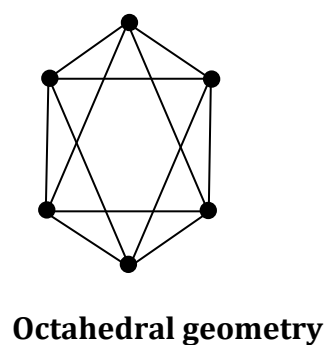
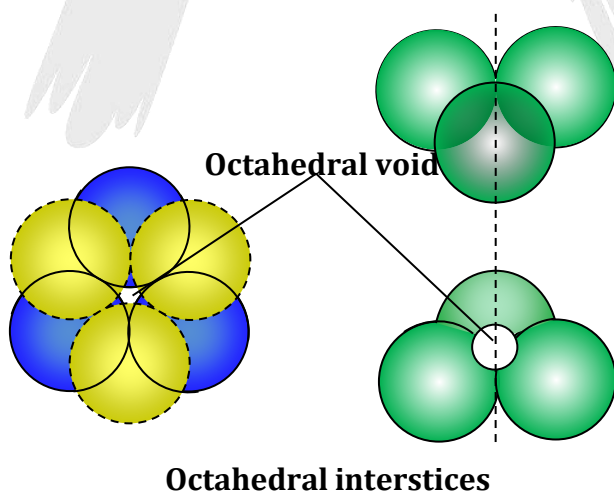


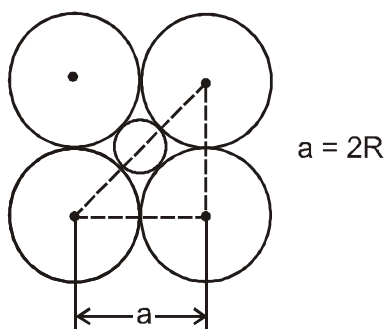


$$\sin 54.44^\circ = \left( \frac{R}{R+r} \right) \Rightarrow \frac{r}{R} = 0.225$$

### 7.1.3 Limiting Radius ratio for coordination number 6: (Octahedral Void):

Octahedral void is formed when ever two spheres are placed, one on top and the other below a square arrangement of sphere. This can also be obtained by placing two three ball arrangement on the top of each other.





$$\sqrt{2} a = 2[R + r] \quad ; \quad 2\sqrt{2} R = 2[R + r]. \quad \frac{r}{R} = 0.414$$

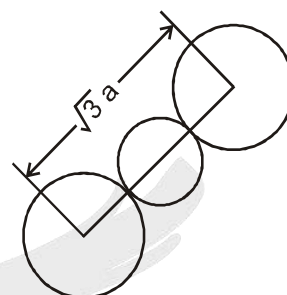
**7.1.4 Limiting Radius ratio for coordination number 8: (Cubic Void):** Void present in the centre of simple cubic unit cell is cubic void

Spheres touch along body diagonal:

$$a\sqrt{3} = 2[R + r]$$

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

$$\frac{r}{R} = 0.732$$



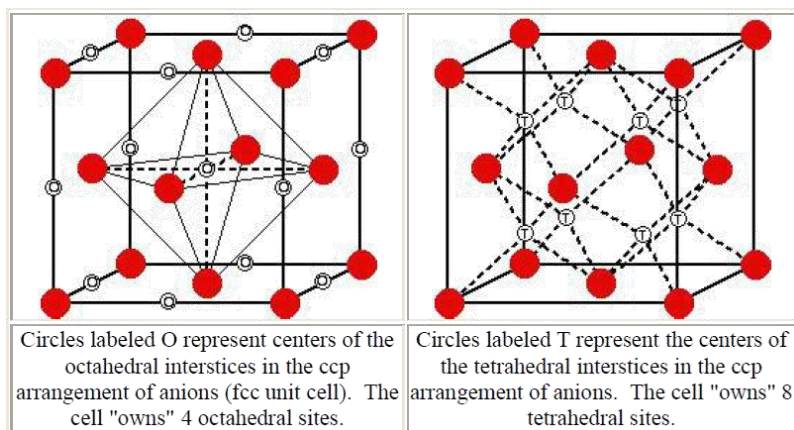
## 7.2. RANGE OF RADIUS RATIOS:

An ionic crystal contains a large number of cations and anions. Generally, cations are smaller in size than that of anions. The cations are surrounded by anions and they touch each other. These ions are arranged in space in such a way to produce maximum stability. The stability of the ionic crystal may be described in terms of radius ratio i.e. the ratio of the radius of cation ( $r$ ) to that of anion ( $R$ ) is ( $r/R$ ). The range of ( $r/R$ ) may be expressed as limiting radius ratio. This value is important to determine the arrangement of the ion in different types of crystals.

Evidently radius ratio ( $r/R$ ) plays a very important role in deciding the stable structure of ionic crystal. Larger cations prefer occupying larger holes (cubic etc.) and smaller cations prefer occupying smaller holes (tetrahedral etc.)

Limiting radius ratio for various types of sites			
Limiting radius ratio = $r/R$	Coordination Number of cation	Structural Arrangement (Geometry of voids)	Example
0.155 - 0.225	3	Plane Trigonal	Boron Oxide
0.225 - 0.414	4	Tetrahedral	ZnS, SiO <sub>2</sub>
0.414 - 0.732	4	Square planner	–
0.414 - 0.732	6	Octahedral	NaCl, MgO <sub>2</sub>
0.732 - 1.000	8	Cubic	CsCl

### 7.3. LOCATION OF OCTAHEDRAL & TETRAHEDRAL VOIDS IN FCC UNIT CELL



#### (a) Tetrahedral void:

- Distance of tetrahedral void from corner is  $\frac{\sqrt{3}a}{4}$  and distance between two tetrahedral void is  $= \frac{a}{2}$
- FCC unit cell has 4 body diagonal and each body diagonal contain 2 tetrahedral void that's why total tetrahedral void = 8.
- If a large size cube is divided in 8 mini-cube then center of each mini-cube contain one tetrahedral void and distance of center of mini-cube from corner is  $\frac{\sqrt{3}a}{4}$ .

#### (b) Octahedral void (OV)

- Each edge center of FCC unit cell have one octahedral void and body center also contain 1 OV.
- Number of octahedral void per unit cell (Z) =  $12 [\text{Edge center}] \times \frac{1}{4} + 1[\text{Body center}] = 4$ .
- For FCC unit cell (Z) = 4 and octahedral void = 4. So octahedral void = Z.

Unit cell	Z	Tetrahedral void = Z $\times 2$	Octahedral Void = Z $\times$ 1
CCP (FCC)	4	8	4
HCP	6	12	6

**Ex.12** In which of the following arrangements octahedral voids are formed?

- (A) hcp                      (B) bcc                      (C) simple cubic                      (D) fcc

**Ans.** (A, D)

**Ex.13** In a close packed structure of mixed oxides, it is found that lattice has  $O^{2-}$  (oxide ions), and one-half of octahedral voids are occupied by trivalent cations ( $A^{3+}$ ) and one-eighth of tetrahedral voids are occupied by divalent cations ( $B^{2+}$ ). Derive formula of the mixed oxide.

**Ans.**  $A_2BO_4$

**Sol.** Number of octahedral voids per ion in lattice = 1

Hence, number of trivalent cations ( $A^{3+}$ ) =  $1 \times \frac{1}{2} = \frac{1}{2}$

number of tetrahedral voids per ion in lattice = 2

Hence, number of divalent cations ( $B^{2+}$ ) =  $2 \times \frac{1}{8} = \frac{1}{4}$

Thus, formula is  $A_{1/2} B_{1/4} O$  or  $A_2BO_4$ .

**Ex.14** A mineral having the formula  $AB_2$  crystallises in the cubic close-packed lattice, with the A atoms occupying the lattice points. What is the coordination number of the A atoms and B atoms? What percentage fraction of the tetrahedral sites is occupied by B atoms?

**Ans.** 100% (all tetrahedral voids are occupied).

**Sol.** C.N. of A atom = 8

C.N. of B atom = 4

Tetrahedral sites occupied by atoms B = 100% (all tetrahedral voids are occupied).

**Ex.15** In a simple cubic lattice of anions, the side length of the unit cell is  $2.88 \text{ \AA}$ . The diameter of the void in the body centre is

- (A)  $1.934 \text{ \AA}$  (B)  $0.461 \text{ \AA}$  (C)  $2.108 \text{ \AA}$  (D)  $4.988 \text{ \AA}$

**Ans.** (C)

**Sol.** For bcc =  $r^+/r^- = 0.732$  and  $a = \frac{2(r^+ + r^-)}{\sqrt{3}}$  and diameter of cubical void ( $2r^+$ ) =  $a(\sqrt{3} - 1)$   
 $= 2.888 \times 0.732 = 2.108 \text{ \AA}$ .

**Ex.16** In a compound, oxide ions are arranged in cubic close packing arrangement. Cations A occupy one-sixth of the tetrahedral voids and cations B occupy one-third of the octahedral voids. The formula of the compound is

- (A)  $A_2BO_3$  (B)  $AB_2O_3$  (C)  $A_2B_2O_2$  (D)  $ABO_3$

**Ans.** (D)

**Sol.** no. of oxide ions = 4

no. of A particles =  $\frac{1}{6} \times 8 = \frac{4}{3}$

no. of B particles =  $\frac{1}{3} \times 4 = \frac{4}{3}$  so formula is  $A_{4/3} B_{4/3} O_4$  or  $ABO_3$

## 8. TYPES OF IONIC STRUCTURES:

### 8.1 Rock salt structure (NaCl type of structure):

$$(0.414 \leq \frac{r_{\text{Na}^+}}{r_{\text{Cl}^-}} < 0.732)$$

(i)  $\text{Cl}^-$  ions form the FCC lattice while  $\text{Na}^+$  ion occupy all the octahedral void.

(ii) Effective number of ion per unit cell=8

(iii) Effective number of  $\text{Cl}^-$  ion per unit cell = 4

Effective number of  $\text{Na}^+$  ion per unit cell = 4

(iv) Formula of unit cell  $\text{Na}_4\text{Cl}_4$

Formula of ionic compound = NaCl

Effective number of formula unit (Z) = 4

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

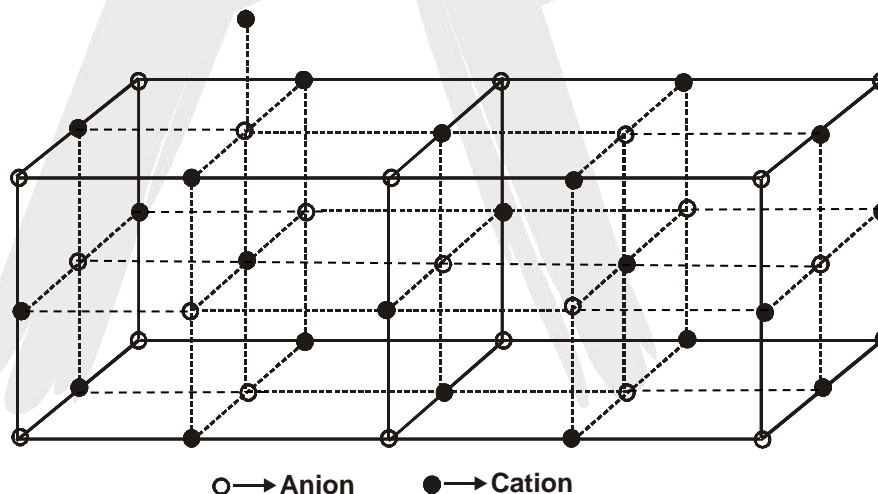
→ Here  $\sqrt{2}a \neq 4R_{\text{Cl}^-}$  → as anion-anion are not in contact.

→  $[r_{\text{Cl}^-} + r_{\text{Na}^+}] = a/2$

(vi) **Coordination number:**

Coordination number of  $\text{Cl}^-$  = Number of  $\text{Na}^+$  ion touching it = 6.

Coordination number of  $\text{Na}^+$  = 6 [placed in octahedral void of  $\text{Cl}^-$  ions].



For  $\text{Cl}^-$  :

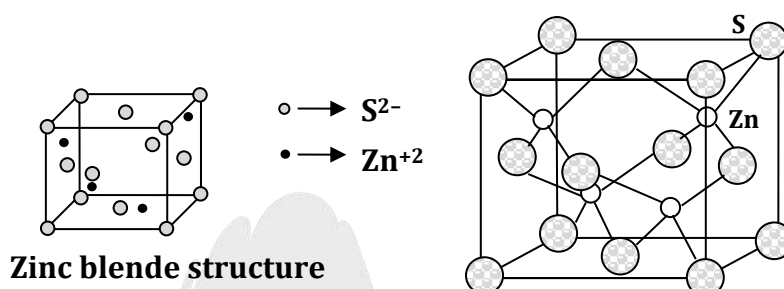
Type of neighbor	Distance	No. of neighbours
(i) Nearest	$\text{Na}^+, \frac{a}{2}$	6
(ii) Next nearest	$\text{Cl}^-, \frac{a}{\sqrt{2}}$	12
(iii) Second next nearest	$\text{Na}^+ \text{ (B.C.)}, \sqrt{\frac{3}{2}}a$	8

**Example:** Halide of Li, Na, K and Rb, AgCl, AgBr, NH<sub>4</sub>Cl.

**Note:** Lattice of NaCl is FCC of Cl<sup>-</sup> in which all octahedral void are occupied by Na<sup>+</sup>.  
or → FCC of Na<sup>+</sup> in which octahedral void are occupied by Cl<sup>-</sup>.

## 8.2 Zinc blende (sphalerite) structure:

$$(0.225 \leq \frac{r_{Zn^{2+}}}{r_{S^{2-}}} < 0.414)$$



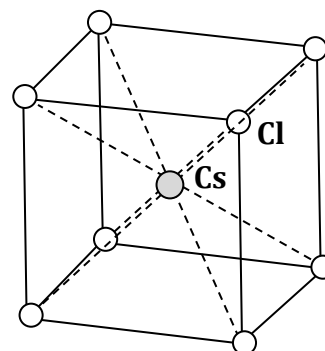
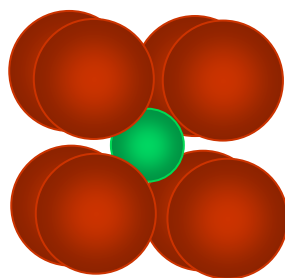
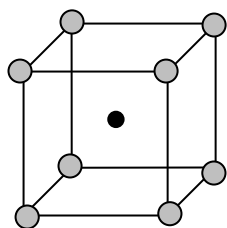
- (i) S<sup>2-</sup> ion form the FCC lattice and Zn<sup>2+</sup> ion occupy alternate (non adjacent) four tetrahedral void.
- (ii) Effective number of ion
  - \* Effective number of S<sup>2-</sup> ion per unit cell = 4.
  - \* Effective number of Zn<sup>2+</sup> ion per unit cell = 4.
- (iii) formula of unit cell = Zn<sub>4</sub>S<sub>4</sub>  
Formula of ionic compound = ZnS
- (v) Density (d) =  $\left[ \frac{Z \times M}{N_A \times a^3} \right]$   
Use  $[r_{Zn^{2+}} + r_{S^{2-}}] = \frac{\sqrt{3}}{4} a_{FCC}$
- (vi) Coordination number:  
Coordination number of Zn<sup>2+</sup> ions = 4.  
Coordination number of S<sup>2-</sup> ions = 4.

**Ex :** ZnS, CuCl, CuBr, CuI, AgI.

## 8.3 Cesium halide structure:

$$0.732 \leq \frac{r_{Cs^+}}{r_{Cl^-}} < 1$$





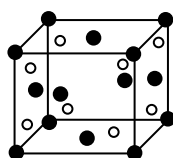
### Cesium chloride structure

- (i)  $\text{Cl}^-$  form simple cubic lattice.  
\*  $\text{Cs}^+$  ion occupies cubical void.
- (ii) Effective number of ion :  
\* Effective number of  $\text{Cs}^+$  ion = 1. & Effective number of  $\text{Cl}^-$  ion = 1.
- (iii) Formula of ionic compound =  $\text{CsCl}$ . So  $Z = 1$ .
- (iv) Density ( $d$ ) =  $\left[ \frac{Z \times M}{N_A \times a^3} \right]$   
 $[r_{\text{Cl}^-} + r_{\text{Cs}^+}] = \frac{a \sqrt{3}}{2}$
- (v) Coordination number of  $\text{Cs}^+$  ion = 8.      (vi) Coordination number of  $\text{Cl}^-$  ion = 8.

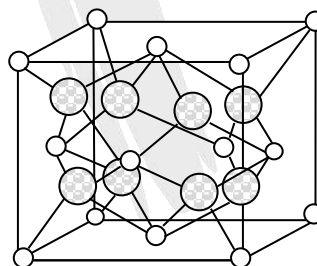
**Ex :  $\text{CsCl}$ ,  $\text{CsBr}$ ,  $\text{CsI}$ .**

### 8.4 Fluorite structure: ( $\text{CaF}_2$ ) $\text{Ca}^{2+}$ forming ccp arrangement and $\text{F}^-$ filling all tetrahedral voids.

$$0.225 \leq \frac{r_-}{r_+} < 0.414$$



### Fluorite structure



- (i)  $\text{Ca}^{2+}$  ion form the FCC lattice and  $\text{F}^-$  ion occupies all tetrahedral voids.
- (ii) Coordination number of  $\text{F}^-$  ion = 4  
Coordination number of  $\text{Ca}^{2+}$  ion = 8
- (iii) Effective number of  $\text{Ca}^{2+}$  ion = 4.  
Effective number of  $\text{F}^-$  ion = 8.
- (iv) Formula of unit cell =  $\text{Ca}_4\text{F}_8$   
Formula of ionic compound =  $\text{CaF}_2$ .

(v) Effective number of formula unit cell (Z) = 4.

(vi) Density =  $\left[ \frac{Z \times M}{N_A \times a^3} \right]$

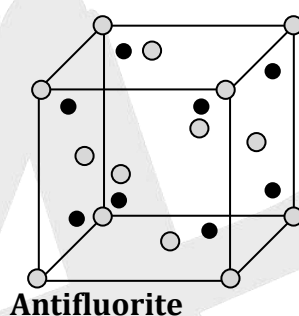
$$[r_{Ca^{2+}} + r_{F^-}] = \frac{\sqrt{3}a}{4}$$

EX:  $CaF_2$   $SrF_2$ ,  $BaF_2$ ,  $BaCl_2$ .

### 8.5 Anti-fluorite structure: ( $Na_2O$ )

$$0.225 \leq \frac{r_{Na^+}}{r_{O^{2-}}} < 0.414$$

$O^{2-}$  ion forms ccp lattice and  $Na^+$  occupies all tetrahedral voids.

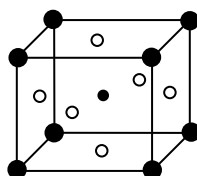


8.6 **Corundum Structure:** ( $Al_2O_3$ )  $O^{2-}$  forming hcp and  $Al^{3+}$  filling 2/3 octahedral voids.

8.7 **Rutile structure:** ( $TiO_2$ )  $O^{2-}$  forming hcp while  $Ti^{4+}$  ions occupy half of the octahedral voids.

Rutile ( $TiO_2$ )	CN
$C^+$	6
$A^-$	3

8.8 **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.



Pervoskite structure

# Perovskite ( $CaTiO_3$ )

POSITION	ION	CN
At BC	$Ca^{++}$	12
At corner	$Ti^{4+}$	6
At Edge centre	$O^{2-}$	2

**8.9 Spinel and inverse spinel structure:**  $(\text{MgAl}_2\text{O}_4)\text{O}^{2-}$  forming fcc,  $\text{Mg}^{2+}$  filling  $1/8$  of tetrahedral voids and  $\text{Al}^{3+}$  taking half of octahedral voids. In an inverse spinel structure,  $\text{O}^{2-}$  ion form FCC lattice,  $\text{A}^{2+}$  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.

STRUCTURES OF SOME CRYSTALS						
S.No.	crystal	C.N.		Z	Structural arrangement	E.g.
		cation	anion	Total Formula unit		
1	NaCl	6	6	$\text{Na}^+ = 4$ $\text{Cl}^- = 4$	$\text{Na}^+ =$ at all octahedral voids $\text{Cl}^- \rightarrow \text{FCC}$	LiCl
2.	ZnS (wurtizite)	4	4	$\text{Zn}^{2+} = 6$ $\text{S}^{2-} = 6$	$\text{Zn}^{2+} = \text{At } 1/2 \text{ TV}$ $\text{S}^{2-} = \text{HCP}$	AgI
3.	ZnS (Blende)	4	4	$\text{Zn}^{2+} = 4$ $\text{S}^{2-} = 4$	$\text{Zn}^{2+} = \text{At } 1/2 \text{ of TV}$ $\text{S}_2^{2-} \text{ FCC}$	CuCl CuBr CuI, CdS
4.	$\text{CaF}_2$ (Fluorite)	8	4	$\text{Ca} = 4$ $\text{F} = 8$	$\text{Ca}^{2+} = \text{FCC}$ $\text{F} = \text{All TV}$	$\text{BaF}_2$ $\text{SrF}_2$
5.	$\text{Na}_2\text{O}$	4	8	$\text{Na}^+ = 8$ $\text{O}^{2-} = 4$	$\text{Na}^+ = \text{All TV}$ $\text{O}^{2-} = \text{FCC}$	
6.	CsCl	8	8	$\text{Cs}^+ = 1$ $\text{Cl}^- = 1$	$\text{Cs}^+ = \text{Body center}$ $\text{Cl}^- = \text{At corners}$	CsCN CsI CaS

**Note :** On increasing pressure  $\rightarrow$  Coordination number tends to increase.

On increasing temperature  $\rightarrow$  Coordination number tends to decrease.



**Ex.17** The number of tetrahedral voids per unit cell in NaCl crystal are:

- (A) 4 (B) 8  
(C) twice the number of octahedral voids. (D) four times the number of octahedral voids.

**Ans.** (B)

**Ex.18** CsCl crystallises in a cubic that has a  $\text{Cl}^-$  at each corner and  $\text{Cs}^+$  at the centre of the unit cell. If  $(r_{\text{Cs}^+}) = 1.69 \text{ \AA}$  and  $r_{\text{Cl}^-} = 1.81 \text{ \AA}$ , what is value of edge length  $a$  of the cube?

**Ans.**  $a = 4.04 \text{ \AA}$

**Sol.** We assume that the closest  $\text{Cs}^+$  to  $\text{Cl}^-$  distance is the sum of the ionic radii of  $\text{Cs}^+$  and  $\text{Cl}^-$ .

$$= 1.69 + 1.81 = 3.50 \text{ \AA}$$

This distance is one-half of the cubic diagonal =  $\frac{a\sqrt{3}}{2}$

$$\therefore \frac{a\sqrt{3}}{2} = 3.50 \text{ \AA} \quad \therefore a = 4.04 \text{ \AA}$$

**Ex.19** A solid AB has the NaCl structure, If radius of cation  $A^+$  is 120 pm, calculate the maximum possible value of the radius of the anion  $B^-$ .

**Sol.** We know for the NaCl structure, for maximum radius of  $B^-$ , the ratio  $r^+/r^-$  should be minimum for octahedral void i.e. 0.414.

$$\frac{r_{A^+}}{r_{B^-}} = 0.414$$

$$r_{B^-} = \frac{r_{A^+}}{0.414} = \frac{120}{0.414} = 290 \text{ pm.}$$

**Ex.20** The effective radius of an iron atom is 1.42 Å. It has a rock-salt structure. Calculate its density (Fe = 56).

**Sol.** Due to rock-salt (fcc) structure, number of atoms in a unit cell ( $z$ ) = 4.

$$\text{Thus, } d (\text{density}) = \frac{zM}{a^3 N_0} \quad a = 2\sqrt{2}r = 2\sqrt{2} \times 1.42 \times 10^{-8} \text{ cm}$$

$$d = \frac{4 \times 56}{6.02 \times 10^{23} \times (2\sqrt{2} \times 1.42 \times 10^{-8})^3} = 5.743 \text{ g/cm}^3$$

**Ex.21** An element crystallises as face-centred cubic lattice with density as 5.20 g/cm<sup>3</sup> and edge length of the side of unit cell as 300 pm. Calculate mass of the element which contains  $3.01 \times 10^{24}$  atoms.

**Sol.**  $z = 4$  in fcc lattice  $M = ?$ ,  $d = 5.20 \text{ g/cm}^3$

$$a = 300 \text{ pm} = 3 \times 10^{-8} \text{ cm}$$

$$\therefore a^3 = 27 \times 10^{-24} \text{ cm}^3$$

$$N_0 = 6.02 \times 10^{23}$$

$$\therefore M = = 21.13 \text{ g mol}^{-1}$$

$$\text{Thus, } 6.02 \times 10^{23} \text{ atoms have} = 21.13 \text{ g}$$

$$\therefore 3.01 \times 10^{24} \text{ atoms have} = \times 3.01 \times 10^{24} \text{ g} = 105.65 \text{ g}$$

## DO YOURSELF-3

- In the zinc blende structure, zinc ions occupy alternate tetrahedral voids and  $S^{2-}$  ions exist as ccp. The radii of  $Zn^{2+}$  and  $S^{2-}$  ions are  $0.83 \text{ \AA}$  and  $1.74 \text{ \AA}$  respectively. The edge length of the  $ZnS$  unit cell is  
 (A)  $2.57 \text{ \AA}$  (B)  $5.14 \text{ \AA}$  (C)  $5.93 \text{ \AA}$  (D)  $4.86 \text{ \AA}$
- If the distance between  $Na^+$  and  $Cl^-$  ions in  $NaCl$  crystal is 'a' pm, what is the length of the cell edge?  
 (A)  $2a$  (B)  $\frac{a}{2}$  (C)  $4a$  (D)  $\frac{a}{4}$
- Which of the following statement is incorrect about rock salt type structure ?  
 (A) It has FCC arrangement of  $Na^+$ .  
 (B)  $Na^+$  &  $Cl^-$  ions have co-ordination number of 6 :6.  
 (C) A unit cell of  $NaCl$  consists of four  $NaCl$  units  
 (D) All halides of alkali metals have rock salt type structure.
- In the zinc blende structure  $S^{2-}$  adopt ccp arrangement and  $Zn^{2+}$  occupy.  
 (A) Octahedral sites (B) Hexagonal sites  
 (C) Tetrahedral sites (D) None of these
- The numbers of tetrahedral and octahedral holes in a ccp array of 100 atoms are respectively  
 (A) 200 and 100 (B) 100 and 200 (C) 200 and 200 (D) 100 and 100
- In a face centred cubic arrangement of metallic atoms, what is the relative ratio of the sizes of tetrahedral and octahedral voids?  
 (A) 0.543 (B) 0.732 (C) 0.414 (D) 0.637
- $CsBr$  has b.c.c. structure with edge length  $4.3 \text{ \AA}$ . The shortest inter ionic distance in between  $Cs^+$  and  $Br^-$  is:  
 (A) 3.72 (B) 1.86 (C) 7.44 (D) 4.3
- In the fluorite structure if the radius ratio is  $\left(\sqrt{\frac{3}{2}} - 1\right)$ , how many ions does each cation touch ?  
 (More than one may be correct)  
 (A) 4 anions (B) 12 cations (C) 8 anions (D) No cations

## 9. IMPERFECTIONS IN SOLIDS

Although crystalline solids have short range as well as long range order in the arrangement of their constituent 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.

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 irregularities 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.

**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 those 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:**

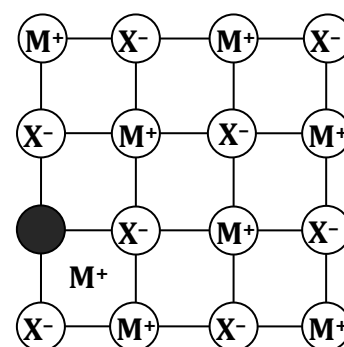
When some of the lattice sites are vacant, the crystal said to have vacancy defect. This results in decrease in density of the substance. This defect can also develop when a substance is heated.

**(b) Interstitial Defect:**

When some constituent particles (atoms or molecules) occupy an interstitial sites then such defects develop. This defect increases the density of the substance. 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 is also called dislocation defect. It not change the density of the solid. Frenkel defect is shown by ionic substance in which there is a



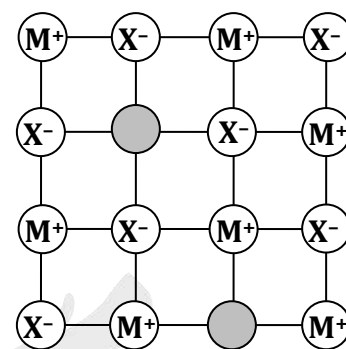
**Frenkel Defect**

large difference in the size of ions, for example, ZnS, AgCl, AgBr and AgI due to small size of  $\text{Zn}^{2+}$  and  $\text{Ag}^+$  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. 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  $10^6$  Schottky pairs per  $\text{cm}^3$  at room temperature. In  $1 \text{ cm}^3$  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.



**Schottky Defect**

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

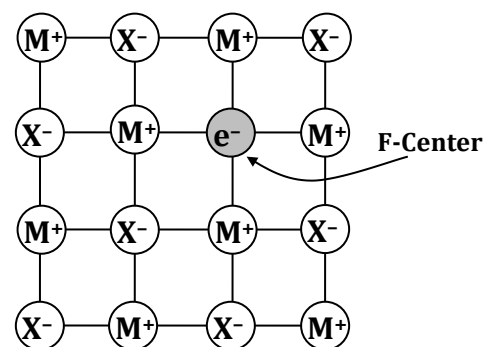
**(ii) Non-Stoichiometric Defects**

The defects discussed so far do not disturb the stoichiometry of the crystalline substances. 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**

Metal excess defect due to anionic vacancies: Alkali halides like NaCl and KCl show this 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  $\text{Cl}^-$  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  $\text{Na}^+$  ions. Metal excess defects due to anion vacancies the released electrons diffuse



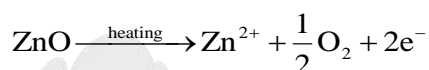
**Metal excess defects due to anion vacancies**



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.

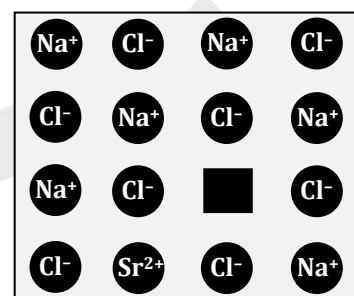
The colour results by excitation of these electrons when they absorb energy from the visible light falling on the crystals. Similarly, excess of lithium makes LiCl crystals pink and excess of potassium makes KCl crystals violet (or lilac).

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.



### (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  $\text{Fe}_{0.95}\text{O}$ . It may actually range from  $\text{FeO}_{0.93}$  to  $\text{Fe}_{0.96}\text{O}$ . In crystals of FeO some  $\text{Fe}^{2+}$  cations are missing and the loss of positive charge is made up by the presence of required number of  $\text{Fe}^{3+}$  ions.



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

### (iii) Impurity Defects

If molten NaCl containing a little amount of  $\text{SrCl}_2$  is crystallised, some of the sites of  $\text{Na}^+$  ions are occupied by  $\text{Sr}^{2+}$ . Each  $\text{Sr}^{2+}$  replaces two  $\text{Na}^+$  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  $\text{Sr}^{2+}$  ions. Another similar example is the solid solution of  $\text{CdCl}_2$  and  $\text{AgCl}$ .

**Ex.22** Which of the following is/are correct ?

- (A) Schottky defect lowers the density
- (B) Frenkel defect increases the dielectric constant of the crystals
- (C) Stoichiometric defects make the crystals electrical conductors
- (D) In the Schottky defect, equal number of extra cations and electrons are present in the interstitial sites.

**Ans.** (ABC)

**Sol.** These are facts.

**Ex.23** When LiCl is heated into the vapour of lithium, the crystal acquires pink colour. This is due to

- (A) Schottky defects (B) Frenkel defects  
(C) Metal excess defect leading to F-centers (D) Electronic defect

**Ans. (C)**

**Ex.24** Which of the following statements are correct in context of point defects in a crystal ?

- (A) AgCl has anion Frenkel defect and CaF<sub>2</sub> has Schottky defects  
(B) AgCl has cation Frenkel defects and CaF<sub>2</sub> has anion Frenkel defects  
(C) AgCl as well as CaF<sub>2</sub> has anion Frenkel defects  
(D) AgCl as well as CaF<sub>2</sub> has Schottky defects

**Ans. (B)**

**Sol.** Since Ag<sup>+</sup> (cation) is smaller than Cl<sup>-</sup> (anion) & hence cation is present in voids.

In CaF<sub>2</sub>, F<sub>anion</sub><sup>-</sup> is smaller.

**Ex.25** Ferrous oxide (FeO) is experimentally found to have the formula Fe<sub>0.93</sub>O. Find the %age of Fe ions in +3 state.

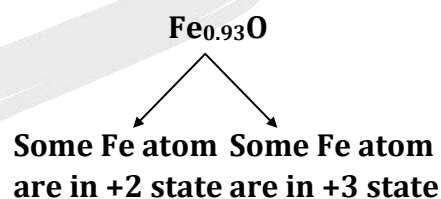
**Sol.** Let there is x Fe atom in +3 state

$$3x + 2(93 - x) = 200$$

$$x = 14$$

$$\% \text{ Fe}^{3+} = \frac{14}{93} \times 100\% = \frac{1400}{93} \%$$

$$\approx 15.54\%$$



## 10. ELECTRICAL PROPERTIES

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

- (i) Conductors:** The solids with conductivities ranging between 10<sup>4</sup> to 10<sup>7</sup> ohm<sup>-1</sup> m<sup>-1</sup> are called conductors. Metals conductivities in the order of 10<sup>7</sup> ohm<sup>-1</sup> m<sup>-1</sup> are good conductors.
- (ii) Insulators:** These are the solids with very low conductivities ranging between 10<sup>-29</sup> to 10<sup>-10</sup> ohm<sup>-1</sup> m<sup>-1</sup>.
- (iii) Semiconductors:** These are the solids with conductivities in the intermediate range from 10<sup>-6</sup> to 10<sup>4</sup> Ohm<sup>-1</sup> m<sup>-1</sup>.

**10.1 : 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.

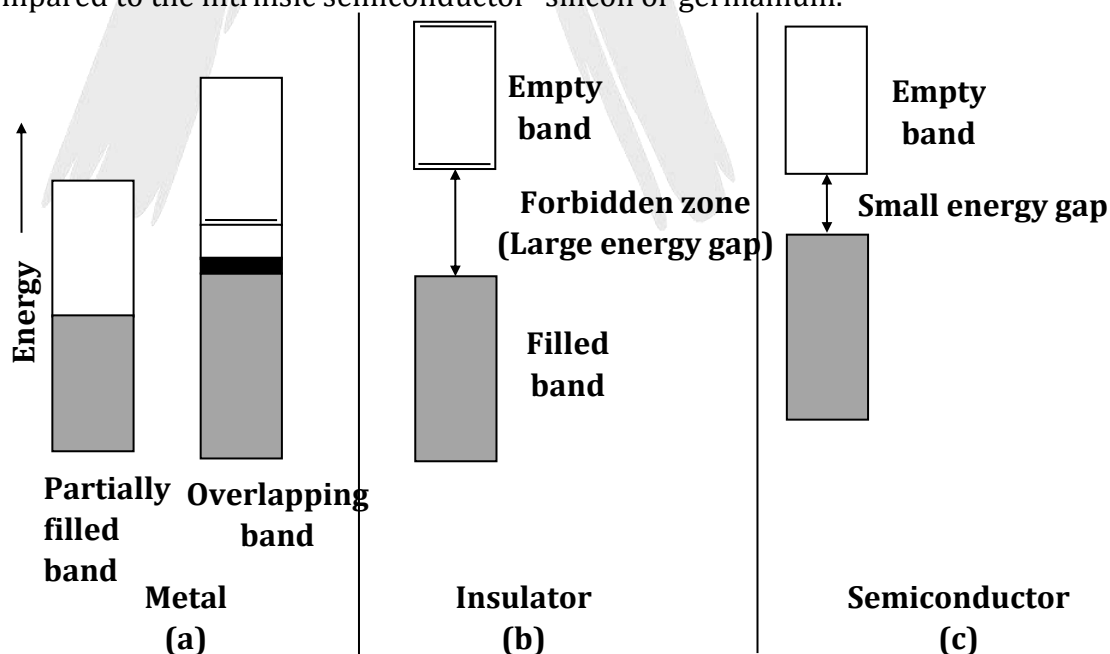
Metals conduct electricity in solid as well as molten state. The conductivity of metals depend upon the number of valence electrons available per atom. The atomic orbital's of metal atoms form molecular orbital's which are so close in energy to each other as to form a band. If this band is partially 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.

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

**10.2 : 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 semiconductors 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.

The conductivity of these intrinsic 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.



**Distinction among (a) metals (b) insulators and (c) semiconductors.**

**In each case, an unshaded area represents a conduction band.**

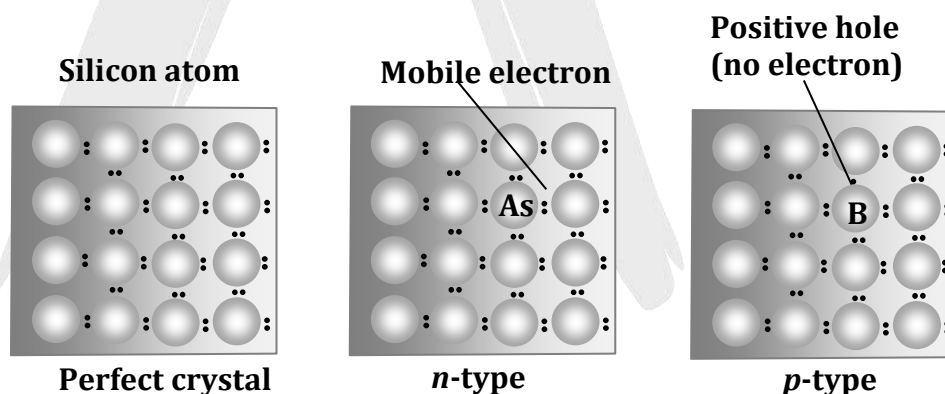
**(a) Electron - rich impurities**

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 neighbour. 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.

All 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 is called p-type semiconductors.



**Fig. :** Creation of n-type and p-type semiconductors 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 high energy into electrical energy.

Germanium 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 In Sb, AlP and GaAs. Gallium arsenide (GaAs) 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 electro negativities of the two elements. It is interesting to learn that transition metal oxides show marked differences in electrical properties. TiO, CrO<sub>2</sub> and ReO<sub>3</sub> behave like metals. Rhenium oxide like ReO<sub>3</sub> is like metallic copper in its conductivity and appearance. Certain other oxides like VO, VO<sub>2</sub>, VO<sub>3</sub>, and TiO<sub>3</sub> show metallic or insulating properties depending on temperature.

**Ex.26** What type of semiconductor is obtained when Si is doped with boron?

**Ans.** p-type semiconductor

### 11. 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, 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.

#### 11.1 Paramagnetic substances:

Substances which are weakly attracted into the magnetic field are called paramagnetic. These substances lose their magnetism on removing the magnetic field. Paramagnetism is caused by the presence of unpaired electrons and since most of the transition metal atoms have unpaired d-electrons. They are paramagnetic in behavior. These possess permanent magnetic dipole.

**Ex.** TiO, VO<sub>2</sub>, CuO, O<sub>2</sub>, FeSO<sub>4</sub>, Ti<sub>2</sub>O<sub>3</sub>, VO

**11.2 Diamagnetic substances:**

Diamagnetic substances are weakly repelled by a magnetic field.  $\text{H}_2\text{O}$ ,  $\text{NaCl}$  and  $\text{C}_6\text{H}_6$  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. Since most of the transition metal ions have unpaired d-electrons, they show paramagnetic behavior. The exceptions are  $\text{Sc}^{3+}$ ,  $\text{Ti}^{4+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^+$ , etc. which do not contain any unpaired d-electrons and hence these are diamagnetic.

**11.3 Ferromagnetic substances:**

The substances possessing unpaired electrons are further classified in three different groups based on the alignment of magnetic moments of unpaired electrons.

(a) Ferromagnetic substances

(b) Antiferromagnetic substances

(c) Ferrimagnetic substances

**(a) Ferromagnetic substances:** The substances which are strongly attracted by magnetic field are termed as ferromagnetic substances. This type of substance have alignment of all the unpaired electrons in the same direction (orientation) These substances are permanently magnetised i.e. these substances show magnetism even in the absence of magnetic field. Examples:  $\text{Ni}$ ,  $\text{Fe}$ ,  $\text{Gd}$ ,  $\text{Co}$  and  $\text{CrO}_2$ .

**(b) Antiferromagnetic substances :** Substances like  $\text{MnO}$  showing antiferromagnetism have domain structure similar to ferromagnetic substance, but their domains are oppositely oriented and cancel out each other's magnetic moment

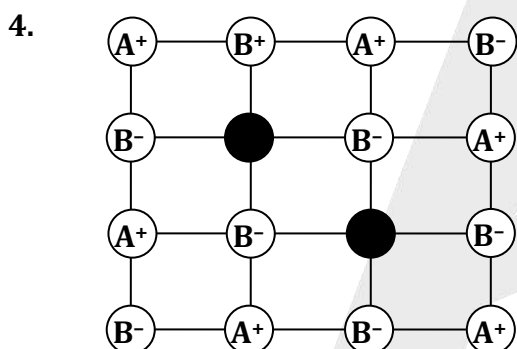
**Example.**  $\text{MnO}$ ,  $\text{Mn}_2\text{O}_3$  and  $\text{MnO}_2$ .

**(c) Ferrimagnetic substances:** 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.  $\text{Fe}_3\text{O}_4$  (magnetite) and ferrites like  $\text{MgFe}_2\text{O}_4$  and  $\text{ZnFe}_2\text{O}_4$  are examples of such substances. These substances also lose ferrimagnetism on heating and become paramagnetic. Example  $\text{Fe}_3\text{O}_4$  is ferrimagnetic at room temperature but becomes paramagnetic at 850 K.



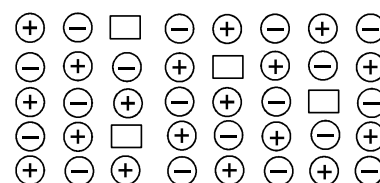
## DO YOURSELF-4

- In a crystal some ions are missing from normal sites. This is an example of  
 (A) F-centre (B) Interstitial defect  
 (C) Frenkel defect (D) Schottky defect
- When an ion leaves its correct lattice site and occupies interstitial sites in its crystal lattice, it is called  
 (A) Crystal defect (B) Frenkel defect (C) Schottky defect (D) None of these
- AgCl is crystallized from molten AgCl containing a little  $\text{CdCl}_2$ . The solid obtained will have  
 (A) cationic vacancies equal to number of  $\text{Cd}^{2+}$  ions incorporated  
 (B) cationic vacancies equal to double the number of  $\text{Cd}^{2+}$  ions  
 (C) anionic vacancies  
 (D) neither cationic nor anionic vacancies



Which of the following is correct

- The defect is known as schottky defect.
  - The defect is known as Frenkel defect.
  - Density of compound in the defect increases.
  - Stoichiometry of compound will change slightly.
- Which of the following is incorrect  
 (A) The defect is known as schottky defect  
 (B) Density of compound in the defect decreases  
 (C)  $\text{NaCl(s)}$  is example which generally shows this defect  
 (D) Stoichiometry of compound will change slightly.



- Analysis show that nickel oxide consist of nickel ion with 96% ions having  $d^8$  configuration and 4% having  $d^7$  configuration. Which amongst the following best represents the formula of the oxide.  
 (A)  $\text{Ni}_{1.02}\text{O}_{1.00}$  (B)  $\text{Ni}_{0.96}\text{O}_{1.00}$   
 (C)  $\text{Ni}_{0.98}\text{O}_{1.98}$  (D)  $\text{Ni}_{0.98}\text{O}_{1.00}$



7. The correct statement(s) regarding defects solids is (are) [More than one may be correct]
- (A) Schottky defect is usually favoured by small difference in the sizes of cation and anion.
  - (B) Schottky defect lowers the density of solids.
  - (C) Compounds having F-centres are diamagnetic.
  - (D) Frenkel defect is a dislocation defect.

A

## EXERCISE (O-I)

## PROBLEMS BASED ON CLASSIFICATION OF SOLIDS

1. How many of the following are covalent network solids?  
S<sub>8</sub>, Bronze, SiO<sub>2</sub>, Diamond, ZnSO<sub>4</sub>, Si, AlN, SiC, CO<sub>2</sub>.  
(A) 4 (B) 5 (C) 6 (D) 6
2. 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
3. Which of the following is not a characteristic of a crystalline solid?  
(A) Definite and characteristic heat of fusion.  
(B) Isotropic nature.  
(C) A regular periodically repeated pattern of arrangement of constituent particles in the entire crystal.  
(D) A true solid
4. Which of the following is an amorphous solid?  
(A) Graphite (C) (B) Quartz glass (SiO<sub>2</sub>)  
(C) Chrome alum (D) Silicon carbide (SiC)
5. Which of the following is true about the value of refractive index of quartz glass?  
(A) Same in all directions (B) Different in different directions  
(C) Cannot be measured (D) Always zero
6. Which of the following statement is not true about amorphous solids?  
(A) On heating they may become crystalline at certain temperature.  
(B) They may become crystalline on keeping for long time.  
(C) Amorphous solids can be moulded by heating.  
(D) They are anisotropic in nature.
7. The sharp melting point of crystalline solids is due to \_\_\_\_\_.  
(A) a regular arrangement of constituent particles observed over a short distance in the crystal lattice.  
(B) a regular arrangement of constituent particles observed over a long distance in the crystal lattice.  
(C) same arrangement of constituent particles in different directions.  
(D) different arrangement of constituent particles in different directions.

## PROBLEMS BASED ON CRYSTAL SYSTEMS, UNIT CELLS

8. Which of the following are the correct axial distances and axial angles for rhombohedral system?
- (A)  $a = b = c, \alpha = \beta = \gamma \neq 90^\circ$  (B)  $a = b \neq c, \alpha = \beta = \gamma = 90^\circ$   
 (C)  $a \neq b = c, \alpha = \beta = \gamma = 90^\circ$  (D)  $a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$
9.  $a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$  represents
- (A) tetragonal system (B) orthorhombic system  
 (C) monoclinic system (D) triclinic system
10. The most unsymmetrical system is:
- (A) Cubic (B) Hexagonal (C) Triclinic (D) Orthorhombic
11. A match box exhibit -
- (A) Cubic geometry (B) Monoclinic geometry  
 (C) Tetragonal geometry (D) Orthorhombic geometry
12. The crystal system of a compound with unit cell dimensions,  $a = 0.387$  and  $b = 0.387$  and  $c = 0.504\text{nm}$  and  $\alpha = \beta = 90^\circ$  and  $\gamma = 120^\circ$  is :
- (A) Cubic (B) Hexagonal (C) Orthorhombic (D) Rhombohedral

## PROBLEMS BASED ON SIMPLE CUBIC AND BBC

13. Which of the following is incorrect for simple cubic metallic crystal -
- (A) The coordination number of an atom is 6  
 (B) The atom along the edge length of the cube touches each other  
 (C) Each atom is surrounded by 6 cubic voids  
 (D) Each atom is surrounded by 8 cubic voids
14. What is incorrect regarding bcc unit cell -
- (A)  $Z = 2$  (B)  $a\sqrt{3} = 4r$  (C) C.N. = 6 (D) Packing fraction = 0.68
15. A metal crystallizes in a body centered cubic lattice (bcc) with the edge of the unit cell  $5.2\text{\AA}$ . The distance between the two nearest neighbours is
- (A)  $10.4\text{\AA}$  (B)  $4.5\text{\AA}$  (C)  $5.2\text{\AA}$  (D)  $9.0\text{\AA}$
16. Fraction of edge length covered by atoms in BCC structure is -
- (A) 1 (B)  $\sqrt{3}\pi/8$  (C)  $1/\sqrt{2}$  (D)  $\sqrt{3}/2$
17. Iron has body centred cubic lattice structure. The edge length of the unit cell is found to be  $286\text{ pm}$ . What is the radius of an iron atom?
- (A)  $r = 124\text{ pm}$  (B)  $r = 128\text{ pm}$   
 (C)  $r = 124\text{\AA}$  (D)  $r = 128\text{\AA}$

18. In a FCC unit cell  
 (A)  $\sqrt{3}a = 4r$  (B)  $\sqrt{2}a = 4r$  (C)  $a = 2r$  (D)  $\sqrt{2}a = 2r$
19. Which is incorrect for FCC lattice -  
 (A)  $a\sqrt{2} = 4R$  (B) Co-ordination number = 12  
 (C) Void fraction = 0.32 (D) No of atoms per unit cell = 4
20. An element crystallizes in both fcc & bcc lattices. Then ratio of edge length of fcc unit cell to bcc unit cell will be -  
 (A)  $1 : 2\sqrt{2}$  (B)  $\sqrt{3} : \sqrt{2}$  (C)  $\sqrt{2} : \sqrt{3}$  (D)  $\sqrt{6} : 1$
21. Which one of the following schemes of ordering closed packed sheets of equal sized spheres generate crystal of minimum packing fraction.  
 (A) ABCABC (B) ABACABAC (C) ABBAABBA (D) ABCBCABCBC

### PROBLEMS BASED ON HCP UNIT CELL

22. What is not true regarding hexagonal close packing (hcp)-  
 (A) packing fraction is 0.74  
 (B) coordination number is 12  
 (C) ABCABC type packing  
 (D) No of atoms per prism = 6
23. The shortest distance between 1<sup>st</sup> and V<sup>th</sup> layer of HCP arrangement is:  
 (A)  $8\sqrt{\frac{2}{3}}r$  (B)  $4\sqrt{\frac{3}{2}}r$  (C)  $16\frac{\sqrt{2}}{3}r$  (D)  $8\sqrt{\frac{3}{2}}r$
24. Volume of HCP unit cell is:  
 (A)  $24\sqrt{2}r^3$  (B)  $8\sqrt{2}r^3$  (C)  $16\sqrt{2}r^3$  (D)  $24\sqrt{3}r^3$

### PROBLEMS BASED ON DENSITY

25. At 912°C and  $10^5$  Pa,  $\alpha$ -Iron (bcc form) may be transformed into  $\gamma$ -iron (fcc form). If density of  $\alpha$ -iron is  $\rho$  then what is density of  $\gamma$ -iron (assume no change in radius of iron atom) -  
 (A)  $\rho/0.74$  (B)  $\frac{\rho \times 0.68}{0.74}$  (C)  $\frac{4\rho}{3\sqrt{1.5}}$  (D)  $\frac{3 \times \rho \sqrt{1.5}}{4}$
26.  ${}^{39}_{19}\text{K}$  (Specific gravity = 0.89) crystallized in bcc arrangement. What is radius of K atom (in cm)  
 (A)  $\left( \frac{2\sqrt{3} \times 39}{\pi^2 \times 0.89 N_A} \right)^{1/3}$  (B)  $\left( \frac{3\sqrt{3} \times 39}{32 \times 0.89 N_A} \right)^{1/3}$   
 (C)  $\left( \frac{4\sqrt{3} \times 39}{\pi^2 \times 0.89 N_A} \right)^{1/3}$  (D)  $\left( \frac{3\sqrt{3} \times 39}{64 \times 0.89 N_A} \right)^{1/3}$

## PROBLEMS BASED ON TV AND OV

27. 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.
28. 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
29. In a lattice of X and Y atoms, if X atoms are present at corners and Y atoms at the body centre & one X atom is removed from a corner from each unit cell, then the formula of the compound will be :  
 (A)  $X_7Y$  (B)  $X_8Y_7$  (C)  $X_7Y_8$  (D)  $X_7Y_7$
30. If 'Z' is the number of atoms in the unit cell that represents the closest packing sequence ---ABCABC---, the number of tetrahedral voids in the unit cell is equal to  
 (A) Z (B) 2Z (C)  $Z/2$  (D)  $Z/4$
31. 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)  $C_3A_2$

## PROBLEMS BASED ON IONIC CRYSTAL

32. If  $x$  = radius of  $Na^+$  &  $y$  = radius of  $Cl^-$  &  $a$  is the unit cell edge length for NaCl crystal, then which of the given relation is correct?  
 (A)  $x + y = a$  (B)  $2x + 2y = a$  (C)  $x + y = 2a$  (D)  $x + y = a\sqrt{2}$
33. Edge length of  $M^+X^-$  (NaCl structure) is  $7.2 \text{ \AA}$ . Radius of  $X^-$  ion is ( $r_{M^+} = 1.6 \text{ \AA}$ ):  
 (A)  $2.0 \text{ \AA}$  (B)  $5.6 \text{ \AA}$  (C)  $2.8 \text{ \AA}$  (D)  $38 \text{ \AA}$
34. How many unit cells are there in 1 gram 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)  $\frac{N_A}{58.5 \times 8}$
35. A compound XY crystallizes in 8 : 8 lattice with unit cell edge length 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
36. 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  $Cl^-$

37. Diamond belongs to the crystal system:  
(A) Cubic (B) triclinic (C) tetragonal (D) hexagonal
38. 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
39. 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

**PROBLEMS BASED ON DEFECTS IN SOLIDS**





40. Which of the following is the most likely to show schottky defect  
(A)  $CaF_2$  (B) ZnS (C) AgCl (D) CsCl
41. 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) atom of tetrahedral voids displaces into octahedral voids  
(D) equal number of extra cations and electrons are present in the interstitial sites
42. F-centers are  
(A) the electrons trapped in anionic vacancies  
(B) the electrons trapped in cation vacancies  
(C) presence of cations in the interstitial sites  
(D) presence of anions in the interstitial sites
43. Strongly heated ZnO crystal can conduct electricity. This is due to  
(A) Movement of extra  $Zn^{2+}$  ions present in the interstitial sites  
(B) Movement of electrons present in the interstitial sites  
(C) Movement of oxide ions  
(D) None of these
44. Which of the following oxides behaves as conductor or insulator depending upon temperature?  
(A) TiO (B)  $SiO_2$  (C)  $TiO_3$  (D) MgO
45. Cations are present in the interstitial sites in \_\_\_\_\_.  
(A) Frenkel defect (B) Schottky defect  
(C) Vacancy defect (D) Metal deficiency defect
46. Schottky defect is observed in crystals when \_\_\_\_\_.  
(A) some cations move from their lattice site to interstitial sites.  
(B) equal number of cations and anions are missing from the lattice.  
(C) some lattice sites are occupied by electrons.  
(D) some impurity is present in the lattice.

47. Which of the following defects is also known as dislocation defect?
- (A) Frenkel defect (B) Schottky defect  
(C) Non-stoichiometric defect (D) Simple interstitial defect

**PROBLEMS BASED ON ELECTRICAL PROPERTIES**

48. Which of the following oxides shows electrical properties like metals?
- (A)  $\text{SiO}_2$  (B)  $\text{MgO}$  (C)  $\text{SO}_2(\text{s})$  (D)  $\text{CrO}_2$
49. The lattice site in a pure crystal cannot be occupied by \_\_\_\_\_.  
(A) molecule (B) ion (C) electron (D) atom
50. Graphite cannot be classified as \_\_\_\_\_.  
(A) conducting solid (B) network solid  
(C) covalent solid (D) ionic solid
51. Which kind of defects are introduced by doping?  
(A) Dislocation defect (B) Schottky defect  
(C) Frenkel defects (D) Electronic defects
52. Silicon doped with electron-rich impurity forms \_\_\_\_\_.  
(A) p-type semiconductor (B) n-type semiconductor  
(C) intrinsic semiconductor (D) insulator

**PROBLEMS BASED ON MAGNETIC PROPERTIES**

53. Which of the following arrangements shows schematic alignment of magnetic moments of antiferromagnetic substances?
- (A) 
- (B) 
- (C) 
- (D) 
54. Which of the following statements is not true?
- (A) Paramagnetic substances are weakly attracted by magnetic field.  
(B) Ferromagnetic substances cannot be magnetised permanently.  
(C) The domains in antiferromagnetic substances are oppositely oriented with respect to each other.  
(D) Pairing of electrons cancels their magnetic moment in the diamagnetic substances.



55. A ferromagnetic substance becomes a permanent magnet when it is placed in a magnetic field because \_\_\_\_\_.  
(A) all the domains get oriented in the direction of magnetic field.  
(B) all the domains get oriented in the direction opposite to the direction of magnetic field.  
(C) domains get oriented randomly.  
(D) domains are not affected by magnetic field.
56. The value of magnetic moment is zero in the case of antiferromagnetic substances because the domains \_\_\_\_\_.  
(A) get oriented in the direction of the applied magnetic field.  
(B) get oriented opposite to the direction of the applied magnetic field.  
(C) are oppositely oriented with respect to each other without the application of magnetic field.  
(D) cancel out each other's magnetic moment.
57. Which of the following statements are correct?  
(A) Ferrimagnetic substances lose ferrimagnetism on heating and become paramagnetic.  
(B) Ferrimagnetic substances do not lose ferrimagnetism on heating and remain ferrimagnetic.  
(C) Antiferromagnetic substances have domain structures similar to ferromagnetic substances and their magnetic moments are not cancelled by each other.  
(D) In ferromagnetic substances all the domains get oriented in the direction of magnetic field and remain as such even after removing magnetic field.

## EXERCISE (S-I)

## PROBLEMS BASED ON CLASSIFICATION OF SOLIDS

- Classify each of the following solids.
 

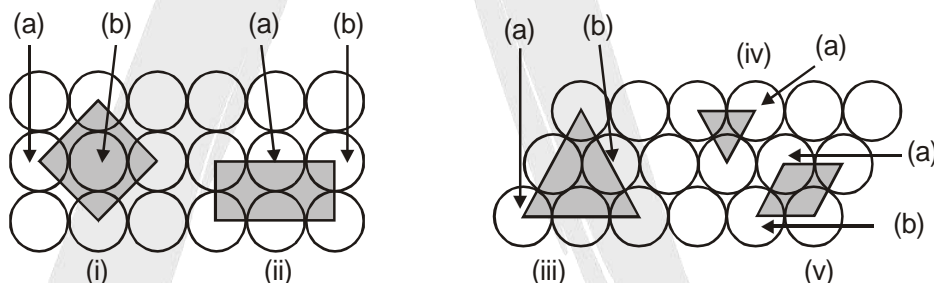
(a) Tetra phosphorus decaoxide ( $P_4O_{10}$ )	(b) Graphite
(c) Brass	(d) Ammonium phosphate $[(NH_4)_3PO_4]$
(e) SiC	(f) Rb
(g) $I_2$	(h) LiBr
(i) $P_4$	(j) Si
(k) Plastic.	

## PROBLEMS BASED ON CRYSTAL SYSTEMS, UNIT CELLS

- How many Bravais lattices are possible in 3D ?
- What are the crystallographic parameters of hexagonal, monoclinic and triclinic unit cell respectively.

## PROBLEMS BASED ON 2D ARRANGEMENT

- Given below are two dimensions lattices with nicely shaded regions. You just have to find the contributions (in fractions) of particles marked to the shaded regions and the total number of particles in the regions.



- What is the coordination number in a square close packed structure in two dimensions?

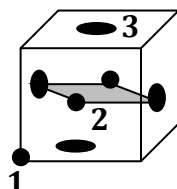
## PROBLEMS BASED ON SC, BCC AND FCC

- A metal crystallises in bcc. Find the % fraction of edge length not covered and also % fraction of edge length covered by atom is:
- A closed packed structure of uniform spheres has the edge length of 534 pm. Calculate the radius of sphere, if it exists in
 

(a) Simple cubic lattice	(b) BCC lattice	(c) FCC lattice
--------------------------	-----------------	-----------------
- Xenon crystallises in the face-centred cubic lattice and the edge of the unit cell is 620 pm. What is the nearest neighbour distance and what is the radius of xenon atom?

9. Following figure shows an FCC unit cell with atoms of radius  $r$  marked 1(corner), 2(face center), 3(face center). A quadrilateral is also shown by joining the centers of 4 face centered atoms.

Find: (i) The distances between atoms 1 & 2, 2 & 3 and 1 & 3.  
(ii) The shape and dimensions of the quadrilateral.



### PROBLEMS BASED ON DENSITY

10. The effective radius of the iron atom is  $1.42 \text{ \AA}$ . It has FCC structure. Calculate its density (Fe = 56 amu)
11. Gold crystallizes in a face centered cubic lattice. If the length of the edge of the unit cell is  $407 \text{ pm}$ , calculate the density of gold as well as its atomic radius assuming it to be spherical. Atomic mass of gold = 197 amu.
12. An element crystallizes in a structure having FCC unit cell of an edge  $200 \text{ pm}$ . Calculate the density, if  $200 \text{ g}$  of this element contains  $24 \times 10^{23}$  atoms.
13. Iron crystallizes in several modifications. At about  $910^\circ\text{C}$ , the body-centered cubic ' $\delta$ ' form undergoes a transition to the face-centered cubic ' $\gamma$ ' form. Calculate the ratio of the density of  $\delta$  iron to that of  $\alpha$  iron at the transition temperature.
14. Iron occurs as bcc as well as fcc unit cell. If the effective radius of an atom of iron is  $124 \text{ pm}$ . Compute the density of iron in both these structures.

### PROBLEMS BASED ON RADIUS RATIO

15. The two ions  $A^+$  and  $B^-$  have radii  $88$  and  $200 \text{ pm}$  respectively. In the closed packed crystal of compound AB, predict the co-ordination number of  $A^+$ .
16. If the radius of  $\text{Mg}^{2+}$  ion,  $\text{Cs}^+$  ion,  $\text{O}^{2-}$  ion,  $\text{S}^{2-}$  ion and  $\text{Cl}^-$  ion are  $0.65 \text{ \AA}$ ,  $1.69 \text{ \AA}$ ,  $1.40 \text{ \AA}$ ,  $1.84 \text{ \AA}$ , and  $1.81 \text{ \AA}$  respectively. Calculate the co-ordination numbers of the cations in the crystals of MgS, MgO and CsCl.

### PROBLEMS BASED ON TV AND OV

17. What is the number and closest distance between octahedral voids and tetrahedral voids in fcc unit cell?
18. In a compound, oxide ions are arranged in cubic close packing arrangement. Cations A occupy one-sixth of the tetrahedral voids and cations B occupy one-third of the octahedral voids. The formula of the compound is  $A_xB_yO_z$ , then find the value of  $x + y + z$ .

19. 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 formula of compound?
20. 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?
21. Spinel is an important class of oxides consisting of two types of metal ions with the oxide ions arranged in CCP pattern. The normal spinel has one-eighth 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  $\text{Zn}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{O}^{2-}$ , with  $\text{Zn}^{2+}$  in the tetrahedral holes. Give the formulae of spinel.

### PROBLEMS BASED ON NaCl STRUCTURE

22. KF crystallizes in the NaCl type structure. If the radius of  $\text{K}^+$  ions is 132 pm and that of  $\text{F}^-$  ion is 135 pm, what is the shortest K-F distance? What is the edge length of the unit cell? What is the closest K-K distance?
23. The density of KBr is  $2.75 \text{ g cm}^{-3}$ . The length of the edge of the unit cell is 654 pm. Find the number of formula unit of KBr present in the single unit cell.  
( $N = 6.023 \times 10^{23} \text{ mol}^{-1}$ , Atomic mass : K = 39, Br = 80)
24. A crystal of lead (II) sulphide has NaCl structure. In this crystal the shortest distance between  $\text{Pb}^{+2}$  ion and  $\text{S}^{2-}$  ion is 297 pm. What is the length of the edge of the unit cell in lead sulphide? Also calculate the unit cell volume.
25. Percentage of void space in AB solid having rock salt structure if  $\frac{r_+}{r_-} = \frac{1}{2}$  having cation anion contact.  
Given  $\pi = 3.15$ .

### PROBLEMS BASED ON ZnS, CsCl STRUCTURE

26. CsCl has the bcc arrangement and its unit cell edge length is 400 pm. Calculate the inter ionic distance in CsCl.
27. If the length of the body diagonal for CsCl which crystallises into a cubic structure with  $\text{Cl}^-$  ions at the corners and  $\text{Cs}^+$  ions at the centre of the unit cells is  $7 \text{ \AA}$  and the radius of the  $\text{Cs}^+$  ion is  $1.69 \text{ \AA}$ , what is the radius of  $\text{Cl}^-$  ion?
28. RbI crystallizes in CsCl structure in which each  $\text{Rb}^+$  is surrounded by eight iodide ions each of radius  $2.17 \text{ \AA}$ . Find the length of one side of RbI unit cell.

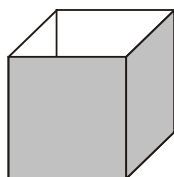
## PROBLEMS BASED ON DEFECTS IN SOLIDS

29. The composition of a sample of wustite is  $\text{Fe}_{0.93}\text{O}_{1.0}$ . What percentage of iron is present in the form of  $\text{Fe(III)}$ ?
30. If  $\text{NaCl}$  is dopped with  $10^{-3}$  mol %  $\text{SrCl}_2$ , what is the numbers of cation vacancies per mole of  $\text{NaCl}$ ?
31. A non-stoichiometric compound  $\text{Fe}_7\text{S}_8$  consist of iron in both  $\text{Fe}^{+2}$  and  $\text{Fe}^{+3}$  form and sulphur is present as sulphide ions. Calculate cation vacancies as a percentage of total cation in the sample.

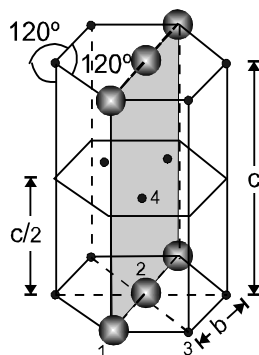
A

## EXERCISE (S-II)

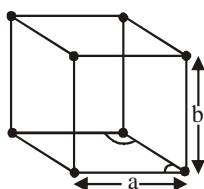
1. How many spherical balls of radii 2 cm can be placed completely inside a cubical box of edge = 8 cm?



2. Calculate the density of diamond from the fact that it has face centered cubic structure with two atoms per lattice point and unit cell edge length of  $3.569 \text{ \AA}$ .
3. 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 atoms on one of its body diagonals. If the volume of this unit cell is  $24 \times 10^{-24} \text{ cm}^3$  and density of element is  $7.2 \text{ g cm}^{-3}$ , calculate the number of atoms present in 200 g of element.
4. What is the percent by mass of titanium in rutile, a mineral that contain Titanium and oxygen, if structure can be described as a closet packed array of oxide ions, with titanium in one half of the octahedral holes. What is the oxidation number of titanium? (Ti = 48)
5. A solid  $A^+$  and  $B^-$  had NaCl type closed packed structure. If the anion has a radius of 250 pm, what should be the ideal radius of the cation? Can a cation  $C^+$  having a radius of 180 pm be slipped into the tetrahedral site of the crystal of  $A^+B^-$ , without disturbing the crystal? Give reasons for your answer.
6. 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.
7. For ABCABC packing distance between two successive tetrahedral void is X and distance between two successive octahedral void is y in a unit cell, then  $\frac{y\sqrt{2}}{X}$  is.
8. Calculate the perimeter of given plane in HCP unit cell (Given that radius of atoms =  $R \text{ \AA}$ ).



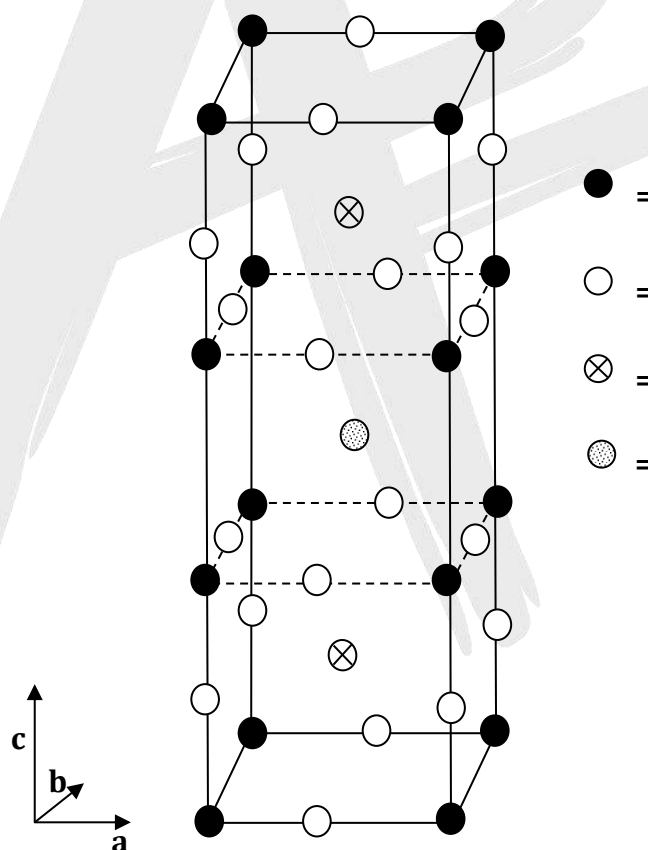
9. An element 'M' crystallizes in ABAB....type packing if adjacent layer A & B are  $10 \frac{\sqrt{2}}{\sqrt{3}}$  pm apart, then calculate radius of largest sphere which can be fitted in the void. (in pm) without disturbing the lattice arrangement (Given:  $\sqrt{2} = 1.414$ )  
Fill your answer as sum of digits (excluding decimal places) till you get the single digit answer.
10. Find packing fraction of unit cell of AAAAAA.....type hypothetical arrangement in which hexagonal packing is taken in layer.
11. 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  $0.65 \text{ \AA}$  and that of  $\text{F}^-$  ion is  $1.36 \text{ \AA}$ .
12. Potassium crystallizes in a body-centered cubic lattice with edge length,  $a = 5.2 \text{ \AA}$ .  
(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?
13. AgCl has the same structure as that of NaCl. The edge length of unit cell of AgCl is found to be  $555 \text{ pm}$  and the density of AgCl is  $5.561 \text{ g cm}^{-3}$ . Find the percentage of sites that are unoccupied.
14. KCl crystallizes in the same type of lattice as does NaCl. Given that  $\frac{r_{\text{Na}^+}}{r_{\text{Cl}^-}} = 0.5$  and  $\frac{r_{\text{Na}^+}}{r_{\text{K}^+}} = 0.7$   
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.
15. Prove that void space in fluorite structure per unit volume of unit cell is  $0.374$ .
16. Ice crystallizes in a hexagonal lattice. At the low temperature at which the structure was determined, the lattice constants where  $a = 4.53 \text{ \AA}$ , and  $b = 7.60 \text{ \AA}$  How many molecules are contained in a given unit cell?  
[density (ice) =  $0.92 \text{ gm/cm}^3$ ]





17. The olivine series of minerals consists of crystals in which Fe and Mg ions may substitute for each other causing substitutional impurity defect without changing the volume of the unit cell. In olivine series of minerals, oxide ion exist as FCC with  $\text{Si}^{4+}$  occupying  $1/4$ th of octahedral voids and divalent ions occupying  $1/4$ th of tetrahedral voids. The density of forsterite (magnesium silicate) is 3.21 g/cc and that of fayalite (ferrous silicate) is 4.34 g/cc. Find the formula of forsterite and fayalite minerals and the percentage of fayalite in an olivine with a density of 3.88 g/cc.
18. In the 1980's a class of ceramic materials was discovered that exhibits superconductivity at the unusually high temperature of 90 K. One such material contains yttrium, barium, copper and oxygen and is called "YBCO". It has a nominal composition of  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , but its actual composition is variable according to the formula  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  ( $0 < \delta < 0.5$ ).

(a) One unit cell of the idealized crystal structure of YBCO is shown below. Identify which circles correspond to which elements in the structure.

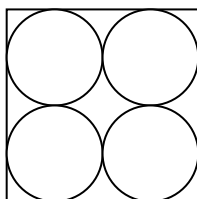


The true structure is actually orthorhombic ( $a \neq b \neq c$ ), but it is approximately tetragonal, with  $a \approx b \approx (c/3)$ .

- (b) Estimate the density of this sample of YBCO (with  $\delta = 0.25$ ) in  $\text{g cm}^{-3}$ . Use  $a = 500 \text{ pm}$  and  $c = 1500 \text{ pm}$ . Ba (137.33), Y (88.91), Cu (63.5), O (16).

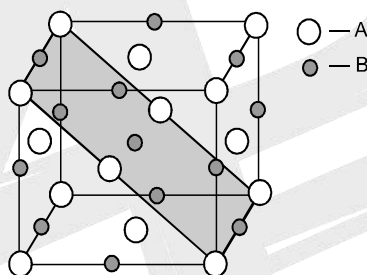
## EXERCISE (O-II)

1. Identical 4 spheres are taken and are arranged in a layer of square packing touching each other as shown

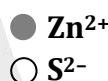
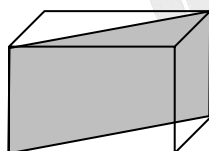


The percentage of vacant space is

- (A)  $100\left(1 - \frac{3\pi}{8}\right)$  (B)  $100\left(1 - \frac{\pi}{6}\right)$  (C)  $100 - \frac{3\pi}{8}$  (D)  $\frac{\pi}{6}$
2. A crystal is made of particles A and B. A forms FCC packing and B occupies all the octahedral voids. If all the particles along the plane as shown in figure are removed, then, the formula of the crystal would be :



- (A) AB (B)  $A_5B_7$  (C)  $A_7B_5$  (D) None of these
3. In a solid,  $S^{2-}$  ions are packed in fcc lattice.  $Zn^{2+}$  occupies half of the tetrahedral voids in an alternating arrangement. Now if a plane is cut (as shown) then the cross-section would be:



4. The density of  $CaF_2$  (fluorite structure) is  $3.18 \text{ g/cm}^3$ . The length of the side of the unit cell is  
(A) 253 pm (B) 344 pm (C) 546 pm (D) 273 pm
5. Correct statement(s) for the packing of identical disc in two dimensions is/are:  
(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.
6. Choose the correct option/options-

- (A) Two adjacent face centre atoms present on a horizontal plane doesn't touch each other in fcc unit cell
- (B) If the radius of cations and anions are  $0.2 \text{ \AA}$  and  $0.95 \text{ \AA}$  then coordination number of cation in the crystal is 4.
- (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) NaCl is a 'AB' crystal lattice that can be interpreted to be made up of two individual fcc unit cells of  $A^+$  and  $B^-$  fused together in such a manner that the corner of one unit cell becomes the edge centre of the other.
7. Which of the following statement(s) is/are correct –
- (A) In a face centred cubic unit cell, the edge centre is an octahedral void.
- (B) In a face centred cubic unit cell, the body centre is an octahedral void.
- (C) In FCC unit cell, octahedral and tetrahedral voids are equal in number.
- (D) Coordination number of FCC unit cell is 12
8. Which of the following statements is/are correct?
- (A) In an anti-fluorite structure anions form FCC lattice and cations occupy all tetrahedral voids.
- (B) Number of nearest  $Na^+$  ions of another  $Na^+$  in  $Na_2O$  crystal will be 8.
- (C) Each sphere is surrounded by six voids in two dimensional hexagonal close packed layers
- (D) 8  $Cs^+$  ions occupy the second nearest neighbour locations of a  $Cs^+$  ion
9. Which of the following are true -
- (A) Ratio of nearest neighbours in simple cubic cell to next nearest neighbours in FCC is 1
- (B) Packing efficiency of a unit cell in which atoms are present at each corner and each edge centre is 26 % in metallic crystal.
- (C) Ratio of nearest neighbours in simple cubic cell to next nearest neighbours in BCC 1
- (D) If number of unit cell along one edge are 'x' then total number of unit cell in cube =  $x^3$
10. Which statements is correct about HCP and CCP lattice
- (A) Number of tetrahedral voids are twice of octahedral holes
- (B) 2 tetrahedral and 1 octahedral voids are present in HCP unit cell per atom.
- (C) Tetrahedral voids =  $2 \times$  octahedral voids, is valid for ccp and hcp.
- (D) Distance between two hexagonal planes in CCP or HCP arrangement is same for a metal exist in both forms.
11. Correct statement for ccp is:
- (A) Each octahedral void is surrounded by 6 spheres and each sphere is surrounded by 4 octahedral voids

- (B) Each octahedral void is surrounded by 6 spheres and each sphere is surrounded by 6 octahedral voids
- (C) Each octahedral void is surrounded by 6 spheres and each sphere is surrounded by 8 octahedral voids
- (D) Each octahedral void is surrounded by 6 spheres and each sphere is surrounded by 12 octahedral voids
12. Which of the following statements is correct in the rock-salt structure of 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.
13. Select write statement(s)
- (A) Density of crystal always increases due to substitutional impurity defect.
- (B) An atom/ion is transferred from a lattice site to an interstitial position in Frenkel defect.
- (C) In AgCl, the silver ion is displaced from its lattice position to an interstitial position. Such a defect is called a Frenkel defect
- (D) By defects in solids density of solids either remains constant or decreases but it can never increase.
14. Select the correct statement (s) :
- (A) CsCl mainly shows Schottky defect
- (B) ZnS mainly shows Frenkel defect
- (C) NaCl unit cell contain  $4\text{Na}^+$  and  $4\text{Cl}^-$
- (D) In NaCl one  $\text{Na}^+$  is surrounded by 6  $\text{Cl}^-$  then 12  $\text{Na}^+$  and then 8  $\text{Cl}^-$ .

**Comprehension: (Q. 15 & 16)**

Solid balls of radius 17.32 cm crystallises in bcc pattern, during one such crystallisation some oxygen gas is trapped. This trapped oxygen at 640K creates pressure of 5 atm.

**Assume:**

- (i) BCC arrangement is not disturbed due to trapping of gas.
- (ii) Gas is uniformly distributed inside unit cell

[Take  $R = 0.08 \text{ atm-litre/mole-K}$ ,  $N_A = 6 \times 10^{23}$ , Mass of a solid ball = 64 g]

15. Calculate number of oxygen molecules present in a unit cell
- (A)  $24 \times 10^{23}$       (B)  $12 \times 10^{23}$       (C)  $6 \times 10^{23}$       (D)  $3 \times 10^{23}$
16. Calculate percentage increase in density due to trapping of gas
- (A) 16.67 %      (B) 33.33 %      (C) 100%      (D) 50%

**Comprehension: (Q. 17 to 19)**

Calcium crystallizes in a cubic unit cell with density 3.2 g/cc. Edge-length of the unit cell is 437 pm

17. The type of unit cell is:  
(A) Simple cubic      (B) BCC      (C) FCC      (D) Edge-centred
18. The nearest neighbour distance is:  
(A) 154.5 pm      (B) 309 pm      (C) 218.5 pm      (D) 260 pm
19. The number of nearest neighbours of a Ca atom are:  
(A) 4      (B) 6      (C) 8      (D) 12
20. If the metal is melted, density of the molten metal was found to be 3 g/cc. What will be the percentage of empty space in the liquid metal?  
(A) 31%      (B) 36%      (C) 28%      (D) 49%

**Comprehension: (Q. 21 & 22)**

There is large variety of non-stoichiometric inorganic solids which contain an excess or deficiency of one of the elements. Such solids showing deviations from the ideal stoichiometric composition form an important group of solids. For example in the vanadium oxide,  $\text{VO}_x$ ,  $x$  can be anywhere between 0.6 and 1.3. There are solids which are difficult to prepare in the stoichiometric composition. Thus, the ideal composition in compounds such as FeO is difficult to obtain (normally we get a composition of  $\text{Fe}_{0.95}\text{O}$  but it may range from  $\text{Fe}_{0.93}\text{O}$  to  $\text{Fe}_{0.96}\text{O}$ ). Non-stoichiometric behaviour is most commonly found for transition metal compounds though are also known for some lanthanides and actinides.

Zinc oxide loses oxygen reversibly at high temperatures and turns yellow in colour. The excess metal is accommodated interstitially, giving rise to electrons trapped in the neighborhoods. The enhanced electrical conductivity of the non-stoichiometric ZnO arises from these electrons.

Anion vacancies in alkali halides are produced by heating the alkali halide crystals in an atmosphere of the alkali metal vapour. When the metal atoms deposit on the surface they diffuse into the crystal and after ionisation the alkali metal ion occupies cationic vacancy whereas electron occupies anionic vacancy. Electrons trapped in anion vacancies are referred to as F-centers (from Farbe the German word for colour) that gives rise to interesting colour in alkali halides. Thus, the excess of potassium in KCl makes the crystal appear violet and the excess of lithium ions LiCl makes it pink.

21. When LiCl is heated into the vapour of lithium, the crystal acquires pink colour. This is due to  
(A) Schottky defects      (B) Frenkel defects  
(C) Metal excess defect leading to F-centers      (D) Electronic defect

22. AgCl is crystallized from molten AgCl containing a little CdCl<sub>2</sub>. The solid obtained will have
- (A) cationic vacancies equal to number of Cd<sup>2+</sup> ions incorporated
  - (B) cationic vacancies equal to double the number of Cd<sup>2+</sup> ions
  - (C) anionic vacancies
  - (D) neither cationic nor anionic vacancies

**MATCH THE COLUMN**

23. Match the column

**Column I**

- (A) Tetragonal and Hexagonal
- (B) Cubic and Rhombohedral
- (C) Monoclinic and Triclinic
- (D) Cubic and Hexagonal

**Column II**

- (P) are two crystal systems
- (Q)  $a = b \neq c$
- (R)  $a \neq b \neq c$
- (S)  $a = b = c$

24. Match the column:

**Column I**

- (A) Rock salt structure
- (B) Zinc Blend structure
- (C) Fluorite structure

**Column II**

- (P) Co-ordination number of cation is 4
- (Q)  $\frac{\sqrt{3}a}{4} = r_+ + r_-$
- (R) Co-ordination number of cation and anion are same
- (S) Distance between two nearest anion is  $\frac{a}{\sqrt{2}}$

**MATCHING LIST TYPE**

25. Match the column

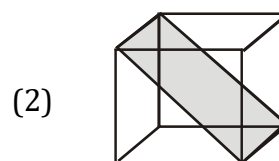
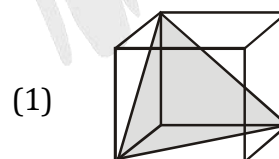
**Column I**

(Arrangement of the atoms/ions)

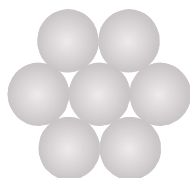


**Column II**

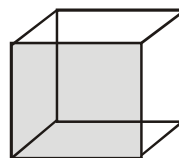
(Planes in fcc lattice)



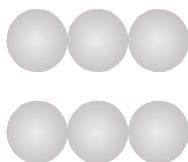
(R)



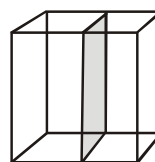
(3)



(S)



(4)



Code:

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

26. Column I

Column II

[Distance in terms of edge length of cube (a)]

(P) 0.866 a

(1) Shortest distance between cation & anion in CsCl structure.

(Q) 0.707 a

(2) Shortest distance between two cation in  $\text{CaF}_2$  structure.

(R) 0.433 a

(3) Shortest distance between carbon atoms in diamond.

(S) 1.414 a

(4) the distance at which second nearest neighbour is present in simple cubic unit cell

Code :

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



## EXERCISE (JEE-MAIN)

1. In a solid AB. A atoms are in ccp arrangement and B atoms occupy all the octahedral sites. If two atoms from the opposite faces are removed, then the resultant stoichiometry of the compound is  $A_xB_y$ . The value of x is \_\_\_\_\_. [nearest integer] **[JEE Main, June 2022]**
2. Metal deficiency defect is shown by  $Fe_{0.93}O$ . In the crystal, some  $Fe^{2+}$  cations are missing and loss of positive charge is compensated by the presence of  $Fe^{3+}$  ions. The percentage of  $Fe^{2+}$  ions in the  $Fe_{0.93}O$  crystals is \_\_\_\_\_. (Nearest integer) **[JEE Main, June 2022]**
3. Select the correct statements. **[JEE Main, July 2021]**
- (A) Crystalline solids have long range order.  
(B) Crystalline solids are isotropic.  
(C) Amorphous solid are sometimes called pseudo solids.  
(D) Amorphous solids soften over a range of temperatures.  
(E) Amorphous solids have a definite heat of fusion.
- Choose the most appropriate answer from the options given below.
- (A) (A), (B), (E) only (B) (B), (D) only  
(C) (C), (D) only (D) (A), (C), (D) only
4. The parameters of the unit cell of a substance are **[JEE Main, July 2021]**  
 $a = 2.5, b = 3.0, c = 4.0, \alpha = 90^\circ, \beta = 120^\circ, \gamma = 90^\circ$ .  
The crystal system of the substance is :  
(A) Hexagonal (B) Orthorhombic  
(C) Monoclinic (D) Triclinic
5. In a binary compound, atoms of element A form a hcp structure and those of element M occupy  $2/3$  of the tetrahedral voids of the hcp structure. The formula of the binary compound is: **[JEE Main, March 2021]**  
(A)  $M_2A_3$  (B)  $M_4A_3$  (C)  $M_4A$  (D)  $MA_3$
6. Given below are two statements.  
Statement I: Frenkel defects are vacancy as well as interstitial defects. **[JEE Main, Aug. 2021]**  
Statement II: Frenkel defect leads to colour in ionic solids due to presence of F-centres.  
Choose the most appropriate answer for the statements from the options given below:  
(A) Statement I is false but Statement II is true  
(B) Both Statement I and Statement II are true  
(C) Statement I is true but Statement II is false  
(D) Both Statement I and Statement II are false

7. A hard substance melts at high temperature and is an insulator in both solid and in molten state.

This solid is most likely to be a / an :

[JEE Main, Mar. 2021]

- (A) Ionic solid (B) Molecular solid  
(C) Metallic solid (D) Covalent solid

8. Match items of List-I with those of List-II :

[JEE Main, Aug. 2021]

List-I (Property)	List-II (Example)
(a) Diamagnetism	(i) MnO
(b) Ferrimagnetism	(ii) O <sub>2</sub>
(c) Paramagnetism	(iii) NaCl
(d) Antiferromagnetism	(iv) Fe <sub>3</sub> O <sub>4</sub>

Choose the most appropriate answer from the options given below:

- (A) (a)–(ii), (b)–(i), (c)–(iii), (d)–(iv)  
(B) (a)–(i), (b)–(iii), (c)–(iv), (d)–(ii)  
(C) (a)–(iii), (b)–(iv), (c)–(ii), (d)–(i)  
(D) (a)–(iv), (b)–(ii), (c)–(i), (d)–(iii)

9. A diatomic molecule X<sub>2</sub> has a body-centred cubic (bcc) structure with a cell edge of 300 pm. The density of the molecule is 6.17 g cm<sup>-3</sup>. The number of molecules present in 200 g of X<sub>2</sub> is: (Avogadro constant (N<sub>A</sub>) = 6 × 10<sup>23</sup> mol<sup>-1</sup>) [Jee Main, 2020]

- (A) 8 N<sub>A</sub> (B) 2 N<sub>A</sub> (C) 4 N<sub>A</sub> (D) 40 N<sub>A</sub>

10. An element with molar mass 2.7 × 10<sup>-2</sup> kg mol<sup>-1</sup> forms a cubic unit cell with edge length 405 pm. If its density is 2.7 × 10<sup>3</sup> kg m<sup>-3</sup>, the radius of the element is approximately \_\_\_ × 10<sup>-12</sup> m (to the nearest integer). [Jee Main, 2020]

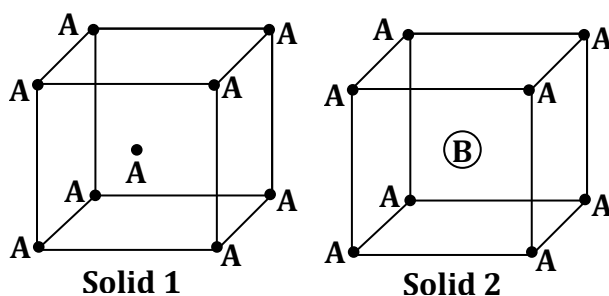
11. An element crystallizes in a face-centred cubic (fcc) unit cell with cell edge a. The distance between the centres of two nearest octahedral voids in the crystal lattice is: [Jee Main, 2020]

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

12. The radius of the largest sphere which fits properly at the centre of the edge of body centred cubic unit cell is : (Edge length is represented by 'a') : [Jee Main, Jan 2019]

- (A) 0.047 a (B) 0.027 a (C) 0.067 a (D) 0.134 a

13. Consider the bcc unit cells of the solids 1 and 2 with the position of atoms as shown below. The radius of atom B is twice that of atom A. The unit cell edge length is 50% more in solid 2 than in solid 1. What is the approximate packing efficiency in solid 2 ? [Jee Main, April 2019]



- (A) 90%                      (B) 45%                      (C) 75%                      (D) 65%
14. Element 'B' forms ccp structure and 'A' occupies half of the octahedral voids, while oxygen atoms occupy all the tetrahedral voids. The structure of bimetallic oxide is : **[Jee Main, April 2019]**  
 (A)  $AB_2O_4$                       (B)  $A_4B_2O$                       (C)  $A_4BO_4$                       (D)  $A_2B_2O$
15. An element has a face-centred cubic (fcc) structure with a cell edge of  $a$ . The distance between the centres of two nearest tetrahedral voids in the lattice is: **[Jee Main, April 2019]**  
 (A)  $\sqrt{2}a$                       (B)  $a$                       (C)  $\frac{a}{2}$                       (D)  $\frac{3}{2}a$
16. Which type of 'defect' has the presence of cations in the interstitial sites? **[Jee Main, 2018]**  
 (A) Metal deficiency defect                      (B) Schottky defect  
 (C) Vacancy defect                      (D) Frenkel defect
17. All of the following share the same crystal structure except :- **[Jee Main, 2018]**  
 (A) RbCl                      (B) CsCl                      (C) LiCl                      (D) NaCl
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]**  
 (A)  $\sqrt{2}a$                       (B)  $\frac{a}{\sqrt{2}}$                       (C)  $2a$                       (D)  $2\sqrt{2}a$
19. Which of the following compounds is metallic and ferromagnetic? **[Jee-Main (offline)-16]**  
 (A)  $CrO_2$                       (B)  $VO_2$                       (C)  $MnO_2$                       (D)  $TiO_2$
20. Sodium metal crystallizes in a body centred cubic lattice with a unit cell edge of  $4.29\text{\AA}$ . The radius of sodium atom is approximately: **[Jee-Main (offline)-15]**  
 (A)  $5.72\text{\AA}$                       (B)  $0.93\text{\AA}$                       (C)  $1.86\text{\AA}$                       (D)  $3.022\text{\AA}$
21. 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]**  
 (A)  $r_{Cs^+} + r_{Cl^-} = \frac{\sqrt{3}}{2}a$                       (B)  $r_{Cs^+} + r_{Cl^-} = \sqrt{3}a$   
 (C)  $r_{Cs^+} + r_{Cl^-} = 3a$                       (D)  $r_{Cs^+} + r_{Cl^-} = \frac{3a}{2}$

22. In a face centered cubic lattice atoms A are at the corner points and atoms B at the face centered points. If atom B is missing from one of the face centered points, the formula of the ionic compound is: [AIEEE-2011, Jee-Main (online)-14]  
(A)  $AB_2$  (B)  $A_2B_3$  (C)  $A_5B_2$  (D)  $A_2B_5$
23. The appearance of colour in solid alkali metal halides is generally due to:  
(A) Frenkel defect (B) F-centres (C) Schottky defect (D) Interstitial position
24. In a monoclinic unit cell, the relation of sides and angles are respectively [Jee-Main (online)-14]  
(A)  $a \neq b \neq c$  and  $\alpha \neq \beta \neq \gamma \neq 90^\circ$   
(B)  $a \neq b \neq c$  and  $\beta = \gamma = 90^\circ \neq \alpha$   
(C)  $a = b \neq c$  and  $\alpha = \beta = \gamma = 90^\circ$   
(D)  $a \neq b \neq c$  and  $\alpha = \beta = \gamma = 90^\circ$
25. The total number of octahedral void(s) per atom present in a cubic close packed structure is :- [Jee-Main (online)-14]  
(A) 1 (B) 2 (C) 3 (D) 4
26. 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]  
(A) 7.01% (B) 4.08% (C) 6.05% (D) 5.08
27. 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]  
(A) 0.96 nm (B) 0.4 nm (C) 0.24 nm (D) 0.56 nm
28. Which one of the following statements about packing in solids is **incorrect**? [Jee-Main (online)-13]  
(A) Void space in ccp mode of packing is 26%  
(B) Coordination number in hcp mode of packing is 12  
(C) Void space in hcp mode of packing is 32%  
(D) Coordination number in bcc mode of packing is 8
29. 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]  
(A)  $AB_2$  (B)  $AB_3$  (C)  $AB_4$  (D)  $A_2B_5$
30. Copper crystallises in fcc with a unit length of 361pm. What is the radius of copper atom? [AIEEE-2011, Jee-Main (online)-13]  
(A) 181pm (B) 128pm (C) 157pm (D) 108pm

## (PHYSICAL CHEMISTRY)

## SOLID STATE

31. 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: [AIEEE-12]  
(A) 152 pm (B) 75 pm (C) 300 pm (D) 240 pm
32. Among the following the incorrect statement is: [Jee-Main (online)-12]  
(A) Density of crystals remains unaffected due to Frenkel defect  
(B) In BCC unit cell the void space is 32%  
(C) Electrical conductivity of semiconductors and metals increases with increase in temperature  
(D) Density of crystals decreases due to Schottky defect
33. 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]  
(A) 314.20 pm (B) 216 pm (C) 200 pm (D) 1.41 pm
34. Ammonium chloride crystallizes in a body centred cubic lattice with edge length of unit cell of 390 pm. If the size of chloride ion is 180 pm, the size of ammonium ion would be: [Jee-Main (online)-12]  
(A) 158 pm (B) 174 pm (C) 142 pm (D) 126 pm
35. 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]  
(A) Octahedral (B) Tetrahedral (C) Pyramidal (D) Trigonal
36. Percentages of free space in cubic close packed structure and in body centered packed structure are respectively [AIEEE-10]  
(A) 48% and 26% (B) 30% and 26% (C) 26% and 32% (D) 32% and 48%
37. The edge length of a face centered 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
38. In a compound, atoms of element Y form ccp lattice and those of element X occupy  $\frac{2}{3}$ 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)  $X_3Y_4$
39. 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)  $\frac{20}{3}\pi r^3$
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

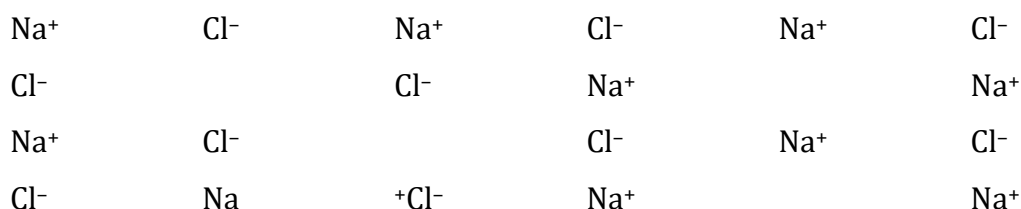
41. An ionic compound has a unit cell consisting of A ions at the corners of a cube and B ions on the centres of the faces of the cube. The empirical formula of this compound would be—

[AIEEE-05]

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

42. What type of crystal defect is indicated in the diagram below?

[AIEEE-04]



- (A) Frenkel defect (B) Schottky defect  
(C) Interstitial defect (D) Frenkel and Schottky defects

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

- (A)  $1.28 \times 10^{21}$  unit cells (B)  $1.71 \times 10^{21}$  unit cells  
(C)  $2.57 \times 10^{21}$  unit cells (D)  $5.14 \times 10^{21}$  unit cells

[AIEEE-03]

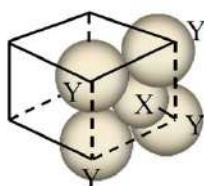
44. The no. of atoms per unit cell in B.C.C. & F.C.C. is respectively:

[AIEEE-02]

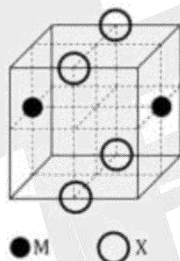
- (A) 8, 10 (B) 2, 4 (C) 1, 2 (D) 1, 3

## EXERCISE (JEE-ADVANCED)

1. Atom X occupies the fcc lattice sites as well as alternate tetrahedral voids of the same lattice. The packing efficiency (in %) of the resultant solid is closest to  
(A) 25 (B) 35 (C) 55 (D) 75 [JEE Adv. 2022]
2. For the given close packed structure of a salt made of cation X and anion Y shown below (ions of only one face are shown for clarity), the packing fraction is approximately  
(packing fraction  $\frac{\text{Packing efficiency}}{100}$ ) [JEE-2021]



- (A) 0.74 (B) 0.63 (C) 0.52 (D) 0.48
3. The cubic unit cell structure of a compound containing cation M and anion X is shown below.



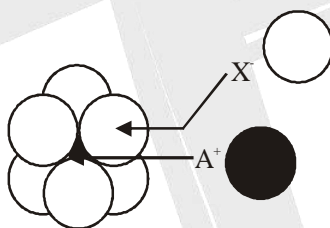
When compared to the anion, the cation has smaller ionic radius. Choose the correct statement(s). [JEE-2020]

- (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.
4. 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]
- Remove all the anions (X) except the central one
  - Replace all the face centered cations (M) by anions (X)
  - Remove all the corner cations (M)
  - Replace the central anion (X) with cation (M)

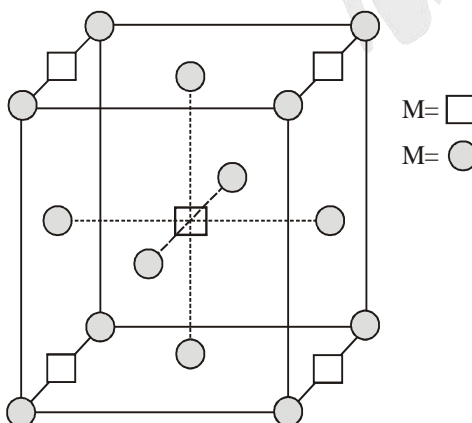
The value of  $\left( \frac{\text{number of anions}}{\text{number of cations}} \right)$  in Z is \_\_\_\_.



5. 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  $8 \text{ g cm}^{-3}$ , then the number of atoms present in 256 g of the crystal is  $N \times 10^{24}$ . The value of  $N$  is [JEE-2017]
6. The CORRECT statement(s) for cubic close packed (ccp) three dimensional structure is (are) [JEE-2016]
- (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%  
 (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. If the unit cell of a mineral has cubic close packed (ccp) array of oxygen atoms with  $m$  fraction of octahedral holes occupied by aluminum 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)  $\frac{1}{4}, \frac{1}{8}$
8. 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]



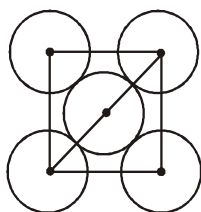
- (A) 104 pm (B) 125 pm (C) 183 pm (D) 57 pm
9. A compound  $M_pX_q$  has cubic close packing (ccp) arrangement of X. Its unit cell structure is shown below. The empirical formula of the compound is: [JEE-2012]



- (A)  $MX$  (B)  $MX_2$  (C)  $M_2X$  (D)  $M_5X_{14}$
10. The number of hexagonal faces that present in a truncated octahedron is. [JEE-2011]

11. Silver (atomic weight =  $108 \text{ g mol}^{-1}$ ) has a density of  $10.5 \text{ g cm}^{-3}$ . The number of silver atoms on a surface of area  $10^{-12} \text{ m}^2$  can be expressed in scientific notation as  $y \times 10^x$ . The value of  $x$  is [JEE 2010]

12. The packing efficiency of the two-dimensional square unit cell shown below is [JEE-2010]



- (A) 39.27%      (B) 68.02%      (C) 74.05%      (D) 78.54%
13. 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.

#### Paragraph for Question No. 14 to 16

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 ' $r$ '.

14. The number of atoms in this HCP unit cells is [JEE 2008]  
 (A) 4      (B) 6      (C) 12      (D) 17
15. 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)  $\frac{64}{3\sqrt{3}} r^3$
16. The empty space in this HCP unit cell is [JEE 2008]  
 (A) 74%      (B) 47.6 %      (C) 32%      (D) 26%
17. 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  $4 \times 4$  matrix given in the ORS. [JEE 2007]

## 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  $90^\circ$

(D) hexagonal and monoclinic

(S) belong to same crystal system.

18. 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]**

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

20. Which of the following FCC structure contains cations in alternate tetrahedral voids? **[JEE 2005]**

(A) NaCl

(B) ZnS

(C)  $\text{Na}_2\text{O}$

(D)  $\text{CaF}_2$

21. (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  $\text{kg m}^{-3}$ . **[JEE-2004]**

(ii) If measured density is  $20 \text{ kg m}^{-3}$ . Identify the type of point defect.

22. 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]**

23. A substance  $\text{A}_x\text{B}_y$  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  $\text{A}_x\text{B}_y$ . **[JEE-2002]**

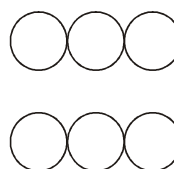
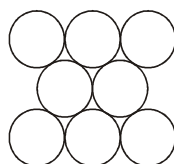
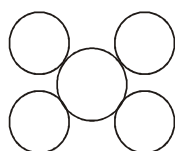
(A)  $\text{AB}_3$

(B)  $\text{A}_4\text{B}_3$

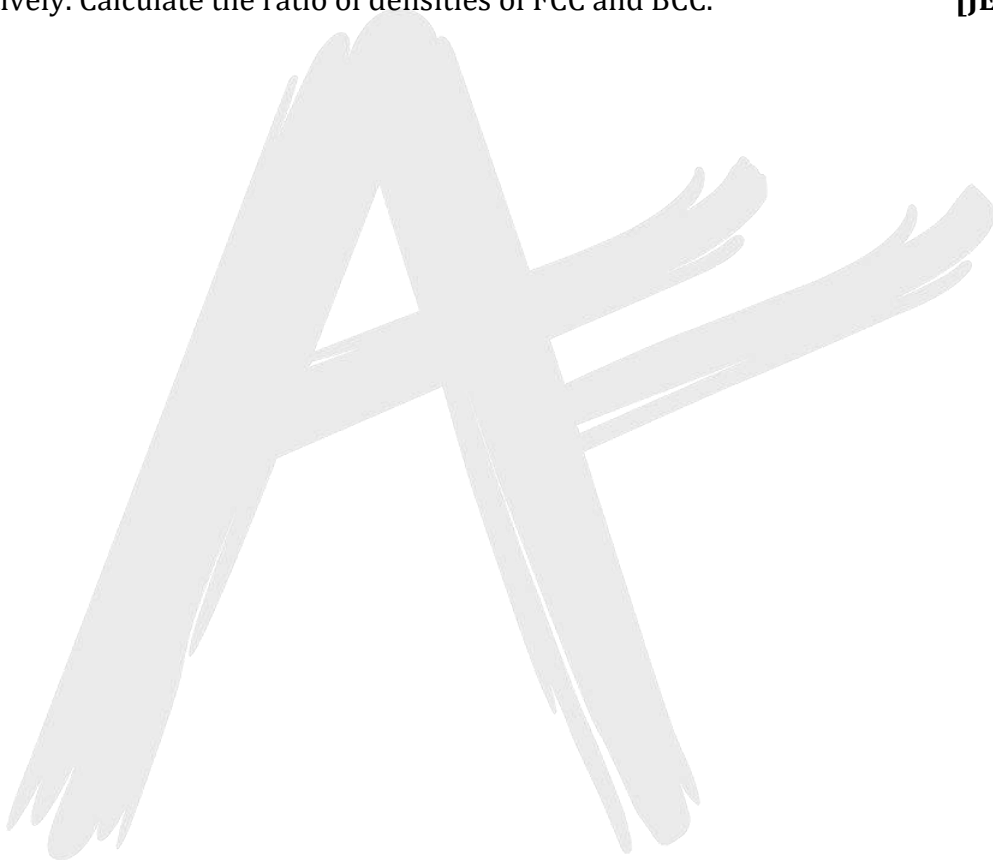
(C)  $\text{A}_3\text{B}$

(D) composition cannot be specified

24. 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]**



25. 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 [JEE-2000]  
(A)  $AB_2$  (B)  $A_2B$  (C)  $A_4B_3$  (D)  $A_3B_4$
26. In any ionic solid [MX] with schottky defects, the number of positive and negative ions are same. [T/F] [JEE-2000]
27. The coordination number of a metal crystallising in a hcp structure is [JEE-2000]  
(A) 12 (B) 4 (C) 8 (D) 6
28. A metal crystallises 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]



ANSWER KEY

EXERCISE (O-I)

1. (B) 2. (C) 3. (B) 4. (B) 5. (A) 6. (D) 7. (B)
8. (A) 9. (D) 10. (C) 11. (D) 12. (B) 13. (C) 14. (C)
15. (B) 16. (D) 17. (A) 18. (B) 19. (C) 20. (B) 21. (C)
22. (C) 23. (A) 24. (A) 25. (C) 26. (B) 27. (C) 28. (C)
29. (C) 30. (B) 31. (C) 32. (B) 33. (A) 34. (C) 35. (B)
36. (A) 37. (A) 38. (B) 39. (C) 40. (D) 41. (B) 42. (A)
43. (B) 44. (C) 45. (A) 46. (B) 47. (A) 48. (D) 49. (C)
50. (D) 51. (D) 52. (B) 53. (D) 54. (B) 55. (A) 56. (C)
57. (A & D)

EXERCISE (S-I)

1. Ionic – LiBr,  $(\text{NH}_4)_3\text{PO}_4$ ; Metallic – Brass, Rb; Molecular –  $\text{P}_4\text{O}_{10}$ ,  $\text{I}_2$ ,  $\text{P}_4$   
Network – SiC, Graphite, Si, Amorphous – Plastic
2. 14
- 3.

Crystal System	Features	Unit cell found	Examples
Monoclinic	$a \neq b \neq c$ $\alpha = \gamma = 90^\circ$ $\beta \neq 120^\circ, \neq 90^\circ, \neq 60^\circ$	S, EC	Monoclinic sulphur, $\text{PbCrO}_4$ $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
Hexagonal	$a = b \neq c$ $\alpha = \beta = 90^\circ, \gamma = 120^\circ$	S	Graphite, ZnO, CdS, Mg, $\text{PbI}_2$ , SiC
Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$	S	$\text{K}_2\text{Cr}_2\text{O}_7$ , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , $\text{H}_3\text{BO}_3$ .

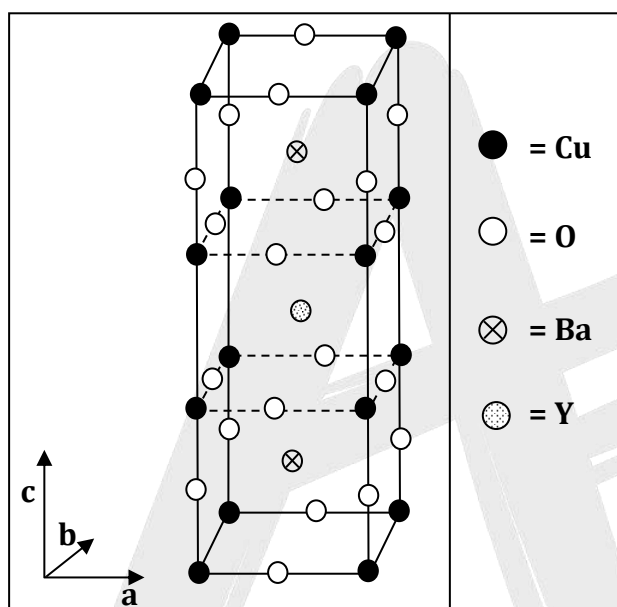
4. Ques. (a) (b) Total particles
  - (i)  $1/4$  1 2
  - (ii)  $1/2$   $1/4$  2
  - (iii)  $1/6$   $1/2$  2
  - (iv)  $1/6$  –  $1/2$
  - (v)  $1/3$   $1/6$  1
5. 4 6. 86.6%
7. (a) 267 pm, (b) 231.2 pm, (c) 188.8 pm

- |     |                           |     |  |     |  |
|-----|---------------------------|-----|--|-----|--|
| 8.  | 438.5 pm, 219.25 pm       | 9.  | (i) $2r$ , $2r$ , $2\sqrt{3}r$ , (ii) Square                                       |     |  |
| 10. | $5.74 \text{ g cm}^{-3}$  | 11. | $19.4 \text{ g/cm}^3$ , 143.9 pm   |     |  |
| 12. | $41.67 \text{ g cm}^{-3}$ | 13. | 1.09   | 14. | $7.922 \text{ g/cc}$ , $8.625 \text{ g/c}$ |
| 15. | (6)                       | 16. | 4, 6, 8  | 17. | $4, 8, \frac{a}{\sqrt{2}}, \frac{a}{2}$    |
| 19. | A, B                      | 20. | $A_2BC$  | 21. | $ZnAl_2O_4$                                |
| 23. | 4                         | 24. | $a = 5.94 \times 10^{-8} \text{ cm}$ , $V = 2.096 \times 10^{-22} \text{ cm}^{-3}$ | 22. | 267 pm, 534 pm, 378 pm                     |
| 26. | $= 346.4 \text{ pm}$      | 27. | $1.81 \text{ \AA}$   | 25. | 30%  |
| 29. | 15.05                     | 30. | $6.02 \times 10^{18}$  | 28. | $4.34 \text{ \AA}$                         |
|     |                           |     |  | 31. | 12.5                                       |



EXERCISE (S-II)

1. 8
2.  $3.5 \text{ g cm}^{-3}$
3.  $3.48 \times 10^{24} \text{ atoms}$
4. 60%, +4
5. 103.4 pm, No
6. 0.7285
7. 2
8. 14.53 R
9. 2.07
10. 0.605
11. (a)  $\text{MnF}_3$ , (b) 6, (c)  $4.02 \text{ \AA}$
12. (a)  $4.5 \text{ \AA}$ , (b)  $5.2 \text{ \AA}$ , (c) 8, (d) 6, (e)  $0.92 \text{ g/cm}^3$
13. 0.24
14. (a) 1.143, (b) 1.172
15. Not Available
16. 4 molecules of  $\text{H}_2\text{O}$
17.  $\text{Mg}_2\text{SiO}_4$ ,  $\text{Fe}_2\text{SiO}_4$ , 66.32%
18. (a)



- (b) density =  $5.90 \text{ g cm}^{-3}$

EXERCISE (O-II)

1. (B)
2. (A)
3. (D)
4. (C)
5. (ABD)
6. (ACD)
7. (ABD)
8. (AC)
9. (ABCD)
10. (ABCD)
11. (B)
12. (D)
13. (BC)
14. (ABCD)

Comprehension: (Q. 15 & 16)

15. (B)
16. (D)

Comprehension: (Q. 17 to 20)

17. (C)
18. (B)
19. (D)
20. (A)

Comprehension: (Q. 20 & 21)

21. (C)
22. (A)
23.  $A \rightarrow P, Q$ ;  $B \rightarrow P, S$ ;  $C \rightarrow P, R$ ;  $D \rightarrow P$
24. (A) Rock salt structure :
25. (A)
26. (B)

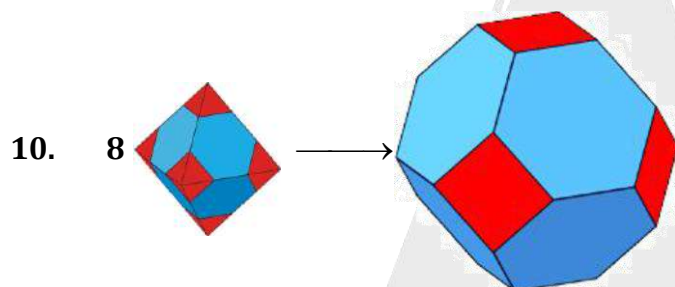


EXERCISE (JEE-MAIN)

1. (3) 2. (85) 3. (D) 4. (C) 5. (B) 6. (C) 7. (D)
8. (C) 9. (C) 10. (143) 11. (A) 12. (C) 13. (A) 14. (A)
15. (C) 16. (D) 17. (B) 18. (B) 19. (A) 20. (C) 21. (A)
22. (D) 23. (B) 24. (B) 25. (A) 26. (B) 27. (B) 28. (C)
29. (C) 30. (B) 31. (A) 32. (C) 33. (C) 34. (A) 35. (A)
36. (C) 37. (A) 38. (A) 39. (C) 40. (C) 41. (D) 42. (B)
43. (C) 44. (B)

EXERCISE (JEE-ADVANCED)

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



11. (7) 12. (D) 13. (BC)

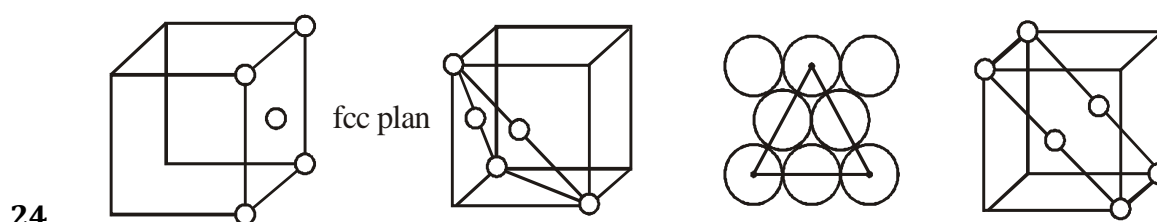
Paragraph for Question No. 14 to 16

14. (B) 15. (A) 16. (D)
17.  $A \rightarrow P, S$ ;  $B \rightarrow P, Q$ ;  $C \rightarrow Q$ ;  $D \rightarrow Q, R$
18. 216.5 pm 19. 117.1 pm 20. (B)
21. (i)  $= 5 \text{ kg m}^{-3}$

(ii) There is huge difference in theoretically calculated density and observed density. It is only possible if some foreign species occupies interstitial space i.e. substitution defect.

22. 18

23. (A)



25. (D) 26. True 27. (A) 28. 1.259

SOLUTION  
EXERCISE (O-I)

1. Covalent network solids are  $\rightarrow$  [SiO<sub>2</sub>, Diamond, Si, AlN & SiC]
2. (C)
7. Factual
8. Factual
9. For triclinic system  
 $a \neq b \neq c$  &  $\alpha \neq \beta \neq \gamma = 90^\circ$ ,  
Hence most unsymmetrical.
10. In match box  
 $a \neq b \neq c$  &  $\alpha = \beta = \gamma = 90^\circ$ ,  
Hence orthorhombic geometry
11. For hexagonal crystal system  
 $a = b \neq c$  &  $\alpha = \beta = 90^\circ$  &  $\gamma = 120^\circ$
14. The distance between 2 nearest neighbor in B.C.C. is  $\frac{\sqrt{3}a}{2}$   
i.e.  $\frac{\sqrt{3} \times 5.2}{2}$   
i.e.  $4.5 \text{ \AA}$
15. In BCC  
 $\sqrt{3}a = 4r$   
Fraction of edge occupied by atoms =  $\frac{2r}{a}$   
 $= \frac{2r}{\frac{4r}{\sqrt{3}}} = \frac{\sqrt{3}}{2}$
16. For B.C.C.  
 $r = \frac{\sqrt{3}a}{4} = \frac{\sqrt{3} \times 286}{4}$  i.e.  $r = 124 \text{ pm}$
20. Factual
22. The shortest distance between 1<sup>st</sup> & V<sup>th</sup> layer of HCP arrangement is  $2C$   
i.e.  $2 \times \left( \sqrt{\frac{2}{3}} \times 4r \right)$   
i.e.  $8\sqrt{\frac{2}{3}} r$

23. Volume of HCP unit CsCl = (Area of Base  $\times$  height)



$$\text{i.e. } \left( 6 \times \frac{\sqrt{3}}{4} \times a^2 \right) \times 2\sqrt{\frac{2}{3}} a$$

$$\text{i.e. } \frac{6\sqrt{3}}{4} \times (2r)^2 + 2\sqrt{\frac{2}{3}} \times (2r) \quad (\text{As } a = 2r)$$

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

24.  $\frac{\rho_{\text{fcc, Fe}}}{\rho_{\text{bcc, Fe}}} = \frac{\pi / 3\sqrt{2}}{\sqrt{3}\pi / 8}$

25. Volume occupied by atoms in an bcc unit cell is -

$$2 \times \frac{4}{3} \pi r^3 = \left[ \frac{2 \times \frac{M}{N_A}}{\rho} \right] \times \frac{\sqrt{3}\pi}{8}$$

26. It is formed by 4 spheres the centres of which form a regular tetrahedron

27. For tetrahedral voids

$$r = 0.225 R$$

& for octahedral voids

$$r = 0.414 R$$

$\Rightarrow$  Size of an octahedral void formed in a closed packed lattice is larger as compared to tetrahedral void.

28. Number of atom X =  $7 \times \frac{1}{8}$

$$\text{Number of atom } y = 1$$

Formula of compound will be  $(X_7 Y_8)$

29. For -----ABCABC----- closed packing sequence, it forms, it forms C.C.P / F.C.C.

Number of tetrahedral voids is twice the number of atoms in the unit cell.

$$\text{Number of tetrahedral void} = 2 \times Z$$

$$\text{Number of octahedral void} = Z$$

30. Number of atom A = 6

$$\text{Number of atom } C = \frac{2}{3} \times 6 \quad \text{i.e. } 4$$

Formula of compounds is  $(A_3 C_2)$

31. For NaCl

$$2(r_{\text{Na}^+} + r_{\text{Cl}^-}) = a$$

$$\Rightarrow 2x + 2y = a$$

32. For F.C.C. of  $\text{M}^+\text{X}^-$   $2(r_{\text{M}^+} + r_{\text{X}^-}) = 7.2$

$$\Rightarrow 2 \times 1.6 + 2r_{\text{X}^-} = 7.2 \quad \Rightarrow r_{\text{X}^-} = 2\text{\AA}$$

33. 1 mole i.e. 58.5 g NaCl contains  $\frac{N_A}{4}$  unit cells

$$\Rightarrow 1 \text{ gm cubic crystal of NaCl contains } \left( \frac{N_A}{58.5 \times 4} \right) \text{ unit cells}$$

34. For compounds (XY) for which crystallizes in 8 : 8 lattice.

$$\Rightarrow r_{\text{X}^+} + r_{\text{Y}^-} = \frac{\sqrt{3}}{2} a$$

$$\Rightarrow r_{\text{X}^+} \left( \frac{\sqrt{3}}{2} \times 480 - 225 \right)$$

$$\Rightarrow r_{\text{X}^+} = 190.68 \text{ pm}$$

35. Number of  $\text{Cs}^+ \rightarrow 8 \times \frac{1}{8}$  i.e 1

Number of  $\text{Cl}^- \rightarrow 1$

36. Factual

37. For ZnS type structure  $\left( \frac{r_{\text{Zn}^{+2}}}{r_{\text{S}^{2-}}} \approx .402 \right)$  it is a 4 : 4 coordination number compound.

$$\Rightarrow \frac{r_{\text{A}^+}}{r_{\text{B}^-}} = 0.225$$

$$\Rightarrow \frac{22.5}{r_{\text{B}^-}} = 0.225$$

$$\Rightarrow r_{\text{B}^-} = 100 \text{ pm}$$

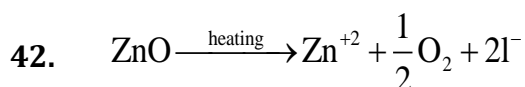
38. For  $\text{CaF}_2 \rightarrow$  Coordination number of cation & Anion is 8 : 4

& For  $\text{CsCl} \rightarrow$  coordination number of cation & Anion is 8 : 8

39. Schottky defect is shown by ionic substances in which the cation & Anion are of almost similar sizes.

40. Schottky defect is basically a vacancy defect in ionic solids. In order to maintain electrical neutrality, the number of missing cation & anions are equal.

41. Factual



So, strongly heated ZnO crystal can conduct electricity, this is due to movement of electrons in the anion vacancies.

EXERCISE (S-I)

1. Molecular solid  $\rightarrow \text{P}_4\text{O}_{10}, \text{I}_2, \text{P}_4$

Ionic solid  $\rightarrow (\text{NH}_4)_3\text{PO}_4, \text{LiBr}$

Metallic solid  $\rightarrow \text{Brass}, \text{Rb}$

Network/covalent solid  $\rightarrow \text{Graphite}, \text{SiC}, \text{Si}$

Amorphous solid  $\rightarrow \text{Plastic}$

2. There are 14 Bravais lattices possible in 3-D.

3.

Crystal system	Features	Unit cell found	Examples
Monoclinic	$a \neq b \neq c$ $\alpha = \gamma = 90^\circ$ $\beta \neq 120^\circ, \neq 90^\circ, \neq 60^\circ$	S, Ec	Monoclinic sulphur, $\text{PbCrO}_4$ , $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
Hexagonal	$a = b \neq c$ $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	S	Graphite, ZnO, cds, Mg, $\text{PbI}_2$ , sic
Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$	S	$\text{K}_2\text{Cr}_2\text{O}_7$ , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , $\text{H}_3\text{BO}_3$ .

4.

Ques. No.	Contributions of particles marked to the shaded region (a)	Contributions of particles marked to the shaded region (b)	Total no. of Particles
(i)	$\frac{1}{4}$	1	$(\frac{1}{4} \times 4 + 1)$ i.e. 2
(ii)	$\frac{1}{2}$	$\frac{1}{4}$	$(\frac{1}{2} \times 2 + \frac{1}{4} \times 4)$ i.e. 2
(iii)	$\frac{1}{6}$	$\frac{1}{2}$	$(\frac{1}{6} \times 3 + \frac{1}{2} \times 3)$ i.e. 2
(iv)	$\frac{1}{6}$	—	$(\frac{1}{6} \times 3)$ i.e. $\frac{1}{2}$
(v)	$\frac{1}{3}$	$\frac{1}{6}$	$(\frac{1}{3} \times 2 + \frac{1}{6} \times 2)$ i.e. 1

5. IN B.C.C,  $r = \frac{\sqrt{3}a}{4}$

also, edge length of unit cell = a

radius of atom = r

∴ Edge length not covered by atom = a - 2r

or  $a - \frac{\sqrt{3}a}{2} = a \frac{[2 - \sqrt{3}]}{2}$

∴ Percentage fraction not covered =  $\frac{a \left[ \frac{2 - \sqrt{3}}{2} \right]}{a} \times 100$

i.e. 13.4 %

∴ Percentage fraction of Edge length covered is (100 - 13.4)

i.e. 86.6 %

6. Edge length (a) = 534 pm

(a) simple cubic lattice :  $a = 2r \Rightarrow r = \frac{a}{2} \quad r = \frac{534}{2}$

i.e.  $r = 267 \text{ pm}$

(b) BCC lattice :  $r = \frac{\sqrt{3}a}{4} \Rightarrow r = \frac{\sqrt{3} \times 534}{4}$

i.e.  $r = 231.2 \text{ pm}$

(c) FCC lattice :  $r = \frac{a}{2\sqrt{2}} \Rightarrow r = \frac{534}{2\sqrt{2}}$

i.e.  $r = 188.8 \text{ pm}$

7. Edge length (a) → 620 pm

(i) Nearest neighbour distance for F. C. C =  $\frac{a}{\sqrt{2}} = \frac{620}{\sqrt{2}}$

i.e.  $438.5 \text{ pm}$

(ii) For F. C. C, radius i.e.  $r = \frac{a}{2\sqrt{2}} = \frac{620}{2\sqrt{2}}$

i.e.  $r = 219.2 \text{ pm}$

8. For F.C.C,  $a = 2\sqrt{2}r$

(i) Distance between atoms 1 and 2 :  $= \left( \frac{a}{\sqrt{2}} \right) = \frac{2\sqrt{2}r}{\sqrt{2}}$  i. e.  $2r$

Distance between atoms 2 & 3:  $\sqrt{\left(\frac{a}{2}\right)^2 + \left(\frac{a}{2}\right)^2}$   
 $= \frac{a}{\sqrt{2}} = \frac{2\sqrt{2}r}{\sqrt{2}}$  i.e.  $2r$

Distance between 1 and 3:  $\sqrt{(2\sqrt{2}r)^2 + (2r)^2}$   
 $= \sqrt{12r^2}$   
 $= 2\sqrt{3}r$

(ii) Shape = square

Length of square =  $2r$ .

9. For F.C.C  $a = 2\sqrt{2}r$

$a = 2\sqrt{2} \times 142 \text{ Å}$

i.e.  $a = 2\sqrt{2} \times 1.42 \times 10^{-8} \text{ cm.}$

density =  $\frac{Z \times M}{a^3 \times N_A} = \frac{4 \times 56}{(2\sqrt{2} \times 1.42 \times 10^{-8})^3 \times 6.022 \times 10^{23}}$

i.e. density =  $5.74 \text{ g cm}^{-3}$

10. (i) density =  $\frac{Z \times M}{a^3 \times N_A}$   
 $= \frac{4 \times 197}{(407 \times 10^{-10})^3 \times 6.022 \times 10^{23}}$

density =  $19.4 \text{ g cm}^{-3}$

(ii) For F.C.C,  $a = 2\sqrt{2}r$

$r = \frac{a}{2\sqrt{2}} = \frac{407}{2\sqrt{2}}$

i.e.  $r = 143.9 \text{ pm}$

11. 200 gm of this element contains  $24 \times 10^{23}$  atom.

$\Rightarrow$  molar mass =  $\left( \frac{200}{24 \times 10^{23}} N_A \right) \text{ g}$

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



$$= \frac{4 \times 200 N_A}{(200 \times 10^{-10})^3 \times 24 \times 10^{23} N_A} = \text{density} = 41.67 \text{ g cm}^{-3}$$

12. For B.C.C,  $a = \frac{4}{\sqrt{3}} r$  &  $Z = 2$

For F.C.C,  $a = 2\sqrt{2}r$  &  $Z = 4$

$$= \frac{(\text{density}) \gamma}{(\text{density}) \alpha} = \frac{4 \times 56}{(2\sqrt{2}r)^3 \times N_A} \times \frac{\left(\frac{4r}{\sqrt{3}}\right)^3 \times N_A}{2 \times 56} = 1.09$$

13. For B.C.C,  $a = \frac{4r}{\sqrt{3}}$

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

$$= \frac{2 \times 56}{\left(\frac{4 \times 124 \times 10^{-10}}{\sqrt{3}}\right)^3 \times 6.022 \times 10^{23}} = 7.92 \text{ g cm}^{-3}.$$

For F.C.C,  $a = 2\sqrt{2}r$

$$\text{density} = \frac{Z \times M}{a^3 \times N_A} = \frac{4 \times 56}{(2\sqrt{2} \times 124 \times 10^{-10})^3 \times 6.022 \times 10^{23}} = 8.625 \text{ g cm}^{-3}.$$

14.  $\frac{r_{A^+}}{r_{B^-}} = \frac{88}{200} = 0.440$

So, by radius ratio rule is lies in the range i.e.  $\left(0.444 \leq \frac{r^+}{r^-} < 0.732\right)$

So, C. N. of  $A^{\oplus}$  is 6.

15. For MgS:  $\frac{r_{Mg^{+2}}}{r_{S^{-2}}} = \frac{0.65}{1.84} = 0.353$

So, by radius ratio rule, C. N = 4

for MgO:  $\frac{r_{Mg^{+2}}}{r_{O^{-2}}} = \frac{0.65}{1.40} = 0.464$

So, by radius ratio rule, C. N. = 6

for CsCl:  $\frac{r_{Cs^+}}{r_{Cl^-}} = \frac{1.69}{1.81} = 0.933$

So, by radius ratio rule, C. N. = 8

16. For F.C.C.

Number of octahedral voids = 4

Number of tetrahedral voids = 8

Distance between 2 octahedral voids =  $\sqrt{\left(\frac{a}{2}\right)^2 + \left(\frac{a}{2}\right)^2}$

i.e.  $\left(\frac{a}{\sqrt{2}}\right)$

Distance between 2 tetrahedral voids =  $a - \frac{a}{4} - \frac{a}{4} = \left(\frac{a}{2}\right)$

17. Number of oxide ions = 4

Number of A particles =  $\frac{1}{6} \times 8$  i.e.  $\frac{4}{3}$

Number of B particles =  $\frac{1}{3} \times 4$  i.e.  $\frac{4}{3}$

So formula is  $A_{\frac{4}{3}} B_{\frac{4}{3}} O_4$  or  $ABO_3$

$x + y + z = 5$

18. Number of atom A = 1

Number of atom B =  $8 \times \frac{1}{8}$  i.e. 1

Formula of compound is (AB)

19. Number of atom A = 4

Number of atom B =  $\frac{1}{4} \times 8$  i.e. 2

Number of atom C =  $\frac{1}{2} \times 4$  i.e. 2

So, formula of compound is (A<sub>2</sub>BC).

20. Number of O<sup>-2</sup> = 4

Number of Zn<sup>+2</sup> = 1

Number of Al<sup>+3</sup> = 2

So, formula of spinel is (ZnAl<sub>2</sub>O<sub>4</sub>)

21.  $r_{K^+} = 132$  pm

$r_{F^-} = 135$  pm

(i) Shortest K-F distance is (132 + 135)

i.e. 267 pm

$$\begin{aligned} \text{(ii) Edge length} &= 2(r_{k^+} + r_{f^-}) \\ &= 2 \times 267 \\ &= 534 \text{ pm} \end{aligned}$$

$$\text{(iii) Closest k-k distance} = \sqrt{(267)^2 + (267)^2} = 368 \text{ pm}$$

$$\begin{aligned} 22. \quad Z &= \frac{\rho \times a^3 \times N_A}{M} \\ &= \frac{2.75 \times (654 \times 10^{-10})^3 \times 6.023 \times 10^{23}}{119} = 4 \end{aligned}$$

$\Rightarrow$  Number of formula units of KBr present in single unit cell = 4

$$\text{Also, } r_+ = \frac{r_-}{2} = \frac{a}{3 \times 2}$$

$$\text{i.e. } r_+ = \frac{a}{6}$$

$$\begin{aligned} \text{Packing fraction} &= \frac{4 \times \frac{4}{3} \pi (r_+^3 + r_-^3)}{a^3} \times 100 \\ &= \frac{4 \times \frac{4}{3} \pi \left( \left( \frac{a}{6} \right)^3 + \left( \frac{a}{3} \right)^3 \right)}{a^3} \times 100 = 70 \% \end{aligned}$$

$\Rightarrow$  percentage of void space in AB is 30 %

$$\begin{aligned} 23. \quad \text{(i) Edge length i.e. } a &= 2(r_{\text{Pb}^{+2}} + r_{\text{S}^{2-}}) \\ &= 2(297) \\ &= 594 \text{ pm or } 5.94 \times 10^{-8} \text{ cm} \end{aligned}$$

$$\begin{aligned} \text{(ii) Volume of unit cell} &= a^3 \\ &= (5.94 \times 10^{-8})^3 \\ &= 2.096 \times 10^{-22} \text{ cm}^3 \end{aligned}$$

$$24. \quad r_+ + r_- = \frac{a}{2}, \quad \text{given } \frac{r_+}{r_-} = \frac{1}{2}$$

$$\Rightarrow \frac{r_+}{2} + r_- = \frac{a}{2}$$

$$\Rightarrow \frac{3r_-}{2} = \frac{a}{2} \quad r_- = \frac{a}{3}$$

25. Inter-ionic distance in CsCl is  $\frac{\sqrt{3}a}{2}$

$$= \frac{\sqrt{3}}{2} \times 400$$

$$= 346.4 \text{ pm c}$$

26. For CsCl:  $\sqrt{3}a = 2(r_{\text{Cs}^+} + r_{\text{Cl}^-})$

$$7 = 2 \times 1.69 + 2r_{\text{Cl}^-}$$

$$\Rightarrow r_{\text{Cl}^-} = \frac{3.62}{2}$$

i.e.  $r_{\text{Cl}^-} = 1.81 \text{ \AA}$

27. By radius ratio rule  $= \frac{r^+}{r^-} = 0.732$  for cubical void

$$\Rightarrow \frac{r_{\text{Rb}^+}}{r_{\text{I}^-}} = 0.732 \quad \Rightarrow \quad r_{\text{Rb}^+} = (0.732 \times 2.17) = 1.59 \text{ \AA}$$

Now,  $(r_{\text{Rb}^+} + r_{\text{I}^-}) = \frac{\sqrt{3}}{2} a$

$$\Rightarrow a = \frac{2 \times (1.59 + 2.17)}{\sqrt{3}} \quad \Rightarrow \quad a = 4.34 \text{ \AA}$$

28.  $\text{Fe}_{0.93} \text{O}_{1.0}$

Consider 1 mole of oxide

mole of Fe = 0.93 & mole of  $\text{O}^{2-} = 1$

Let mole of  $\text{Fe}^{+2}$  be x & mole of  $\text{Fe}^{+3}$  be  $(0.93 - x)$

by charge balancing,  $2x + 3(0.93 - x) = 2 \times 1 \quad x = 0.79$

mole of  $\text{Fe}^{+2} = 0.79$

mole of  $\text{Fe}^{+3} = 0.14 \quad \% \text{ of } \text{Fe}^{+3} = \frac{0.14}{0.93} \times 100 = 15.05 \%$

29. Number of  $\text{Se}^{+2}$  ions present = number of cationic vacancies

Number of cation vacancies per mole of NaCl  $= \frac{10^{-3}}{100} \times N_A$

i.e.  $6.022 \times 10^{18}$ .

30. Cation vacancies as a percentage of  $\text{Fe}^{+2}$  initially present in sample is  $\left(\frac{1}{8}\right) \times 100$

EXERCISE (S-II)

1.  $a = 2 \times (\text{diameter of ball})$   
 $\rightarrow$  Number of spherical balls of radii 2 cm that can be placed completely inside a cubical box of edge = 8 cm is 8.

2. Ans. =  $3.5 \text{ g/cm}^3$

$$\text{Density} = \frac{Z \times M}{a^3 \times N_A} = \frac{(4 \times 2) \times 12}{6.022 \times 10^{23} \times (3.569 \times 10^{-8})^3} = 3.5 \text{ g/cm}^3$$

3.  $Z = 8 \times \frac{1}{8} + 2 \quad z = 3$

$$\text{density i.e. } r = \frac{Z \times M}{a^3 \times N_A} \quad M = \frac{\rho \times a^3 \times N_A}{z}$$

$$\rightarrow M = \frac{7.2 \times 24 \times 10^{-24} \times 6.022 \times 10^{23}}{3} \rightarrow M = 34.56 \text{ gm}$$

As, 34.56 gm of element contains  $6 \times 10^{23}$  atoms

$\rightarrow$  200 gm of an element contains

i.e.  $3.48 \times 10^{24}$  atoms

4. Number of  $\text{O}^{2-} = 4$

Number of  $\text{Ti}^{+n} = 2$

$\rightarrow$  By charge balancing,  $2 \times n = 8$

$\Rightarrow n = 4$

$\Rightarrow$  Ti should be present in +4 O.S & the compound should be  $(\text{TiO}_2)$

$$\text{Also, \% be mass of Ti} = \frac{48}{80} \times 100 \quad \text{i.e.} = 60\%$$

5.  $\frac{r_+}{r_-} = 0.414$

$$\Rightarrow r_+ = 0.414 \times 250$$

$$r_+ = 103.5 \text{ pm}$$

Cation  $\text{C}^+$ , having a radius 180 pm cannot be slipped into the tetrahedral site of the crystal of  $\text{A}^+$   $\text{B}^-$ , without disturbing the crystal.

6.  $\text{P.F.} = \frac{1 \times \frac{4}{3} \pi r_+^3 + 1 \times \frac{4}{3} \pi r_-^3}{8(r_+ + r_-)^3} \times 3\sqrt{3}$

$$\frac{1 \times \frac{4}{3} \pi r_+^3 + 1 \times \frac{4}{3} \pi r_-^3}{8(r_+ + r_-)^3} \times 3\sqrt{3}$$

$$= \frac{\frac{4}{3} \pi (r_+ + r_-)^3}{8(r_+ + r_-)^3} \times 3\sqrt{3} = 0.7285$$

7.  $X \longrightarrow \frac{a}{2}$

$$y \longrightarrow \frac{a}{\sqrt{2}}$$

$$\frac{y\sqrt{2}}{X} = \frac{a \times \sqrt{2} \times 2}{\sqrt{2} \times a} = 2$$

8. Perimeter of plane is  $= (2c + 8R)$

$$= 2 \times \sqrt{\frac{2}{3}} \times 4R + 8R$$

$$= 6.53 R + 8R$$

$$= 14.53 R$$

9.  $\sqrt{\frac{2}{3}} \times 2r = 10\sqrt{4_3}$

$$r = 5 \text{ pm.}$$

$$\text{Radius of largest sphere which can be fitted in the void} = 5 \times 0.414 = 2.07 \text{ pm}$$

10. Packing fraction =  $\frac{\left(12 \times \frac{1}{6} + 2 \times \frac{1}{2}\right) \times \frac{4}{3} \pi r^3}{6 \times \frac{\sqrt{3}}{4} \times (2r)^2 \times 2r} = 0.605$

11. (a) Number of  $\text{Mn}^{+3}$  ion  $= 8 \times \frac{1}{8}$  i.e. 1

$$\text{Number of } \text{F}^\ominus \text{ ion} = 12 \times \frac{1}{4} \text{ i.e. } 3$$

Empirical formula of compounds is  $\text{MnF}_3$ .

(b) Coordination number  $= 6 \left( \frac{1 \times 3 \times 8}{4} \right)$

(c) Edge length (a)  $= 2(r_{\text{Mn}^{+3}} + r_{\text{F}^-}) = 2(0.65 + 1.36) \text{ i.e. } 4.02 \text{ \AA}$

12. (a) Distance between nearest neighbor =  $\frac{\sqrt{3}a}{2}$

i.e.  $\frac{\sqrt{3} \times 5.2}{2} = 4.5 \text{ \AA}$

(b) Distance between next nearest neighbor = a i.e. 5.2 \AA

(c) Nearest neighbor for K atom = 8

(d) Next nearest neighbour for K atom = 6

13. For AgCl,  $z = \frac{\rho \times a^3 \times N_A}{M} = \frac{5.561 \times (555 \times 10^{-10})^3 \times 6.023 \times 10^{23}}{143.5} = 3.9902$

Percentage of sites that are unoccupied is

$= \left(100 - \frac{100}{4} \times 3.9902\right) = 0.24 \text{ i.e. } 0.24\%$

14. (a)  $\frac{r_{Na^+}}{r_{Cl^-}} = 0.5$  &  $\frac{r_{Na^+}}{r_{K^+}} = \text{NaCl \& KCl has octahedral structure.}$   $\frac{r_{K^+}}{r_{Cl^-}} = 0.714$

In octahedral Edge length =  $r_{cation} + r_{anion}$ . Let a = Edge length of KCl octahedron

$a = r_{K^+} + r_{Cl^-}$  & b = Edge length of NaCl octahedron

$b = r_{Na^+} + r_{Cl^-}$

Now,  $\frac{r_{Na^+} + r_{Cl^-}}{r_{Cl^-}} = 1.5$  .....(1)

&  $\frac{r_{K^+} + r_{Cl^-}}{r_{Cl^-}} = 1.714$  .....(2)

$\frac{a}{b} = \frac{1.714}{1.5}$

i.e.  $\frac{a}{b} = 1.143$ .

(b)  $\frac{d_{NaCl}}{d_{KCl}} = \left(\frac{M}{a^3}\right)_{NaCl} \times \left(\frac{a^3}{M}\right)_{KCl} = \left(\frac{58.5}{74.5}\right) \times (1.143)^3 = 1.172$

15. Let  $\frac{r_+}{r_-} = 0.732$

P.F =  $\frac{4 \times \frac{4}{3} \pi r_+^3 + 8 \times \frac{4}{3} \pi r_-^3}{64(r_+ + r_-)^3} \times 3\sqrt{3} = \frac{\pi\sqrt{3} \left[ \left(\frac{r_+}{r_-}\right)^3 + 2 \right]}{4 \left[ \frac{r_+}{r_-} + 1 \right]^3} = 62.6 \%$



Void space in favorite structure per unit cell = 0.374

$$16. \quad d = \frac{Z \times M}{a^3 \times N_A}$$

$$0.92 = \frac{Z \times 18}{\left[ 6 \frac{\sqrt{3}}{4} \times (4.53)^2 \times 7.41 \times 10^{-24} \right] \times 6.022 \times 10^{23}} \quad Z = 4$$

$$17. \quad \text{Formula of forsterite} = \text{Mg} \frac{1}{4} \times 8 \frac{\text{Si}_1}{4} \times 4 \text{O}_4 \quad \text{i.e. Mg}_2\text{SiO}_4$$

$$\text{As,} \quad \frac{m_1}{d_1} + \frac{m_2}{d_2} = \frac{m_T}{d}$$

$$\frac{x}{4.34} + \frac{100-x}{3.21} = \frac{100}{3.88} \quad x = 66.3 \%$$

% of fayalite in an olivine is 66.3%

### EXERCISE (O-II)

2. m-(1)

$$\text{Number of atom A} \rightarrow 4 \times \frac{1}{8} + 4 \times \frac{1}{2} \quad \text{i.e.} \quad \frac{5}{2}$$

$$\text{Number of atom B} \rightarrow 10 \times \frac{1}{4} \quad \text{i.e.} \quad \frac{5}{2}$$

Formula of compounds is AB.

m-(2)

$$\text{In new arrangement, A particles} = \left( \frac{1}{8} \times 8 + \frac{1}{2} \times 6 \right) - \left( \frac{1}{8} \times 4 + \frac{1}{2} \times 2 \right)$$

$$\text{i.e.} \quad \frac{5}{2}$$

$$\& \text{ B particle} = \left( \frac{1}{4} \times 12 + 1 \right) - \left( 1 + \frac{1}{4} \times 2 \right) = \frac{5}{2}$$

So, formula is (AB).

3.  $\text{S}^{2-}$  ions for F.C.C. lattice &  $\text{Zn}^{+2}$  ions occupy alternate tetrahedral voids.

4. For  $\text{CaF}_2$   $\text{Ca}^{+2}$  occupy C.C.P & occupy all tetrahedral voids

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

$$a^3 = \frac{4 \times 73}{6.022 \times 10^{23} \times 3.18}$$

$$a = 546 \text{ pm}$$

5. (A) For square close packing, coordination number is 4 is a true statement.  
 (B) For hexagonal closed packing, coordination number is 6 is a true statement.  
 (C) There is only one void per atom in square close packing but 2 in hexagonal close packing is wrong statement.  
 (D) P.F. in Hexagonal close packing is 90.65 %  
 P.F. in square close packing is = 78.5 %  
 Hexagonal close packing is more Efficiently packed then square closed packing.
6. Factual
7. Number of tetrahedral voids =  $2 \times Z$   
 Number of octahedral voids =  $Z$   
 For F.C.C, body centre is occupied by octahedral void  
 Correct options are (A), (B) & (D).
8. Factual
11. F.C.C octahedral voids are present at each edge centre & at the body centre  
 Each octahedral void is surrounded by 6 spheres & Each sphere is surrounded by 6 octahedral voids.
12. for Rock-Salt structure, coordination number of each cation & Anion is six.
13. Factual
14. Correct option are (A), (B), (C) and (D)  
 CsCl mainly shows Schottky defect due to comparable size of cation & Anion.  
 ZnS mainly shows frenkel defect due to variation in size of cation & Anion  
 For NaCl,  
 (i) Unit cell contains  $4\text{Na}^+$  &  $4\text{Cl}^-$   
 (ii) One  $\text{Na}^+$  is surrounded by  $6\text{Cl}^-$  then  $12 \text{Na}^+$  & then  $8\text{Cl}^-$  at a distance  $\frac{a}{2}$ ,  $\frac{a}{\sqrt{2}}$  &  $a$  respectively.

### Comprehension: (Q. 15 & 16)

15. Volume occupied by  $\text{O}_2 = \left( \frac{4 \times 17.32}{\sqrt{3}} \right)^3 \times 0.32 = 20.5 \text{ litres}$

Using,  $PV = nRT$

$$n_{\text{O}_2} = \frac{P.V}{RT} = \frac{5 \times 20.5}{0.08 \times 640} = 2$$

number of oxygen molecules present in unit cell =  $2 \times N_A = 2 \times 6 \times 10^{23} = 12 \times 10^{23}$

Correct option is (B)

$$16. \quad \text{Total density} = \frac{2 \times (64 + 64)}{\left(\frac{4 \times 17.22}{\sqrt{3}}\right)^3 \times 6 \times 10^{23}} = 6.6 \times 10^{-27}.$$

$$\% \text{ increase in density} = \left(\frac{6.6 - 3.3}{6.6}\right) \times 100 = 50 \%$$

Correct option is (D).

### Comprehension: (Q. 17 to 19)

Calcium crystallizes in a cubic unit cell with density 3.2 g/cc. Edge-length of the unit cell is 437 pm

$$17. \quad d = \frac{Z \times M}{a^3 \times N_A}$$

$$Z = \frac{3.2 \times (437 \times 10^{-10})^3 \times 6.022 \times 10^{23}}{40} \quad Z = 4$$

F.C.C.

Correct option is (C)

$$18. \quad \text{Nearest neighbour distance} = \frac{a}{\sqrt{2}} = \frac{437}{\sqrt{2}} = 309 \text{ pm}$$

Correct option is (B)

$$19. \quad \text{Nearest neighbours are at a distance } \frac{a}{\sqrt{2}} \text{ and the number is 12}$$

Correct option is (D).

$$20. \quad \text{Density of molten metal is } 3 \text{ g cm}^{-3}.$$

$$Z = \frac{3 \times (437 \times 10^{-10})^3 \times 6.022 \times 10^{23}}{40}$$

$$Z = 3.76$$

Now, If  $Z = 4$  the % occupancy 74%

$$\text{For } Z = 3.76 \text{ the \% occupancy} = \frac{74}{4} \times 3.76 = 69 \%$$

% Empty space = 31%

### Comprehension: (Q. 21 & 22)

21. This is due to metal Excess defect

⇒ Correct option is (C)

22. This is impurity defect ⇒ Correct option is (A)

MATCH THE COLUMN

23. (A) For tetragonal & Hexagonal  
(P) are two crystal systems  
(Q)  $a = b \neq c$
- (B) For cubic & Rhombohedral  
(P) are two crystal systems  
(S)  $a = b = c$
- (C) For monoclinic & Triclinic  
(P) are two crystal systems  
(R)  $a \neq b \neq c$
- (D) For cubic & Hexagonal  
(P) are two crystal systems
24. (A) Rock salt structure :  
(R) Coordination number of cation & anion are 6. i.e. same  
(S) Distance between 2 nearest anion is  $\frac{a}{\sqrt{2}}$
- (B) Zinc blend structure :  
(P) Coordination number of cation is 4.  
(Q)  $\frac{\sqrt{3}a}{4} = r_+ + r_-$   
(R) Coordination number of cation & anion are same  
(S) Distance between two nearest anion is  $\frac{a}{\sqrt{2}}$
- (C) Fluorite structure  
(Q)  $\frac{\sqrt{3}a}{4} = r_+ + r_-$

MATCHING LIST TYPE

25. Correct option is (A)
26. Correct option is (B)

EXERCISE (JEE-MAIN)

1.  $A \rightarrow 4 - \left(2 \times \frac{1}{2}\right) = 3$

$B \rightarrow 12 \times \frac{1}{4} + 1 \times 1 = 4$

So, Compound is  $A_3B_4$

The value of x is 3.

2. In  $Fe_{0.93}O$  for every 93 Fe ions 14 are  $Fe^{+3}$  and  $(93 - 14) = 79$  are  $Fe^{+2}$  ions

$\therefore \% Fe^{+2} = \frac{79}{93} \times 100 = 84.9\%$

$\therefore$  nearest integer = 85%

6. Theory based.

9.  $Density = \frac{Z \times M}{N_A \times a^3}$

$6.17 = \frac{2 \times M}{6 \times 10^{23} \times (300 \times 10^{-10})^3}$

$M = 50$

$\therefore$  Number of molecules in 200 gm. =  $\frac{200 \times N_A}{50} = 4 N_A$

10.  $\therefore$   $Density = \frac{Z \times M}{N_A \times a^3}$

$2.7 \times 10^3 = \frac{Z \times 2.7 \times 10^{-2}}{6.02 \times 10^{23} \times (405 \times 10^{-12})^3}$

$Z = 4$

$\therefore$  Structure is FCC.

So,  $a = 2\sqrt{2}R$

$R = \frac{405 \times 10^{-12}}{2\sqrt{2}} \text{ m}$

$= 143 \times 10^{-12} \text{ m}$

11. min distance between two octahedral voids in fcc =  $\frac{a}{\sqrt{2}}$

(Distance between edge centre and body centre)

12. The radius of largest sphere which fits properly at the centre of edge of a body centred cubic unit cell =  $\frac{a - 2r}{2}$

$= \frac{a - \frac{2\sqrt{3}a}{4}}{2}$

$$= 0.067 a$$

13. Length of body diagonal =  $\sqrt{3}a$

$$= 2r_A + 2r_B$$

$$= 2r_A + 4r_A \quad [\because r_B = 2r_A]$$

$$= 6r_A$$

$$\Rightarrow a = 2\sqrt{3}r_A$$

$$P.F = \frac{\text{Volume of Particle}}{\text{Volume of unit cell}} = \frac{\frac{4}{3}\pi r_A^3 + \frac{4}{3}\pi(2r_A)^3}{a^3}$$

$$= \frac{\frac{4}{3}\pi(9r_A^3)}{(2\sqrt{3}r_A)^3}$$

$$= 906 \text{ i.e. } 90\%$$

14.  $\therefore$  B forms CCP structure So its effective number in a unit cell = 4

$\therefore$  A occupies half of the octahedral holes

So, its effective number in a unit cell = 2

$\therefore$  Oxygen atoms occupy all the tetrahedral holes

So, its effective number in a unit cell = 8

$\therefore$  Simplest ratio of A, B and oxygen atom = 1 : 2 : 4

15. Let AE be the Edge length = a.

BD be the nearest distance b/w 2 tetrahedral voids.

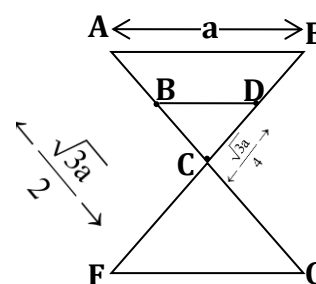
$$AC = \frac{\sqrt{3}a}{2} \quad \& \quad CD = \frac{\sqrt{3}a}{4}$$

$\Rightarrow$  by properties of triangle,

$$\frac{AE}{AC} = \frac{BD}{BC}$$

$$\Rightarrow \frac{a \times 2}{\sqrt{3}a} = \frac{BD \times 4}{\sqrt{3}a}$$

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



16. In Frenkel defect, smaller ion displaces from its actual lattice site into the interstitial sites.

18. The closest approach between 2 atoms in metallic crystal in F.C.C. structure is  $\frac{a}{\sqrt{2}}$

19.  $\text{CrO}_2$  is magnetic & ferromagnetic both

20. For B.C.C.  $r = \frac{\sqrt{3}a}{4} \Rightarrow r = \frac{\sqrt{3} \times 4.29}{4}$

i.e.  $r = 1.86 \text{ \AA}$

21. For CsCl  $r_{\text{Cs}^+} + r_{\text{Cl}^-} = \frac{\sqrt{3}}{2} a$

22. Number of atom A =  $8 \times \frac{1}{8}$  i.e. 1

Number of atom B =  $5 \times \frac{1}{2}$

$\Rightarrow$  Formula compounds is  $(\text{AB}_{5/2})$  i.e.  $\text{A}_2\text{B}_5$

23. The appearance of colour in solid-alkali metal halide is generally due to F-centers.

24. For monoclinic unit cell :

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

25. The total number of octahedral void per atom present in cubic close packed structure is 1.

26.  $\text{M}_{0.98}\text{O}_1$

Consider 1 mole of oxide

mole of M = 0.98, mole of  $\text{O}^{2-} = 1$

Let moles of  $\text{M}^{+3} = x$

& moles of  $\text{M}^{+2} = (0.98 - x)$

$\Rightarrow$  By charge balancing  $(0.98 - x) \cdot 2 + 3x - 2 = 0$ .

$\Rightarrow x = 0.04 \Rightarrow \% \text{ of } \text{M}^{+3} = \frac{0.04}{0.98} \times 100$  i.e. 4.08 %

27. For F.C.C

$a = 2\sqrt{2} r \Rightarrow a = 2\sqrt{2} \times 0.14$

i.e.  $a = 0.4 \text{ nm}$

28. The only incorrect statement is (3) i.e. void space in hcp mode of packing is 32%

29. Number of atom A =  $6 \times \frac{1}{8}$  i.e.  $\frac{3}{4}$

Number of atom B =  $6 \times \frac{1}{2}$  i.e. 3  $\Rightarrow$  Formula of compound is  $\text{AB}_4$

30. For F.C.C.

$r = \frac{a}{2\sqrt{2}} = \frac{361}{2\sqrt{2}}$  i.e.  $r = 128 \text{ pm}$

31. For B.C.C.



$$r = \frac{\sqrt{3}a}{4} = \frac{\sqrt{3} \times 351}{4} \quad \text{i.e. } r = 152 \text{ pm}$$

32. The only incorrect statement is (3) i.e. electrical conductivity of semiconductors & metals increases with Increases in temperature.

33. For B.C.C

The distance of Nearest Approach between atom is equal to  $\frac{\sqrt{3}a}{2}$

$$\frac{\sqrt{3}a}{2} = 1.73$$

$$a = 2\text{\AA} \text{ or } 200 \text{ pm}$$

34. For  $\text{NH}_4\text{Cl}$  in B.C.C lattice:

$$(r_{\text{NH}_4^+} + r_{\text{Cl}^-}) = \frac{\sqrt{3}a}{2}$$

$$\Rightarrow r_{\text{NH}_4^+} + 180 = \frac{\sqrt{3} \times 390}{2}$$

$$\Rightarrow r_{\text{NH}_4^+} = \frac{\sqrt{3} \times 390}{2} - 180$$

$$\Rightarrow r_{\text{NH}_4^+} = 158 \text{ pm}$$

35. For  $\text{CaO}$  :  $\frac{r_{\text{Ca}^{+2}}}{r_{\text{O}^{2-}}} = \frac{94}{146} = 0.643$

$\Rightarrow$  By radius ratio rule it should be octahedral.

36. For C.C.P.

% Of free space = 26 %

For B.C.C.

% Of free space = 32 %

37.  $(r_+ + r_-) = \frac{a}{2}$

$$110 + r_- = \frac{508}{2}$$

$$\Rightarrow r_- = \frac{508}{2} - 110$$

$$\Rightarrow r_- = 144 \text{ pm}$$

38. Number of Atom X =  $\frac{2}{3} \times 8$

Number of Atom Y = 4

$\Rightarrow$  Formula of compound is  $\frac{X_{16}}{3} Y_4$  or  $X_4 Y_3$

39. Total volume of atoms present in a face. centred unit cell of metal is  $4 \times \frac{4}{3} \pi r^3$

i.e.  $\frac{16}{3} \pi r^3$

40. Lattice energy of an ionic compounds depends on  $\rightarrow$  (3)

i.e. charge on the ion & size of the ion.

41. Number of Atom A =  $4 \times \frac{1}{8}$  i.e. 1

Number of Atom B =  $6 \times \frac{1}{2}$  i.e. 3

Formula of compound is  $AB_3$

42. Schottky defect

43. 58.5 gm of NaCl contains  $\frac{6.022 \times 10^{23}}{4}$  unit cells

$\Rightarrow$  1 gm of NaCl should contain  $\frac{6.022 \times 10^{23} \times 1}{58.5 \times 4}$  i.e.  $2.57 \times 10^{21}$  unit cells

44. 2,4

EXERCISE (JEE-ADVANCED)

$$1. \quad \text{Packing fraction (P.E.)} = \frac{1 \times \frac{4}{3} \pi r_-^3 + 3 \times \frac{4}{3} \pi r_+^3}{a^3}$$

$$\frac{r_+}{r_-} = 0.414 \text{ (Square planar void), } a = 2r_-$$

We get,

$$\text{P.F.} = \frac{\frac{4}{3} \pi (r_-^3 + 3r_+^3)}{8r_-^3}$$

$$= \left[ \frac{\pi}{6} (1 + 3(0.414)^3) \right] = 0.63$$

2. The given compound has CsCl type structure in which anion  $x$  form simple cubic unit cell and  $M^+$  cation is present in cubic void.

$$\therefore r_{M^+} + r_{X^-} = \frac{a\sqrt{3}}{2}$$

$$\therefore \frac{r_{M^+} + r_{X^-}}{a} = \frac{\sqrt{3}}{2} = 0.866$$

Coordination no. of  $M^+ = 8$

Coordination no. of  $X^- = 8$

$$\text{And } 0.732 \leq \frac{r_{M^+}}{r_{X^-}} < 1 \quad \therefore \text{Correct Ans. (A), (C)}$$

$$3. \quad \text{For F.C.C : Density (r)} = \frac{z \times m}{a^3 \times N_A}$$

$$\Rightarrow m = \frac{\rho \times a^3 \times N_A}{z} = \frac{8 \times (4 \times 10^{-8})^3 \times N_A}{4} = 128 \times 10^{-24} N_A$$

$$\text{Number of Atoms} = \frac{256}{m} \times N_A = \frac{256 \times N_A}{128 \times 10^{-24} N_A} = 2 \times 10^{24} \quad N = 2$$

4. (a) Nearest neighbor in the top most layer of CCP structure is 9 thus incorrect.

$$(b) \quad \text{Packing efficiency is 74\% thus correct. \% of packing efficiency} = \frac{4 \times \frac{4}{3} \pi r^3}{a^3} \times 100$$

$$= \frac{4 \times \frac{4}{3} \pi r^3}{(2\sqrt{2}r)^3} \times 100 \quad \text{i.e. 74 \%}$$

(c) Number of tetrahedral void per atom = 2

Number of octahedral void per atom = 1

this correct

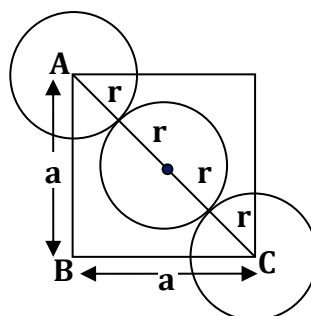
(d) In DABC

$$AC^2 = AB^2 + BC^2$$

$$\Rightarrow (4r)^2 = a^2 + a^2$$

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

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



5. In CCP,  $O^{2-}$  ions are 4

Hence total negative charge = - 8

Let number of  $Al^{+3}$  ions be x

& number of  $Mg^{+2}$  ion be y

$$\Rightarrow \text{Total position charge} = 3x + 2y$$

$$\Rightarrow 3x + 2y = 8$$

This relation is satisfied only by  $x = 2$  &  $y = 1$

Hence number of  $Al^{+3} = 2$

& number of  $Mg^{+2} = 1$

$$\Rightarrow m \text{ i.e. fraction of octahedral holes occupied by } Al^{+3} \text{ ions} = \frac{2}{4} \text{ i.e. } \frac{1}{2}$$

$$\text{and } n \text{ i.e. fraction of tetrahedral holes occupied by } Mg^{+2} \text{ ions} = \frac{1}{8}$$

6. The given arrangement is octahedral void arrangement.

$$\frac{r_{A^+}}{r_{X^-}} \approx 0.414 \Rightarrow r_{A^+} \approx 0.414 \times 250$$

$$\text{i.e. } r_{A^+} \approx 103.5 \text{ pm}$$

$$\frac{r_{A^+}}{r_{X^-}} < 0.732 \Rightarrow r_{A^+} < 183 \text{ pm.}$$

So, the radius of  $A^+$  is 104 pm.

$$7. \text{ No. of M atoms} = \frac{1}{4} \times 4 + 1 = 2$$

$$\text{Number of X atoms} = \frac{1}{2} \times 6 + \frac{1}{8} \times 8 = 3 + 1 = 4$$

So, empirical formula of compound is  $(MX_2)$ .

8. Fig → copy from solution given of back.

Explanation : The truncated octahedron is the 14-faced Archimedean solid with 14 total faces :  
6 square & 8 regular hexagons.

The truncated octahedron is formed by removing the six right square pyramids one from each point of regular octahedron.

Truncated octahedron unfolded in two dimensions.

9.  $4R = L\sqrt{2}$

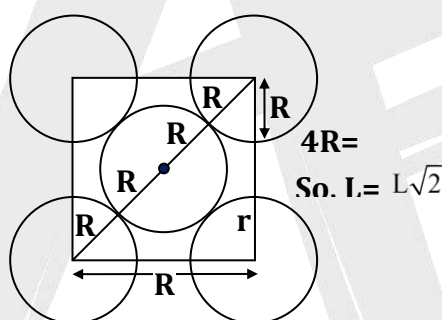
So,  $L = 2\sqrt{2} R$

Area of square unit cell =  $(2\sqrt{2} R)^2 = 8R^2$

11.  $4R = L\sqrt{2}$

So,  $L = 2\sqrt{2} R$

⇒ Area of square unit cell =  $(2\sqrt{2} R)^2 = 8R^2$



Area of atoms present in 1 unit cell =  $\pi R^2 + 4 \left( \frac{\pi R^2}{4} \right) = 2\pi R^2$

⇒ Packing efficiency =  $\frac{2\pi R^2}{8R^2} \times 100 = 78.54 \%$

12. Frenkel defect is a dislocation defect Trapping of an electron in the lattice leads to the formation of F-centres

**Paragraph for Question No. 13 to 15**

13. Total number of atoms in 1 unit cell =  $\left( 12 \times \frac{1}{6} \right) + 3 + \left( 2 \times \frac{1}{2} \right) = 6$

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

Area of Base =  $6 \times \frac{\sqrt{3}}{4} (2r)^2$

$$\Rightarrow \text{volume of Hexagon} = \text{Area of base} \times \text{height} = \left(6 \frac{\sqrt{3}}{4} \times 4r^2\right) \times \left(\sqrt{\frac{2}{3}} \times 4r\right) = 24\sqrt{2} r^3$$

$$15. \text{ Packing fraction} = \frac{\text{Volume of atom in 1 unit cell}}{\text{Volume of 1 unit cell}} \times 100 = \frac{6 \times \frac{4}{3} \pi r^3}{24\sqrt{2} r^3} \times 100 = 74\%$$

$$\Rightarrow \text{Empty space} = 26\%$$

16. (A) simple cubic & FCC

Have the cell parameters  $a = b = c$  &  $a = b = c = a$  & are 2 crystal systems (Q)

(C) Cubic & Tetragonal are 2 crystal system. (Q)

(D) Hexagonal & Monoclinic are 2 crystal system (Q) have 2 crystallographic angles of  $90^\circ$  (R).

$$17. r = \frac{Z \times M}{a^3 \times N_A}$$

$$\Rightarrow Z = \frac{\rho \times a^3 \times N_A}{M} = \frac{2 \times (5 \times 10^{-8})^3 \times 6 \times 10^{23}}{75} = 2$$

So, it is a B.C.C. unit cell

$$\Rightarrow R = \frac{\sqrt{3} a}{4} = \frac{\sqrt{3} \times 5}{4} \Rightarrow R = 216.5 \text{ pm}$$

18. In a cubic crystal system, there are 2 types of void known as octahedral & Tetrahedral voids.

It  $r_1$  is the radius of void &  $r_2$  is the radius of atom creating these voids, then

$$\left(\frac{r_1}{r_2}\right)_{\text{octahedral}} = 0.414$$

$$\left(\frac{r_1}{r_2}\right)_{\text{tetrahedral}} = 0.225$$

The above radius ratio values indicate that octahedral void has larger radius, have for maximum diameter of atom to be present in interstitial space

$$r_1 = 0.414 r_2$$

$$\text{Also in F.C.C., } 4r_2 = \sqrt{2} a$$

$$\Rightarrow \text{Diameter required } (2r_1) = 2 \times 0.414 r_2 = \frac{2 \times 0.414 \times a}{\sqrt{2}} = \frac{0.414 \times 400}{\sqrt{2}}$$

$$\text{i.e. } 117.1 \text{ pm}$$

16. In C.C.P, number of tetrahedral voids =  $2 \times$  number of atoms.

As there are  $4S^{-2}$  ions at lattice points & they need  $4zn^{+2}$ , which are adjusted in alternate tetrahedral voids.

17. (i)  $5 \text{ kg m}^{-3}$

(ii) There is a huge difference density & observed density. It is only possible if some foreign species occupy interstitial space i.e. substitution defect.

(i) In Rock salt like crystal AB, there are 4 AB units per unit cell

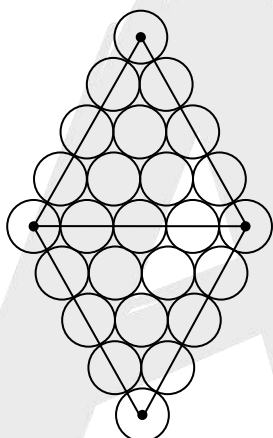
$$\Rightarrow \text{density} = \frac{Z \times M}{a^3 \times N_A} = \frac{4 \times 6.023y}{8y \times 10^{-27} \times 6.023 \times 10^{23}}$$

$$= 5 \times 10^3 \text{ g/m}^3 \quad [\because a = 2y^{1/3} \text{ nm} \quad \text{or} \quad 2y^{1/3} \times 10^{-9} \text{ m}]$$

$$\text{or } 5 \text{ kg/m}^3$$

18. To have maximum number of spheres, the packing must be hcp.

Maximum number of spheres = 25.



Area of figure =  $2 \times$  Area of equilateral triangle of side = 40 mm or 4 cm.

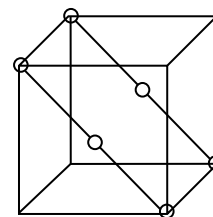
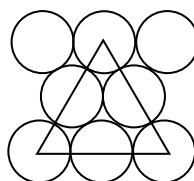
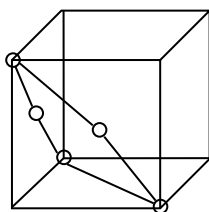
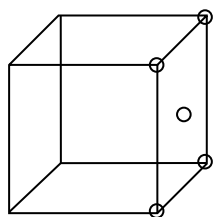
$$= 2 \times \frac{\sqrt{3}}{4} (4)^2 = 13.856 \quad \frac{25}{13.856} = 1.804 \text{ marbles/cm}^2$$

19. Number of atom of A per unit cell =  $8 \times \frac{1}{8}$  i.e. 1

Number of atoms of B per unit cell =  $6 \times \frac{1}{2}$  i.e. 3

$\Rightarrow$  formula is  $\text{AB}_3$

20.



21. Number of atoms A per unit cell =  $\left( \frac{1}{8} \times 8 + 4 \times \frac{1}{2} \right) = 3$



$$\text{Number of atom B per unit cell} = 4 \cdot \left( 12 \times \frac{1}{4} + 1 \right) \Rightarrow \text{Formula is } (A_3B_4)$$

22. Factual

23. 3 - consecutive layers of atom in hcp are there.

Atom X is in correct of 12 like atoms, 6 from layer B and 3 from to and bottom layer A each.

$$\Rightarrow \text{C.N.} = (6 + 3 + 3) \text{ i.e } 12$$

24. Density  $\propto \frac{Z}{a^3}$

$$\frac{d_{\text{F.C.C}}}{d_{\text{B.C.C}}} = \frac{4}{(3.5)^3} \times \frac{(3)^3}{2} = 1.259$$

