

Class 12

2017-18



CHEMISTRY

FOR JEE MAIN & ADVANCED

SECOND
EDITION



Topic Covered
Solid State

Exhaustive Theory ◀
(Now Revised)

Formula Sheet ◀

9000+ Problems ◀
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Key Take Aways, Problem Solving Tactics

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Questions recommended for revision



19. SOLID STATE

1. INTRODUCTION

We know that solids are substances which have a definite volume and a definite shape. A solid is a nearly incompressible state of matter with a well-defined shape, rigidity and volume.

2. CLASSIFICATION OF SOLIDS

Solids can be broadly classified into two types:

1. Crystalline
2. Amorphous

Table 19.1: Difference between crystalline and amorphous solids

S.No.	Property	Crystalline solids	Amorphous solids
1.	Geometry	These have definite regular geometry which extends throughout the crystals i.e., these solids have long range order.	These do not have definite orderly arrangement.
2.	Melting Points	These have sharp m.p.	These do not have sharp m.p.
3.	Symmetry	These possess symmetry.	These do not possess any symmetry.
4.	Heat of Fusion	These have definite heat of fusion.	These do not have definite heat of fusion.
5.	Interfacial angles	Crystals are always guarded by planes so that a definite angle exists between two planes called interfacial angle.	These do not possess interfacial angle.
6.	Volume change	There is a sudden change in volume when it melts.	There is no sudden change in volume on melting.
7.	Isotropy and Anisotropy	These are anisotropes i.e., their physical properties such as refractive index, conductivity etc. have different values in different directions.	These are isotropic i.e., their physical properties such as refractive index, conductivity etc. have same value in all the directions.

PLANCESS CONCEPTS**Glass Transition Temperature**

An important property of amorphous polymer is glass transition temperature at which a glassy polymer transforms into flexible rubber-like mass capable of taking on shapes and forms. This property is used in the processing of polymers.

Vaibhav Krishnan (JEE 2009 AIR 22)

3. TYPES OF CRYSTALLINE SOLIDS

On the basis of the nature of the constituent particles and the interparticle forces, crystalline solids may be divided into four classes.

Table 19.2: Characteristics of various types of solids

Characteristics	Molecular Solids	Covalent Network	Metallic Solids	Ionic Solids
1. Units that occupy	Atoms or molecules	Atoms	Positive ions in a 'sea of electrons'	Positive and negative ions
2. Binding forces	Vander Waal's forces (weak intermolecular forces) of following two types (i) London (dispersion) forces (ii) Dipole-dipole forces	Covalent bonding (shared pair of electrons)	Metallic bonding (extreme delocalised bond) – positively charged atomic cores surrounded by 'sea' of delocalised electrons	Ionic bonding (electrostatic attraction between positive and negative ions)
3. Physical Properties	(i) Very soft. (ii) Low melting points (iii) Non conductors	(i) Very hard (ii) Very high melting points (iii) Non conductors	(i) Hard or soft (ii) Moderate high melting points (iii) Good conductors	(i) Quite hard and brittle (ii) Fairly high melting points
4. Example	Solid Ne, Solid NH_3 , ice (Solid H_2O), dry ice (Solid CO_2)	Diamond, Carborundum (SiC), quartz (SiO_2)	Cu, Fe, Ag	NaCl , KNO_3 , Na_2SO_4

PLANCESS CONCEPTS

Stability of a crystal is reflected in the value of its melting point. A more stable structure would require higher energy and hence melt at higher temperature.

Nikhil Khandelwal (JEE 2009 AIR 94)

4. SALIENT FEATURES OF CYRSTALS

A crystal possesses the following characteristic features:

- 1. Faces:** The surfaces are usually planar and arranged on a definite plane (as a result of internal geometry). The planes which bind the crystal, are called faces. Faces are of two types:
 - (i) Like:** A crystal having all faces alike, e.g. Fluorspar.
 - (ii) Unlike:** A crystal having all faces not alike, e.g. Galena.
- 2. Form:** All the faces corresponding to a crystal are said to constitute a form.
- 3. Edges:** The intersection of two adjacent faces forms an edge.
- 4. Interfacial Angle:** The angle between the normals to the two intersecting faces is called interfacial angle.
- 5. Zone and Zone Axis:** The faces of a crystal occur in sets called zones, which meet in parallel edges or would do so if the planes of the faces are extended. Each zone forms a complete belt around the crystal.

A line passing through the centre of a crystal in a direction parallel to the edge of zone is known as **zone axis**.

Space Lattice: A three dimensional arrangement of points that shows how the atoms or ions are arranged in space is called a Space Lattice. Each point is individually called a lattice point.

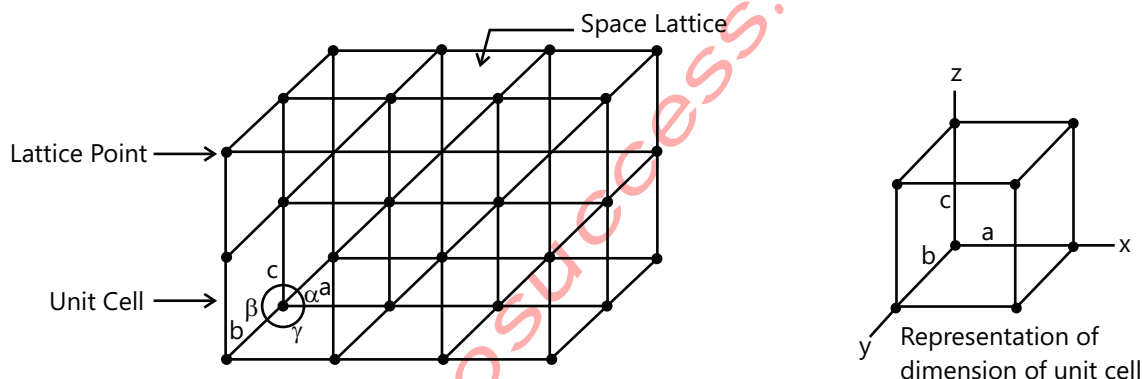


Figure 19.1: Representation of space lattice and unit cell

Crystal Lattice: A space lattice is called a crystal lattice when the lattice points in the space are replaced by actual atoms or ions.

Crystal System: The unit cell in a 3-dimension lattice is characterized by the length a , b , c and their angles α , β , γ . These are known as unit cell parameters.

Bravais Lattices: An arrangement of spheres as given above leads to simple or primitive unit cell, when there are points only at the corner of the unit lattice. However, certain unit cells have lattice points on other sides also in addition to the corners. Such unit cell are called non-primitive unit cells. Bravais (1848) showed from geometrical considerations that there can be only 14 different ways in which similar points (spheres) can be arranged.

These fourteen types of lattice are known as Bravais lattices. They can be divided into seven crystal systems as shown below:

Table 19.3: Crystal system table

S.No.	Crystal System	Axial Characteristics	Examples
1.	Cubic (Most symmetrical)	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	NaCl, KCl, CsCl, zinc blende, Cu, Ag, diamond
2.	Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	White tin, SnO_2 , TiO_2

3.	Orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	Rhombic sulphur, PbCO_3 , PbSO_4 , KNO_3
4.	Monoclinic	$a \neq b \neq c$ $\alpha = \gamma = 90^\circ; \beta \neq 90^\circ$	Monoclinic sulphur, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
5.	Rhombohedral or trigonal	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	Calcite, quartz, As, Sb, NaNO_3 , ICl
6.	Triclinic (Most unsymmetrical)	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$	$\text{K}_2\text{Cr}_2\text{O}_7$, H_3BO_3 , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
7.	Hexagonal	$a = b \neq c$ $\alpha = \beta = 90^\circ; \gamma = 120^\circ$	Graphite

PLANCESS CONCEPTS

The relationship between the plane faces (F), straight edges (e) and interfacial angle (C) for a given crystal can be written as:

$$F + C = e + 2$$

Saurabh Gupta (JEE 2010 AIR 443)

4.1 Laws of Crystallography

The geometric crystallography (the outward spatial arrangement of crystal planes and shape of crystals) is based on the following three fundamental laws:

- The Laws of Constancy of Interfacial Angles:** The crystals of a substance can have different shapes depending upon the number and size of the faces but the angle at which the two adjacent faces intersect remains always constant. Depending on the number and size of the faces, the crystals of a substance can have different shapes. However, the angle at which two adjacent faces intersect always remains constant.
- Haüy's Law of Rationality of Indices:** The intercepts of any face of plane of a crystal on suitable crystallographic axes can be expressed by small multiples of three unit distances a, b, c or some simple integral multiple (m, n, p) of these unit distances, i.e., ma: nb: pc or fraction of whole numbers.
- The Law of Constancy of Symmetry:** According to this law, all crystals of the same substance possess the same elements of symmetry.

5. SYMMETRY IN A CRYSTAL

- Centre of Symmetry:** Centre of symmetry of a crystal may be defined as an imaginary point within a crystal such that any line passing through it, intersects the crystal at equal distances in both directions e.g. staggered form of ethane possesses a centre of symmetry.

Every Crystal Possesses Only One Centre of Symmetry

- Plane of Symmetry:** It is an imaginary plane passing through the crystal which can divide it into two equal parts in such a way that one part is an exact mirror image of the other. Thus, they are also referred to as mirror planes. There are two types of mirror planes (as shown below).

(A) Rectangular mirror planes

(B) Diagonal mirror plane

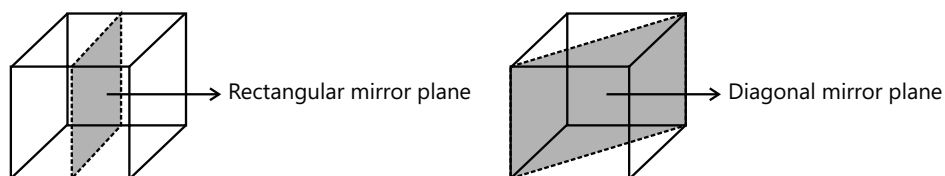


Figure 19.2: Representation of type of plane of symmetry present in a unit cell

5.1 Axis of Symmetry or Axis of Rotation

An axis of symmetry or axis of rotation is an imaginary line, passing through the crystal such that when the crystal is rotated about this line, it presents the same appearance more than once in one complete rotation. I.e. through 360° .

When the same appearance of crystal is repeated, on rotating through an angle of $\frac{360^\circ}{n}$ around an imaginary axis it is called n-fold axis of symmetry where n- is known as order of axis.

Two-Fold Axis: If a similar appearance occurs two times in one complete rotation i.e. after a rotation through 180° , the axis is called two fold axis of symmetry or dyad axis.

Three-Fold Axis: If the original appearance occurs thrice, then it is called three fold axis of symmetry.

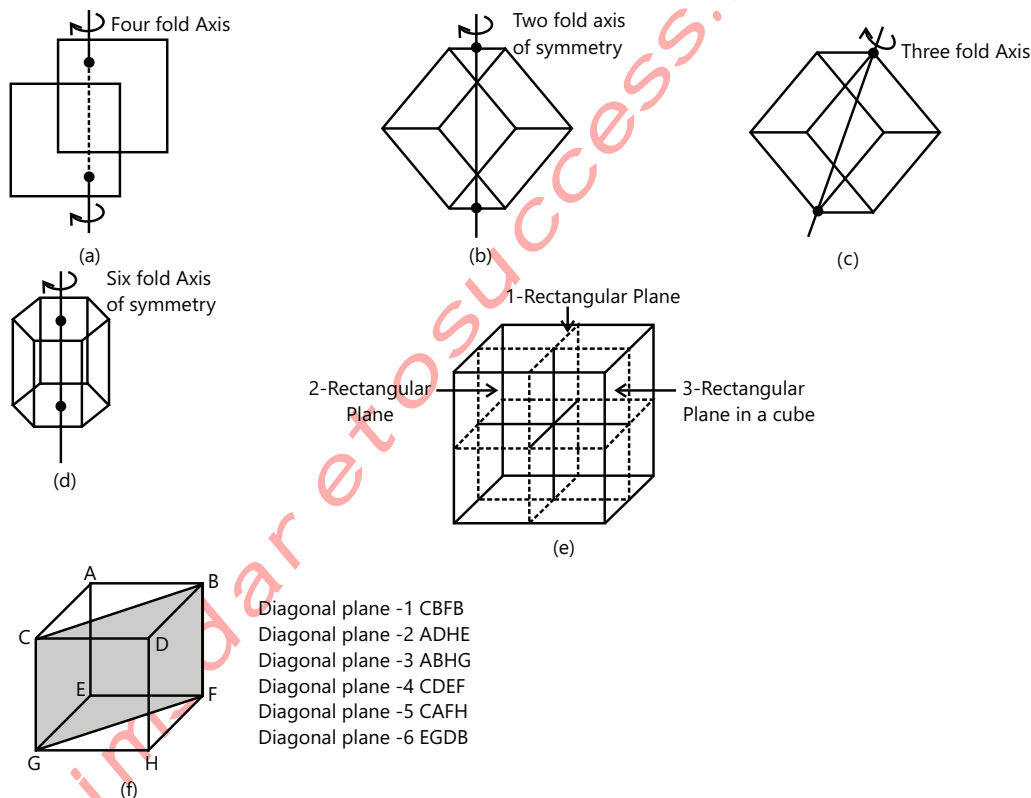


Figure 19.3: Representation of axis of symmetry present in a unit cell

PLANCESS CONCEPTS

A crystal may have a number of planes or axis of symmetry but it possesses only one centre of symmetry.

Neeraj Toshniwal (JEE 2009 AIR 21)

5.2 Total Elements of Symmetry in a Cubical Crystal

Total planes of symmetry = $3 + 6 = 9$
 Axis of symmetry = 4 (3-fold axis)
 3 (Four fold axis)
 6 (Six fold axis) = 13 Axes of symmetry
 Centre of symmetry = 1
 Hence, a cube has 23 elements of symmetry.

6. UNIT CELL

The smallest repeating pattern in a space lattice is called a unit cell.

6.1 Types of Unit Cell

Unit cells are classified as simple or primitive, body centred, face centred and end centred. This classification depends on the position of constituent particles in a unit cell.

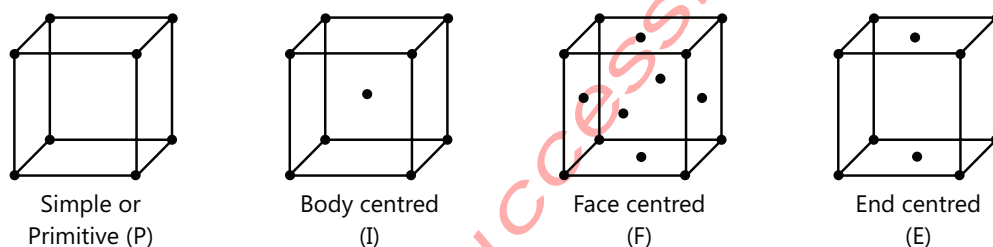


Figure 19.4: Different types of unit cell

6.2 Number of Atoms in a Unit Cell

- A point lying at the corner of a unit cell is shared equally by eight unit cells and therefore, only one-eighth ($1/8$) portion of each of such a point belongs to the given unit cell.
- A point present on an edge is distributed among the four unit cells, therefore only one-fourth ($1/4$) of such a point belongs to the given unit cell.
- A face-centred point is shared between two unit cells. Therefore one-half ($1/2$) part lies in each unit cell.
- A body-centred point belongs entirely to one unit cell since it is not shared by any other unit cell. Therefore, its contribution to the unit cell is one.

Table 19.4: Number of atoms in different type of unit cell

Type of cell	Number of atoms at corners	Number of atoms in faces	Number of atoms in the body of cube	Total
Simple or primitive cubic	$8 \times \frac{1}{8} = 1$	0	0	1
Body-centred cubic (bcc)	$8 \times \frac{1}{8} = 1$	0	$1 \times 1 = 1$	2
Face-centred cubic (fcc)	$8 \times \frac{1}{8} = 1$	$6 \times \frac{1}{2} = 3$	0	4

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

Sol: X atom is occupying simple cubic structure, y atom occupies body center and O occupies edge centre. So calculate the no of atoms of X, Y and O present in a unit cell.

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

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

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

O atom is present at each of the edge centre (number of edges of cube = 12)

And each O atom present at edge centre will make $\frac{1}{4}$ contribution towards the unit cell.

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

The formula of the compound is, therefore XYO_3 .

Illustration 2: A cubic crystalline solid contains P atoms at the corners and Q atoms at the body centres. If one atom from the corner is missing, what will be the simplest formula of the resulting solid? **(JEE MAIN)**

$$\text{Sol: } Z_p = 7 \times \frac{1}{8} = \frac{7}{8}$$

$$Z_Q = 1$$

\therefore The simplest formula is $\text{P}_{\frac{7}{8}}\text{Q} = \text{P}_7\text{Q}_8$.

Illustration 3: A compound alloy of gold and copper crystallizes in a cube lattice in which the gold atoms occupy the lattice points at the corners of a cube and the copper atoms occupy the centres of each of the cube faces. Determine the formula of this compound. **(JEE MAIN)**

Sol: Determine the number of atoms of Au (Occupying simple primitive structure) present in one unit cell and no. of atoms of Cu (occupying face center arrangement) present in one unit cell .

One-eighth of each corner atom (Au) and one-half of each face-centred atom (Cu) are contained within the unit cell of the compound.

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

$$\text{Number of Cu atoms per unit cell} = 6 \times \frac{1}{2} = 3.$$

The formula of the compound is AuCu_3 .

Illustration 4: A compound formed by elements A and B crystallizes in cubic structure where A atoms are at the corners of a cube and B atoms are at the body centre of the cube. What is the formula of the compound? **(JEE MAIN)**

Sol: Determine the number of atoms of A (Occupying Corner of a cube) present in one unit cell and no. of atoms of Ag (occupying Body center arrangement) present in one unit cell

An atom at the corner of the cube is shared by 8 cubes and hence, contributes only $\frac{1}{8}$ to a particular cube. There are eight corners of a cube.

$$\therefore \text{The number of A atoms in the unit cell} = 8 \times \frac{1}{8} = 1$$

An atom at the body centre of cube belongs only to one unit cell.

$$\therefore \text{Number of atoms of B in the unit cell} = 1 \times 1 = 1.$$

Thus, formula is AB.

6.3 Coordination Number

The number of nearest neighbours that an atom has in a unit cell is called the coordination number. In ionic crystal, the number of oppositely charged ions surrounding each ion is called its co-ordination number. The co-ordination number of a crystal depends upon its structure.

- (a) **Simple Cubic Structure:** It is clear from the Figure that each atom say (A) has 4 nearest neighbours 2, 3, 4 and one to the left of A of another unit cell in one plane. In addition, it also possesses one atom vertically above of another unit cell. Thus, in all, A possesses six neighbour atoms and therefore, a simple cubic structure reveals a co-ordination number of six, e.g., NaCl.

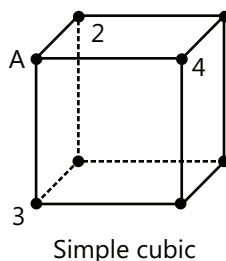


Figure 19.5-a: Diagrammatic representation of simple unit cell

- (b) **Face Centred Cubic Structure (fcc):** It is clear, from the figure, that the nearest neighbour of a corner atom is the face centred atom and thus, each atom say (A) has 4 nearest neighbours 1, 2, 4 and the other is on its left side from another cell. In addition, it also possesses four face centred atoms in planes below and above it. Thus, in all, A possesses 12 neighbour atoms and therefore, face centred cubic structure reveals a co-ordination number of twelve, e.g., Copper.

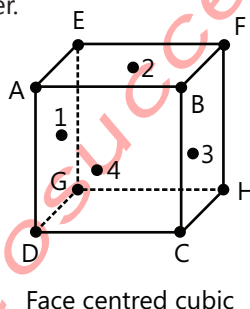


Figure 19.5-b: Diagrammatic representation face centred unit cell

- (c) **Body Centred Cubic Structure (bcc):** It is clear from the figure, that the nearest neighbour of a corner atom is body centred atom. Thus, each atom say (A) has eight body centred atoms of 8 surrounding unit cells as neighbours in one plane, since A is surrounded by 8 surrounding unit cells. Thus, a body centred cubic structure reveals a co-ordination number of eight, e.g., CsCl.

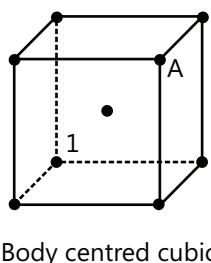


Figure 19.5-c: Diagrammatic representation of body centred unit cell

PLANCESS CONCEPTS

Pressure and temperature changes the coordination number of a crystal.

- High pressure increases the co-ordination number.
- High temperature decreases the co-ordination number.

Aman Gour (JEE 2012 AIR 230)

6.4 Density of Lattice Matter

It is defined as the ratio of mass per unit cell to the Volume of unit cells.

$$\text{Density of lattice matter} = \frac{\text{mass per unit cell}}{\text{volume of unit cell}}$$

$$\text{Mass per unit cell} = \text{No. of Atoms} \times \text{Mass of one of atom} = n \times \frac{\text{Atomic mass}}{\text{Avog. No.}}$$

$$\text{Density of lattice matter} = \frac{n \times \text{at. wt.}}{\text{Av.no.} \times \text{volume of unit cell}}$$

$$\rho = \frac{n \times \text{atomic mass (or molar mass)}}{N_A \times V}$$

$$\rho = \frac{n \times \text{atomic mass}}{N_A \times a^3}$$

Where 'a' is edge length of cube. (in cm)

Where 'n' is number of atoms per unit cell; volume of unit cell is to be derived for given crystal system. It is equal to a^3 for cubic crystal systems.

Illustration 5: The edge length of a cubic crystal of an element is found (by X-ray diffraction) to be 'a' picometres. Show how you can calculate its density. **(JEE MAIN)**

Sol: The density of the unit cell is the same as the density of the substance.

$$\text{Edge length of unit cell} = a \text{ pm} = a \times 10^{-10} \text{ cm}$$

$$\text{Volume of the unit cell} = a^3 \times 10^{-30} \text{ cm}^3$$

$$\text{Density of the unit cell} = \frac{n \times M}{a^3 \times N_A \times 10^{-30}} \text{ gcm}^{-3}$$

Illustration 6: Chromium metal crystallizes with a body centred cubic lattice. The edge length of the unit cell is found to be 287 pm. Calculate the atomic radius. What would be the density of chromium in g/cm^3 ? (At. wt. of Cr = 51.99) **(JEE MAIN)**

Sol: From the given value of edge length first determine the atomic radius for a bcc crystal lattice and density can be determined using the following formula,

$$\text{Density} = \frac{n \times \text{at. wt.}}{V \times \text{Av. no.}} = \frac{n \times \text{at. wt.}}{a^3 \times \text{Av. no.}}$$

$$\text{For bcc lattice, } r = \frac{\sqrt{3}a}{4} = \frac{\sqrt{3}}{4} \times 287 = 124.27 \text{ pm}$$

$$\text{Now, Density} = \frac{n \times \text{at. wt.}}{V \times \text{Av. no.}} = \frac{n \times \text{at. wt.}}{a^3 \times \text{Av. no.}}$$

$$n = 2 \text{ for bcc; } a = 287 \text{ pm} = 287 \times 10^{-10} \text{ cm}$$

$$\therefore \rho = \frac{2 \times 51.99}{(287 \times 10^{-10})^3 \times (6.023 \times 10^{23})} = 7.31 \text{ g/cm}^3$$

Illustration 7: An element (density 6.8 g cm^{-3}) occurs in bcc structure with unit cell edge of 290 pm . Calculate the number of atoms present in 200 g of the element. **(JEE ADVANCED)**

Sol: First determine the molecular mass of the element by using following equation,

$$\text{Density} = \frac{n \times M}{\text{Av. no.} \times a^3}$$

And from molecular mass determine the number of atoms present in 200 g of the element.

Let M be the molecular mass of the element.

$$\text{Volume of the unit cell} = a^3 = (290 \times 10^{-10} \text{ cm})^3 = 24.4 \times 10^{-24}$$

In a body centred cubic (bcc) structure $n = 2$.

$$\text{Density} = \frac{n \times M}{\text{Av. no.} \times a^3}$$

$$6.8 = \frac{2 \times M}{6.023 \times 10^{23} \times 24.4 \times 10^{-24}}$$

$$M = \frac{6.8 \times 6.023 \times 10^{23} \times 24.4 \times 10^{-24}}{2} = 50 \text{ g}$$

$\therefore 50 \text{ g}$ of the element contain 6.023×10^{23} atoms

$$200 \text{ g of the element would contains} = \frac{6.023 \times 10^{23} \times 200}{50} = 24.09 \times 10^{23} \text{ atoms}$$

6.5 Nearest Neighbouring Distance in Case of Identical Spheres

Nearest neighbouring distance is the distance between the centres of any two touching spheres.

(a) In case of SCC (Simple Cubic Lattice)

In a simple cubic lattice the edge length (a) = Nearest neighbouring distance

$$a = d = 2r$$

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

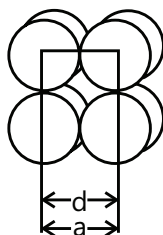


Figure 19.6-a: Nearest neighbouring distance in case of SCC

(b) Body Centred

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

$$\Rightarrow (\text{Body Diagonal})^2 = (\text{Face Diagonal})^2 + (\text{edge})^2$$

$$= 2(\text{edge})^2 + (\text{edge})^2 = 3(\text{edge})^2$$

$$\Rightarrow (\text{Body Diagonal})^2 = 3(\text{edge})^2 = 3a^2$$

$$\therefore \text{body diagonal} = \sqrt{3} a$$

$$\text{Also Body Diagonal} = r + 2r + r = 4r$$

$$\Rightarrow 24r = \sqrt{3}a \Rightarrow r = \frac{\sqrt{3}}{4}a$$

$$d = 2r \Rightarrow d = \frac{\sqrt{3}}{2}a = \text{nearest neighbouring distance}$$

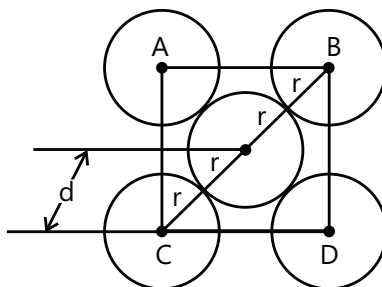


Figure 19.6-b: Nearest neighbouring distance in case of BCC

(c) Face Centred Cubic Lattice

$$\text{Here } (\text{Face diagonal})^2 = (\text{edge})^2 + (\text{edge})^2$$

$$\therefore (\text{face diagonal})^2 = a^2 + a^2 = 2a^2$$

$$\therefore \text{face diagonal} = \sqrt{2} a$$

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

$$r = \frac{\sqrt{2}}{4}a \Rightarrow r = \frac{1}{2\sqrt{2}}a \Rightarrow d = \frac{\sqrt{2}}{2}a = \frac{1}{\sqrt{2}}a$$

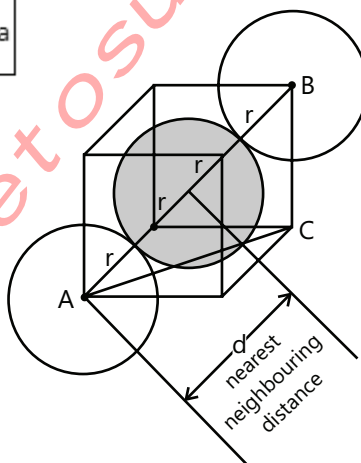


Figure 19.6-c-Nearest neighbouring distance in case of FCC

6.6 Packing Fraction

Packing Fraction in Case of Identical Spheres

Packing fraction is the ratio of volume occupied by sphere to the total volume of the cube

$$\text{Packing Fraction} = \frac{\text{Volume occupied by sphere}}{\text{Total volume of cube}} = \frac{\frac{4}{3}\pi r^3 \times z}{a^3}$$

where a = edge of cube, z = number of sphere per unit cell

Packing fraction of SCC

$$r = \frac{a}{2}, z = 1; \quad PF = \frac{\frac{4}{3}\pi\left(\frac{a}{2}\right)^3 \times z}{a^3} = \frac{4\pi}{8 \times 3} = \frac{\pi}{6}$$

$$\Rightarrow PF = \frac{\pi}{6} = 0.524$$

$$\Rightarrow \% \text{ volume occupied by sphere} = \frac{\pi}{6} \times 100 = 52.4\%$$

$$\Rightarrow \% \text{ Free space} = 100 - 52.4 = 47.6\%$$

Packing fraction for BCC

$$r = \frac{\sqrt{3}}{4}a, z = 2; \quad PF = \frac{\frac{4}{3}\pi\left(\frac{\sqrt{3}}{4}a\right)^3 \times 2}{a^3} = \frac{4}{3} \times \frac{\pi \times 3\sqrt{3} \times 2}{64} = \frac{\sqrt{3}\pi}{8} = 0.68$$

$$\Rightarrow \% \text{ volume occupied} = 100 \times 0.68 = 68\%$$

$$\% \text{ Free space} = 100 - 68 = 32\%$$

Packing Fraction for FCC

$$r = \frac{\sqrt{2}}{4}a, z = 4 \quad PF = \frac{\frac{4}{3}\pi\left(\frac{\sqrt{2}}{4}a\right)^3 \times 4}{a^3} = \frac{4}{3} \times \frac{\pi \times 2\sqrt{2} \times 4}{64} = \frac{\sqrt{2}\pi}{6} = 0.7407$$

$$\Rightarrow PF = \frac{\sqrt{2}\pi}{6} = 0.740$$

$$\% \text{ volume occupied} = 100 \times 74 = 74\%$$

$$\% \text{ Free space} = 100 - 74 = 26\%$$

PLANCESS CONCEPTS

The packing density data reveals that close packing of atoms in cubic structure follow the order, FCC > BCC > SCC, i.e., more closely packed atoms are in FCC structure.

B Rajiv Reddy (JEE 2012 AIR 11)

Table 19.5: Summary of Various Characteristics of Different Cubic Systems

S. No.	Cubic	Nuber of effective atoms per unit cell (Z_{eff})	Coordi- nation Number (CN)	Atomic radius (r)	Packing efficiency	Density (ρ) (g cm ⁻³)	Nearest neighbour distance (d)
1.	Simple cube (sc)	1	6	$r = \frac{a}{2}$	$PE = \frac{\pi}{6} \times 100$ $= 52.4\%$	$\rho = \frac{Z_{\text{eff}} \times Mw}{N_A \times a^3 \times 10^{-30}}$ $= \frac{1 \times Mw}{N_A \times a^3 \times 10^{-30}}$	a

2.	Body centred cubic (bcc)	2	8	$r = \frac{\sqrt{3}a}{4}$	$PE = \frac{\sqrt{3}}{8} \pi \times 100$ = 68%	$\rho = \frac{2 \times Mw}{N_A \times a^3 \times 10^{-30}}$	$\frac{\sqrt{3}}{2} a$
3.	Face centred cubic (fcc)	4	12	$r = \frac{a}{2\sqrt{2}}$	$PE = \frac{\sqrt{2}}{6} \pi \times 100$ = 74.04%	$\rho = \frac{4 \times Mw}{N_A \times a^3 \times 10^{-30}}$	$\frac{a}{\sqrt{2}}$

Illustration 8: The density of solid Argon is 1.65 g/mL at -233°C . If the Argon atom is assumed to be sphere of radius 1.54×10^{-8} cm. What percentage of solid Argon is apparently empty space? (Ar = 40) **(JEE ADVANCED)**

Sol: First determine the no. of atoms of Ar present in 1.65 g from this calculate the total volume occupied by all atoms of Ar. we can determine % empty space by subtracting the volume of solid Ar taken and volume occupied by Ar,

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

$$\text{Also, number of atoms in 1.65 g or one cm}^3 = \frac{1.65}{40} \times 6.023 \times 10^{23} = N$$

$$\therefore \text{Total volume of all atoms of Ar in solid state} = \frac{4}{3} \pi r^3 N = \frac{4}{3} \times \frac{22}{7} \times (1.54 \times 10^{-8})^3 \times \frac{1.65}{40} \times 6.023 \times 10^{23} = 0.380 \text{ cm}^3$$

As the volume of solid argon taken = 1 cm^3

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

7. CLOSED PACKING OF CONSTITUENTS

(a) Close Packing in One Dimension: Here, spheres are arranged in a row, touching each other, in a one-dimensional close packed structure as shown below,



Figure 19.7-a: Close packing of spheres in one dimension

(b) Close Packing in Two Dimensions: Two-dimensional close packed structure can be produced by stacking the rows of close packed spheres. This can be done in two different ways as shown in figures (a) and (b).

(i) Square close packing

(ii) Hexagonal close packing

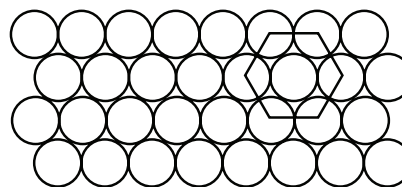
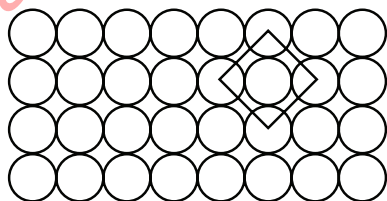


Figure 19.7-b: Close packing of spheres in two dimension

(c) Close Packing in Three Dimensions:

- (i) Hexagonal Close Packing (HCP):** While forming the first layer, minimum space is wasted by utilizing the maximum space possible. In every second row the particles occupy the depressions (also called voids) between the particles of the first row. In the third row, the particles are vertically aligned with those in the first row giving AB AB AB ... type of arrangement. This structure has hexagonal symmetry and is known as hexagonal close packing (HCP). In HCP, the coordination number is 12 and only 26% space is free. A single unit cell has 4 atoms.

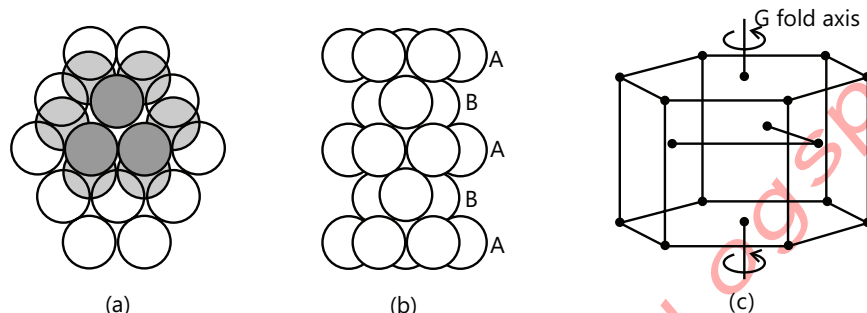


Figure 19.7-c: Hexagonal close packing of spheres in three dimension

- (ii) Cubic Close Packing (CCP):** If we start with hexagonal layer of spheres and second layer of spheres is arranged by placing the spheres over the voids of the first layer, half of these holes can be filled by these spheres. Presume that spheres in the third layer are arranged to cover octahedral holes. When organized this way, the third layer does not resemble either the first or second layer; but the fourth layer is similar to the first layer, fifth layer to second, sixth to third and so on giving pattern ABCABCABC This arrangement has cubic symmetry and is known as cubic closed packed (CCP) arrangement. This is also called face-centred cubic (FCC) arrangement.

The free space available in this packing is 26% and coordination number is 12.

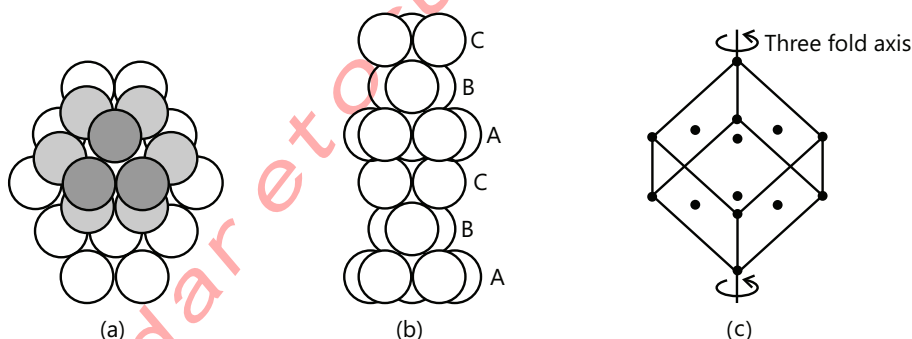


Figure 19.7-d: Cubic close packing of spheres in three dimension

- (iii) Body Centred Close Packing (BCP):** In B.C.P. arrangement, 8 particles are present at the corners and 1 particle is present at the body centre. The coordination number of central sphere is 8. The efficiency of this type of packing is less, only 68% space is occupied and 32% remains unoccupied. A single unit cell has 2 atoms.

PLANCESS CONCEPTS

- In two dimensional hexagonal close packing, there is less free space between sphere than two dimensional square close packing. Thus, hexagonal close packing is denser than square close packing.
- In hexagonal close packing about 60.4% of available space is occupied by spheres whereas square close packing occupies only 52.4% of the space by spheres.
- If only one layer of spheres is to be packed, the spheres arrange themselves in hexagonal close packing.
- In both CCP and HCP, the co-ordination number of spheres remain twelve.

Rohit Kumar (JEE 2012 AIR 79)

Illustration 9: A hexagonal close-packed structure and a cubic close-packed structure for a given element would be expected to have the same density. Explain. **(JEE MAIN)**

Sol: In both the structures, the fraction of the total volume occupied is 0.74. The two structures have the same co-ordination number of 12.

8. VOIDS OR HOLES

The voids/holes are the empty spaces in between closed packed spheres.

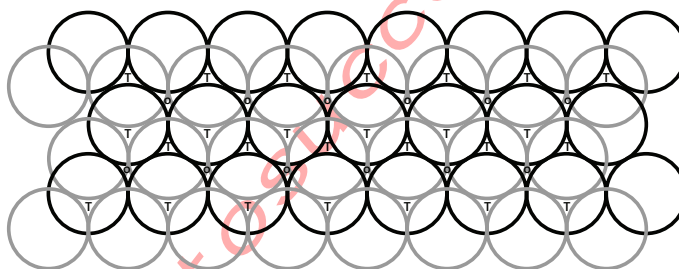


Figure 19.8-a: Representation of a Void

Types of Voids:

- (a) **Octahedral Voids:** This void is surrounded by six spheres and formed by a combination of two triangular voids of the first and second layer. There is one octahedral void per atom in a crystal. The radius ratio ($r_{\text{void}}/r_{\text{sphere}}$) is 0.414.

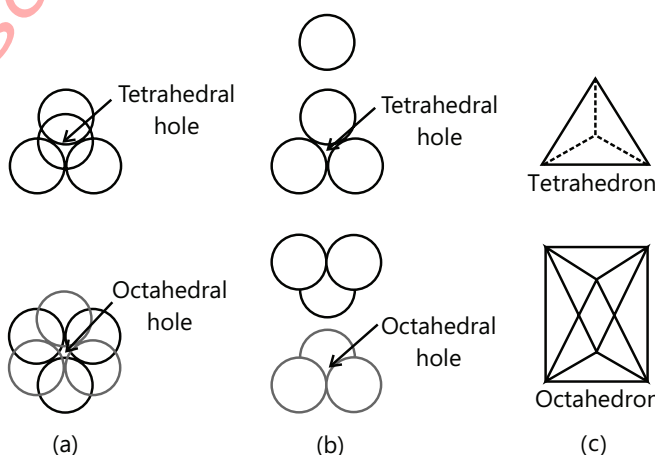


Figure 19.8-b: Tetrahedral and Octahedral Voids (a) top view, (b) exploded side view, and (c) Geometrical shape of the void

- (b) **Tetrahedral Voids:** These voids are surrounded by four spheres, which lie at the vertices of a regular tetrahedron. There are 2 tetrahedral voids per atom in a crystal and the radius ratio is 0.225.
- (c) **Trigonal Voids:** The void enclosed by three spheres in contact is called a trigonal void. There are 8 trigonal voids per atom in a crystal and the radius ratio is 0.155.

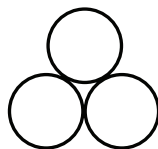


Figure 19.8-c: Trigonal void

Locating Tetrahedral and Octahedral Voids: Both octahedral and tetrahedral voids are present in all closed packed structures. In a CCP pattern, there is one octahedral void at the centre of body and 12 octahedral voids in each of the 12 edges of the cube. Each void on the edge is shared by four other unit cells.

PLANCESS CONCEPTS

The co-ordination number of a tetrahedral void is four. The co-ordination number of an octahedral void is six.

Krishan Mittal (JEE 2012, AIR 199)

Table 19.6: Summary of the Main Characteristics and Examples of Some Simple Ionic Solids

Crystal Structure	Brief description	Examples	Coordination number	Number of formula unit/ units cell	Coordination number
Type AB: Rock salt (NaCl) type	It has fcc arrangement in which Cl^- ion occupy the corners and face centres of a cube while Na^+ ions are present at the body and edge centres.	Halides of Li, Rb, AgF, AgBr, NH_4Cl , NH_4Br , NH_4I	Each Na^+ is surrounded by 6 Cl^- . Each Cl^- is surrounded by 6 Na^+ ; occupy all OVs	General formula A_4B_4 or AB $Z_{\text{eff}} = 4$	6: 6
Radius for fcc	$(r^+ + r^-) = \frac{a}{2}$				
Cesium Chloride (CsCl) type	It has bcc arrangement with Cs^+ at the body centre and Cl^- ions at the corners of a cube or vice versa.	CsCl , CsBr , CsI , CsCN , TlCl , TlBr , TlI and TlCN	Each Cs^+ is surrounded by 8 Cl^- . Each Cl^- is surrounded by 8 Cs^+ .	General formula AB $Z_{\text{eff}} = 1$	8: 8
Radius for bcc type	$(r^+ + r^-) = \frac{\sqrt{3}a}{2}$				
Zinc blende (ZnS) (sphalerite) type	It has ccp arrangement in which S^{2-} ions form fcc and each Zn^{2+} ion is surrounded tetrahedrally by S^{2-} ion vice versa.	CuCl , CuBr , CuI , AgI	Each Zn^{2+} is surrounded by 4 S^{2-} . Each S^{2-} is surrounded by 4 Zn^{2+} . Zn^{2+} are in alternate TVs.	General formula A_4B_4 or AB $Z_{\text{eff}} = 4$	4: 4

Crystal Structure	Brief description	Examples	Coordination number	Number of formula unit/ units cell	Coordination number
Type AB ₂ Fluorite (CaF ₂) type	It has ccp arrangement in which Ca ²⁺ ions form fcc with each Ca ²⁺ ions surrounded by 8 F ⁻ ions and each F ⁻ by 4 Ca ²⁺ ions	BaF ₂ , BaCl ₂ , SrF ₂ , SrC ₂ , CdF ₂ , PbF ₂	Each Ca ²⁺ is surrounded by 8 F ⁻ . Each F ⁻ is surrounded by 4 Ca ²⁺ . F ⁻ ions occupy all the 8 TVs.	General formula A ₄ B ₄ or AB Z _{eff} = 4	8: 4
Type A ₂ B Antifluorite Type	Here O ²⁻ form the ccp arrangement so that each Na ⁺ ion is surrounded by four O ²⁻ ions and each O ²⁻ ion is surrounded by 8 Na ⁺ ions.	Na ₂ O, Li ₂ O	Each Na ⁺ is surrounded by 4 O ²⁻ . Each O ²⁻ is surrounded by 8 Na ⁺ . Na ⁺ ions occupy all the TVs	General formula A ₄ B ₄ or AB Z _{eff} = 4	4: 8

Illustration 10: In a cubic lattice, the closed packed structure of mixed oxides of the lattice is made up of oxide ion; one eighth of the tetrahedral voids are occupied by divalent ions (A²⁺) while one half of the octahedral voids are occupied by trivalent ions (B³⁺). What is the formula of the oxides? **(JEE ADVANCED)**

Sol: Let there be n no. of O²⁻ in the crystal.

∴ Octahedral voids = n

Tetrahedral voids = 2n

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

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

∴ Formula is **AB₂O₄**.

9. RADIUS RATIO

The ratio of radius of cation to anion is known as radius ratio of ionic solids, i.e.,

$$\text{Radius ratio} = \frac{\text{Radius of cation (or } r^+ \text{)}}{\text{Radius of anion (or } r^- \text{)}}$$

Following important conclusions can be drawn from radius ratio of ionic solids.

- If the radius ratio (r^+/r^-) = 0.225, the cation would fit exactly into the tetrahedral voids and have co-ordination number four.
- If the radius ratio (r^+/r^-) = 0.414, the cation would fit exactly into the octahedral voids and have co-ordination number six.

Illustration 11: If the radius of the bromide ion is 0.182 nm, how large a cation can fit in each of the tetrahedral hole? **(JEE MAIN)**

Sol: Radius ratio = $\frac{\text{Radius of cation (or } r^+ \text{)}}{\text{Radius of anion (or } r^- \text{)}}$

For tetrahedral voids (r^+/r^-) = 0.414

From the given value of radius of the bromide ion determine the radius for cation. Depending upon the size of the cation predict the answer.

For tetrahedral voids $(r^+/r^-) = 0.414$ (for maximum value of r^+)

$$r^+ = 0.414 \times 0.182 = 7.53 \times 10^{-2} \text{ nm}$$

Thus, cation of $7.53 \times 10^{-2} \text{ nm}$ will fit exactly in tetrahedral voids.

Illustration 12: In the cubic crystal of CsCl ($d = 3.97 \text{ g cm}^{-3}$) the eight corners are occupied by Cl^- with a Cs^+ at the centre and vice versa. Calculate the distance between neighbouring Cs^+ and Cl^- ions. What is the radius ratio of the two ions? (At. wt. of Cs = 132.91 and Cl = 35.45) **(JEE ADVANCED)**

Sol: In a unit cell, $n = 1$ for cubic crystal

$$\therefore \text{density} = \frac{n \times \text{mol.wt.}}{V \times \text{Av.No.}} = \frac{n \times \text{mol.wt.}}{a^3 \times \text{Av.No.}}$$

$$\therefore 3.97 = \frac{1 \times 168.36}{a^3 \times 6.023 \times 10^{23}}$$

$$a = 4.13 \times 10^{-8} \text{ cm}$$

$$a = 4.13 \text{ \AA}$$

For a cube of side length 4.13 \AA .

$$\text{Diagonal} = \sqrt{3} \times 4.13 = 7.15 \text{ \AA}$$

As it is a bcc with Cs^+ at centre (radius r^+) and Cl^- corners (radius r^-) so,

$$2r^+ + 2r^- = 7.15 \text{ or } r^+ + r^- = 3.57 \text{ \AA}$$

i.e., distance between neighbouring Cs^+ and $\text{Cl}^- = 3.57 \text{ \AA}$

Now assume two Cl^- ions touching each other

So, Length of unit cell $= 2r^- = 4.13 \text{ \AA}$

$$\therefore r^- = 2.06 \text{ \AA}$$

$$\therefore r^+ = 3.57 - 2.06 = 1.51$$

$$\therefore \frac{r^+}{r^-} = \frac{1.51}{2.06} = 0.73$$

10. DEFECTS

Atomic Imperfection: Atomic imperfections are the defects that arise due to irregularity in the arrangement of atoms or ions. These are of following types:

Point Defects: These are caused by missing or misplaced atoms or ions. These involve:

(a) Vacancy defect: If an atom or ion is missing from the lattice site, the defect is known as vacancy defect.

(b) Impurity defect: If a foreign atom or ion occupies a lattice site as an impurity, the defect is called impurity defect. If the foreign atom or ion occupies voids in the structure, the defect is called **interstitial impurity**.

Point Defects: These are caused by a departure from the periodic arrangement in the vicinity of an atom or a group of atoms. Point defects in crystals may be classified as:

(a) Defects in stoichiometric solids, also called as stoichiometric defects.

(b) Defects in non-stoichiometric solids, also called as non-stoichiometric defects.

(c) Impurity defects.

Defects in Stoichiometric Solids: Stoichiometric solids are those in which the number of positive and negative ions are exactly in the ratio indicated by their chemical formulae. These are of 2 types (i) Schottky defect, (ii) Frenkel defect

(i) Schottky Defect: A pair of 'holes' or vacancies exists in the crystal lattice due to one cation and one anion missing from the normal lattice sites. As the number of missing cations and anions remain the same, the crystal as a whole remains the same. This sort of defect occurs in highly ionic compounds with a high coordination number and where the ions (both cations and anions) are of similar size. Alkali metal halides such as NaCl, KCl, KBr, AgBr and CsCl show this defect. In NaCl crystal, at room temperature, there will be one Schottky defect per 10^{16} ions.

Since the presence of large number of Schottky defects in a crystal leads to decrease in the number of ions in the lattice, this results in lowering the density of the solid markedly.

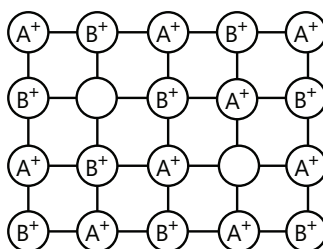


Figure 19.9-a: Schottky defect in a crystal

(ii) Frenkel Defect: When a 'hole' or 'vacancy' exists in the crystal lattice because an ion occupies an interstitial lattice site, it gives rise to Frenkel defect. The crystal remains neutral. The defect occurs more frequently in solids which have low coordination number and possess ions (cations and anions) of different sizes. Since cations are generally smaller than anions, it is more common to find the cations occupying the interstitial sites. For example, in AgBr and ZnS crystals. Ag^+ ions and Zn^{2+} ions are missing from their normal lattice sites and are present in the interstitial positions. AgBr, AgCl and AgI are special cases which show both Schottky and Frenkel defects.

However, the density of the solid remains the same as the presence of Frenkel defect does not change the number of ions in the lattice. The defect causes increase in dielectric constant of the crystals as similar charges come closer.

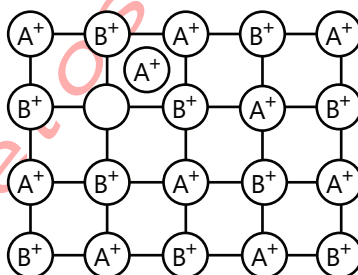
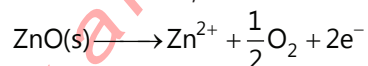


Figure 19.9-b: Frenkel defect observed in a crystal

Illustration 13: Explain, why ZnO becomes yellow on heating?

(JEE ADVANCED)

Sol: Due to Frenkel defect, when ZnO is heated, it loses oxygen reversibly and turns yellow in colour.



The Zn^{2+} ions formed enter the vacant voids in the crystal to form non-stoichiometric solid. The released electrons are trapped in its neighbourhood. It is therefore, non-stoichiometric ZnO is yellow and shows increased conductivity.

Table 19.7: Difference between frenkel and schottky defects

S.No.	Frenkel Defects	Schottky Defects
1.	The ion occupies an interstitial position than its actual lattice position.	Both cations and anions are missing from their lattice positions in the crystal (vacancy defect).

2.	There is no change in the density of the crystal.	The defect decreases the density of the crystal.
3.	It occurs in ionic compounds with low coordination number and with a large difference in the size of cations and anions.	It occurs in compounds with high coordination number and with ions of similar sizes.

Illustration 14: Calculate the concentration of cation vacancies if NaCl is doped with 10^{-3} mole % of SrCl_2 .

(JEE ADVANCED)

Sol: Doping of SrCl_2 to NaCl brings in replacement of two Na^+ ion by each Sr^{2+} ion, but each Sr^{2+} occupies only one lattice point. This produces one cation vacancy.

Thus, doping of 10^{-3} moles of SrCl_2 in 100 mole NaCl will produce cation vacancies = 10^{-3} moles.

\therefore 100 mole NaCl will have cation vacancies after doping = 10^{-3} moles.

\therefore 1 mole of NaCl will have cation vacancies = $\frac{10^{-3}}{100} = 10^{-5}$

\therefore Total cationic vacancies = $10^{-5} \times N_A = 6.02 \times 10^{18}$

11. MAGNETIC PROPERTIES OF SOLIDS

On the basis of their magnetic properties, substances can be classified into five categories.

Table 19.8: Magnetic properties of crystals

Sr. No	Properties	Information	Magnetic Alignment	Example	Application
1.	Diamagnetic	Repelled weakly in magnetic field. Such solids have only paired electrons.	$\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$	Benzene, NaCl, TiO_2 , V_2O_5 , etc.	Insulators
2.	Paramagnetic	Have unpaired electrons; weakly attracted in magnetic field. They cannot be permanently magnetised.	$\uparrow\downarrow \rightarrow \uparrow\downarrow$	O_2 , VO, CuO, TiO	Electronic devices
3.	Ferromagnetic	Also, have unpaired electrons. Strongly attracted in magnetic field. Such solids can be permanently magnetised. On heating to a temperature called Curie Point, these solids change to paramagnetic solid.	$\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow$	Fe, Ni, Co, CrO_2	CrO_2 is used in audio, video tapes.
4.	Antiferromagnetic	In these solids changes electrons align themselves in such a way that resultant magnetic moment is zero.	$\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$	Cr_2O_3 , CoO, Co_3O_4 , Fe_2O_3 , MnO, MnO_2	Used in the instruments of magnetic susceptibility measurement
5.	Ferrimagnetic	unpaired electrons align themselves in such way that there is a net magnetic moment.	$\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$ or $\uparrow\uparrow\downarrow\downarrow\uparrow\uparrow$ $\downarrow\downarrow\uparrow\uparrow$ and so on	Fe_3O_4	–

Curie Temperature: The temperature at which a ferromagnetic substance loses its ferromagnetism and attains paramagnetism only is called Curie temperature. For iron, the Curie temperature is 1033 K, for Ni it is 629 K and for Fe_3O_4 it is 850 K. Below this temperature, paramagnetic substances behave as ferromagnetic substances.

12. ELECTRICAL PROPERTIES OF SOLIDS

Solids are classified into three groups on the basis of their electrical conductivities:

- 1. Conductors:** These generally include metals. Their conductivity is of the order of 10^7 - $10^4 \text{ ohm}^{-1} \text{ m}^{-1}$.
- 2. Semiconductors:** Those solids which have intermediate conductivities ranging from 10^{-6} to $10^4 \text{ ohm}^{-2} \text{ m}^{-1}$ are classified as semiconductors. As the temperature rises there is a rise in conductivity because electrons from the valence band jump to conduction band.
- 3. Insulators:** These are solids which have very low conductivity values ranging from 10^{-10} to $10^{-20} \text{ ohm}^{-1} \text{ m}^{-1}$.

Causes of conductance in solids:

In most of the solids, conduction takes place due to migration of electrons under the influence of electric field. However, in ionic compounds, the movement of the ion is responsible for their conducting behavior. In metals, conductivity strongly depends upon the number of valence electrons available in an atom.

A band is formed due to closeness of molecular orbitals which are formed from atomic orbital.

If this band is partially filled or it overlaps the unoccupied higher energy conduction band, the electrons can flow easily under an applied electric field and the solid behaves as conductor.

If the gap between valence band and next higher unoccupied conduction band is large, electrons cannot jump into it and such a substance behaves as insulator.

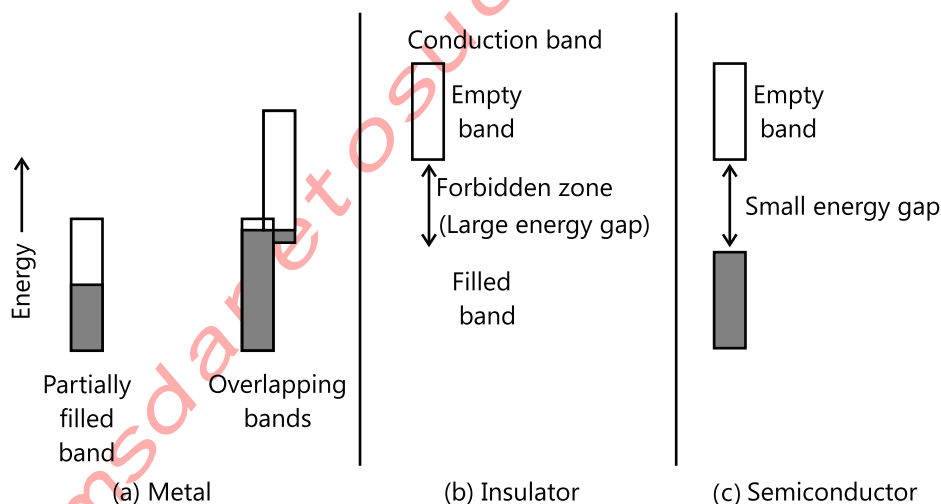


Figure 19.10-a: Distinction among metals, insulators and semiconductors

If the gap between the valence band and conduction band is small, some electrons may jump from valence band to the conduction band. Such a substance shows some conductivity and it behaves as a semiconductor [Fig(c)]. An increase in temperature will increase the electrical conductivity of semiconductors as more electrons can jump from valence to conduction band. Silicon and germanium show this type of behaviour and are called intrinsic semiconductors.

Doping: The process of introducing an impurity into semi-conductors to enhance their conductivity is called doping.

n-type semiconductor: When silicon or germanium crystal is doped with a group 15 element like P or As, the dopant atom forms four covalent bonds like a Si or Ge atom but the fifth electron, not used in bonding, becomes delocalised and contributes its share towards electrical conduction. Thus, silicon or germanium doped with P or As is called n-type semiconductor, n indicative of negative since it is the electron that conducts electricity.

p-type semiconductor: When silicon or germanium is doped with a group 13 element like B or Al, the dopant atom forms three covalent bonds like a B or Al atom, but in place of the fourth electron, a hole is created. This hole moves through the crystal like a positive charge giving rise to electrical conductivity. Thus, Si or Ge doped with B or Al is called p-type of semiconductor (p stands for positive hole), since it is the positive hole that is responsible for conduction.

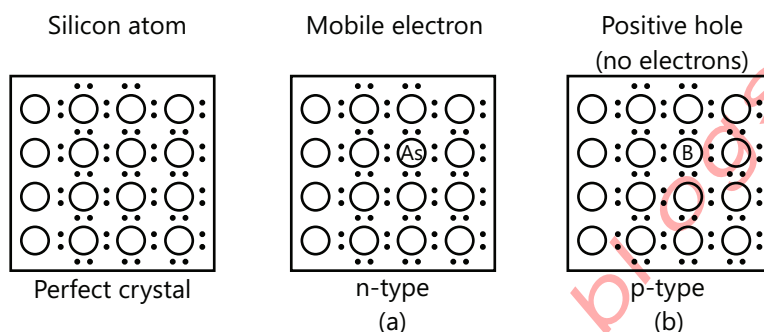


Figure 19.10-b: Distinction among perfect crystal, n-type and p-type semiconductor

Diode: When n-type and p-type semiconductors are combined, what results, is known as a diode. These diodes are used as rectifiers.

Transistors: These are used to detect or amplify radio or audio signals. They consist of pnp or npn Sandwich semiconductors.

Photodiode: These are diodes which are capable of converting light energy into electrical energy and are used in solar cells.

Table 19.9: Electrical properties of crystals

	Properties	Information	Dipolar Property	Example	Application
1.	Piezoelectricity	When a crystal of dielectrics is subjected to mechanical stress, then small magnitude current is produced. It is called direct Piezoelectric effect.	Development of charge in some part of crystal	Quartz and Rochelle salt	–
2.	Anti piezoelectricity	In some solids, electric field develops mechanical effect.	Crystal suffers elastic deformation in an electric field	–	
3.	Ferroelectricity	Piezoelectric crystals having permanent dipoles are said to possess ferroelectricity	↑↑↑↑↑↑	BaTiO ₃ , KH ₂ PO ₄ , Rochelle salt	Electromagnetic appliances
4.	Anti ferroelectricity	Piezoelectric crystals with zero dipole are said to possess anti ferroelectricity.	↑↓↑↓↑↓	PbZrO ₃ , Lead zirconate	
5.	Pyroelectricity	Some polar crystals produce electric impulse on heating.	–	Crystals of tartaric acid	Used in fire alarms, thermostat

13. TYPES OF IONIC STRUCTURES

- (a) **Rock Salt Structure:** (NaCl) Larger atoms form ccp arrangement and smaller atoms fill all octahedral voids.

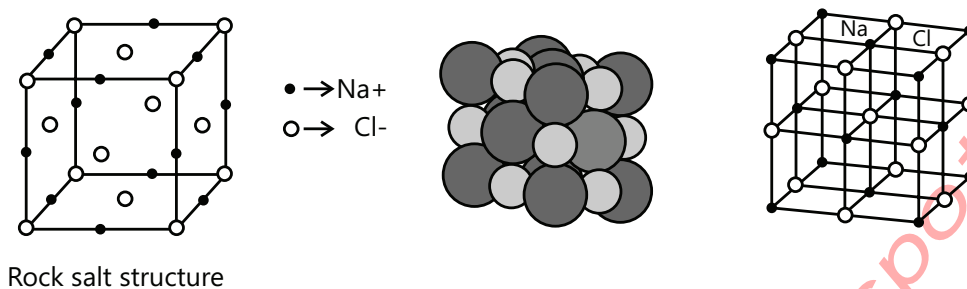


Figure 19.11-a: Arrangement of atoms in rock salt type structure

- (b) **Zinc Blende (Sphalerite) Structure:** (ZnS) Larger atoms form ccp arrangement and smaller atoms fill half of alternate tetrahedral voids.

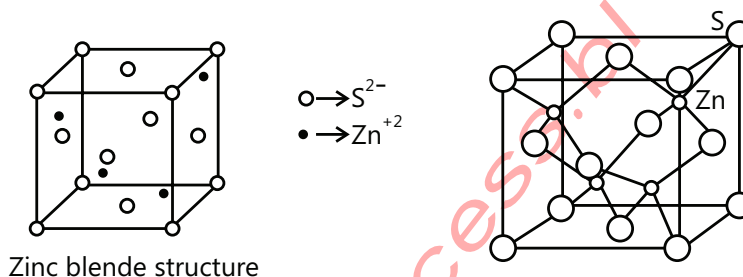


Figure 19.11-b: Arrangement of atoms in Zinc blende type structure

- (c) **Cesium Halide Structure:** (CsCl) Cl⁻ at the corners of cube and Cs⁺ in the centre.

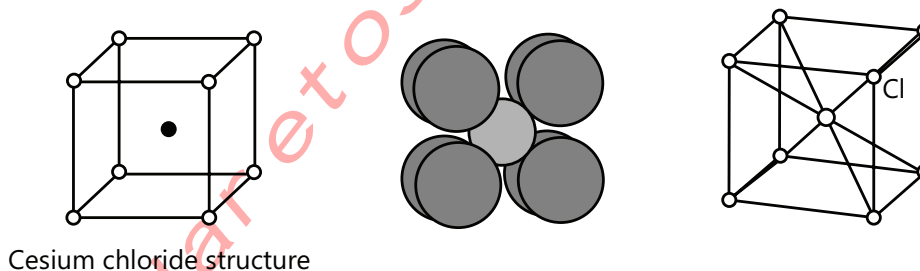


Figure 19.11-c: Arrangement of atoms in cesium chloride type structure

- (d) **Fluorite Structure:** (CaF₂) Ca²⁺ form ccp arrangement and F⁻ fill all tetrahedral voids.

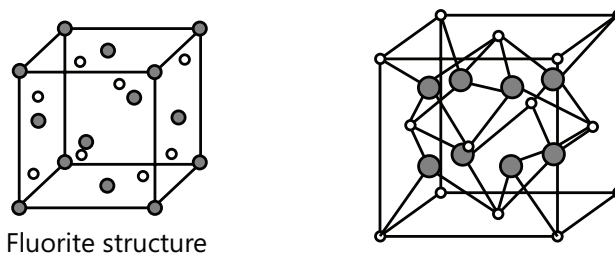
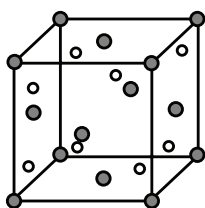


Figure 19.11-d: Arrangement of atoms in fluorite type structure

(e) **Antifluorite Structure:** (Li_2O) O^{2-} ion form ccp and Li^+ take all tetrahedral voids.



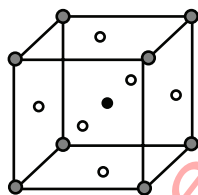
Antifluorite structure

Figure 19.11-e: Arrangement of atoms in antifluorite type structure

(f) **Corundum Structure:** (Al_2O_3) O^{2-} form hcp and Al^{3+} fill $2/3$ octahedral voids.

(g) **Rutile Structure:** (TiO_2) O^{2-} form hcp while Ti^{4+} ions occupy half of the octahedral voids.

(h) **Pervoskite Structure:** (CaTiO_3) Ca^{2+} in the corner of cube, O^{2-} at the face centre and Ti^{4+} at the centre of cube.



Pervoskite structure

Figure 19.11-f: Arrangement of atoms in pervoskite type structure

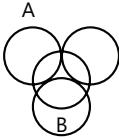
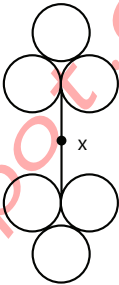
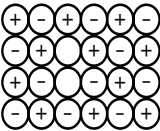
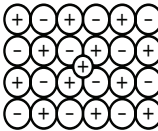
Table 19.10: Summary of some characteristic of some closest and non-closest packed structure

S. No.	Formula	Type of lattice	Type of structure	Z_{eff}	Radius	Packing factor (PF)	TV occupied	OV occupied	Ligancy
1.	AB	Rock salt (NaCl)*	fcc	4	$(r_{A^{\circ}} + r_{B^{\circ}}) = \frac{\pi}{2} a$	$PF = \frac{4 \times \frac{4}{3} \pi r_{A^{\circ}}^2 + 4 \times \frac{4}{3} \pi r_{B^{\circ}}^2}{a^2}$	None	All by Na^{+} ions	6 : 6
2.		ZnS (Zinc blende)	ccp	4	$(r_{A^{\circ}} + r_{B^{\circ}}) = \frac{\sqrt{3}}{4} a$	$PF = \frac{4 \times \frac{4}{3} \pi r_{A^{\circ}}^2 + 4 \times \frac{4}{3} \pi r_{B^{\circ}}^2}{a^2}$	Half by Zn^{2+} ions (Alternate TV)	None	4 : 4
3.		CaCl	hcp	1	$2(r_{A^{\circ}} + r_{B^{\circ}}) = \sqrt{3} a$	$PF = \frac{1 \times \frac{4}{3} \pi r_{A^{\circ}}^2 + 1 \times \frac{4}{3} \pi r_{B^{\circ}}^2}{a^2}$	None	Only one by Cs^{+}	8 : 8
4.	AB_2	CaF_2^{*}	ccp	4	$(r_{A^{\circ}} + r_{B^{\circ}}) = \frac{\sqrt{3}}{4} a$	$PF = \frac{4 \times \frac{4}{3} \pi r_{A^{\circ}}^2 + 8 \times \frac{4}{3} \pi r_{B^{\circ}}^2}{a^2}$	All by Na^{+} ions	None	8 : 4
Note: Here radius rule will change. Now r/r lies in 0.225 – 0.414 as anion lies in TV.						4 : 8			
5.	A_2B	Na_2O (Antifluorite)	ccp	4	$(r_{A^{\circ}} + r_{B^{\circ}}) = \frac{\sqrt{3}}{4} a$	$PF = \frac{8 \times \frac{4}{3} \pi r_{A^{\circ}}^2 + 4 \times \frac{4}{3} \pi r_{B^{\circ}}^2}{a^2}$ $PF = \frac{8 \times \frac{4}{3} \pi r_{A^{\circ}}^2}{a^2} = \frac{\sqrt{3}}{16} \pi = 0.34$	All by Na^{+} ions	None	4 : 8
6.		Diamond Cubic (DC)	fcc	8	$r = \frac{\sqrt{3}}{8} a$	$PF = \frac{8 \times \frac{4}{3} \pi r_{A^{\circ}}^2}{a^2} = \frac{\sqrt{3}}{16} \pi = 0.34$ Height $c = 4 r \frac{\sqrt{2}}{3}$	4 more C – atoms are present in alternate TVs	None	4

S. No.	Formula	Type of lattice	Type of structure	Z_{eff}	Radius	Packing factor (PF)	TV occupied	OV occupied	Ligancy
7.		Hexagonal closed packed (AB AB... packing)	hcp	6	$2r = 4$ $\text{Height (c)} = 4r \frac{\sqrt{2}}{3}$ Base area, $A = 6\sqrt{3} r^2$ $\text{Volume} = 24\sqrt{2} r^3$	$\text{PF} = \frac{\left(6 \times \frac{4}{3} \pi r^3\right)}{24\sqrt{2} r^3} = \frac{\pi}{3\sqrt{2}} = 0.74$ $\text{PF} = \frac{\left(6 \times \frac{4}{3} \pi r^3\right)}{24\sqrt{2} r^3} = \frac{\pi}{3\sqrt{2}} = 0.74$	-	-	-
8.	AB_2O_4	Spinel (ZnAl_2O_4)	fcc	4	$\text{Volume} = a^3 = 16\sqrt{2} r_{\text{O}^{2-}}^3$ For TV, $\frac{r_{\text{Zn}^{2+}}}{r_{\text{O}^{2-}}} = 0.225$ For OV, $\frac{r_{\text{Al}^{3+}}}{r_{\text{O}^{2-}}} = 0.414$	$\text{PF} = \frac{\left[2 \times \frac{4}{3} \pi r_{\text{Al}^{3+}}^3\right] + \left[1 \times \frac{4}{3} \pi r_{\text{Zn}^{2+}}^3\right] + \left[4 \times \frac{4}{3} \pi r_{\text{O}^{2-}}^3\right]}{16\sqrt{2} r_{\text{O}^{2-}}^3}$ $= \frac{\pi}{3\sqrt{2}} \left[\frac{1}{2} \left(\frac{r_{\text{Al}^{3+}}}{r_{\text{O}^{2-}}} \right)^3 + 1 \right]$ $= \frac{\pi}{3\sqrt{2}} \left[\frac{1}{2} (0.414)^3 + \frac{1}{4} (0.225)^3 + 1 \right] = 0.77$	$\text{Zn}^{2+} = \frac{1}{8} \text{ TV}$ $\text{Al}^{3+} = \frac{1}{2} \text{ OV}$ $\text{Al}^{3+} = \frac{2}{3} \text{ OV}$	-	-
9.	Al_2O_3	Corundum (Al_2O_3)	Hcp	6	$\text{Volume of hcp} = 24\sqrt{2} r^3$ For OV, $\frac{r_{\text{O}^{2-}}}{r_{\text{Al}^{3+}}} = 0.414$	$\text{PF} = \frac{\left[6 \times \frac{4}{3} \pi r_{\text{O}^{2-}}^3\right] + \left[4 \times \frac{4}{3} \pi r_{\text{Al}^{3+}}^3\right]}{24\sqrt{2} r_{\text{O}^{2-}}^3}$ $= \frac{\pi}{3\sqrt{2}} \left[1 + \frac{2}{3} \left(\frac{r_{\text{Al}^{3+}}}{r_{\text{O}^{2-}}} \right)^3 \right]$ $= \frac{3.1416}{3 \times 1.414} \left[1 + \frac{2}{3} (0.414)^3 \right] = 0.7756$	$\text{Al}^{3+} = \frac{2}{3} \text{ OV}$	6 : 4	

POINTS TO REMEMBER

Radius Ratio: In a given coordination number, radius ratio has fixed value in the limiting case:	<table border="1"> <tr> <th>C.N</th><th>r^+/r</th></tr> <tr> <td>3</td><td>0.155</td></tr> <tr> <td>4(T_d)</td><td>0.225</td></tr> <tr> <td>4(SP)</td><td>0.414</td></tr> <tr> <td>6</td><td>0.414</td></tr> <tr> <td>8</td><td>0.732</td></tr> </table>	C.N	r^+/r	3	0.155	4(T_d)	0.225	4(SP)	0.414	6	0.414	8	0.732
C.N	r^+/r												
3	0.155												
4(T_d)	0.225												
4(SP)	0.414												
6	0.414												
8	0.732												
Packing fraction [ϕ]: It is the maximum fractional volume of unit cell which can be occupied by atoms or ions. In case of atomic solids of like atoms, following are the values of packing fractions	<table border="1"> <tr> <th>Typing of unit cells</th><th>Packing fractions</th></tr> <tr> <td>Simple cubic</td><td>0.53</td></tr> <tr> <td>Body centred cubic</td><td>0.68</td></tr> <tr> <td>Fcc</td><td>0.74</td></tr> <tr> <td>Hcp</td><td>0.74</td></tr> </table>	Typing of unit cells	Packing fractions	Simple cubic	0.53	Body centred cubic	0.68	Fcc	0.74	Hcp	0.74		
Typing of unit cells	Packing fractions												
Simple cubic	0.53												
Body centred cubic	0.68												
Fcc	0.74												
Hcp	0.74												
Relationship between radius and sides of unit cells in atomic solids (a = edge length, r = atomic radius):	<table border="1"> <tr> <td>SC</td><td>$A=2r$</td></tr> <tr> <td>Bcc</td><td>$\sqrt{3}a = 4r$</td></tr> <tr> <td>Fcc</td><td>$\sqrt{2}a = 4r$</td></tr> <tr> <td>Hcp</td><td>$h = \left(4\sqrt{\frac{2}{3}}\right)r$</td></tr> </table>	SC	$A=2r$	Bcc	$\sqrt{3}a = 4r$	Fcc	$\sqrt{2}a = 4r$	Hcp	$h = \left(4\sqrt{\frac{2}{3}}\right)r$				
SC	$A=2r$												
Bcc	$\sqrt{3}a = 4r$												
Fcc	$\sqrt{2}a = 4r$												
Hcp	$h = \left(4\sqrt{\frac{2}{3}}\right)r$												
Bravias lattices:	Based on the arrangement of atoms or ions, the seven crystal systems are further classified into 14 types known as the bravias lattices.												
Primitive cell:	A primitive cell is a bravias lattice that homes only one atom (effectively) in one unit cell.												
Density of solid [ρ]:	$\rho = \frac{\text{Mass of atoms / ions in one unit cell}}{\text{volume of an unit cell}}$												
Cubic System :	$\rho = \frac{NM}{N_A} \left(\frac{1}{a^3} \right) \text{gcm}^{-3}$ <p> N=number of atoms per unit cell, M=molar mass, N_A =Avogadro's number a^3=volume of unit cell in cm^3 </p>												

<p>Tetrahedral and Octahedral void (Holes) :</p>	<p>(i) Number of tetrahedral voids = $2 \times$ effective number of atoms/unit cell.</p> <p>(ii) Number of octahedral voids = Number of atoms (effectively) per unit cell.</p> <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">  <p>The interstices below B is tetrahedral void</p> </div> <div style="text-align: center;">  <p>x is the central of octahedral void</p> </div> </div>
<p>Crystal defects :</p>	<p>A) Point Defects\Stoichiometric defects</p> <p>Two types:-</p> <p>(i) Schottky Defect –Atoms or ions absent from their normal lattice sites. Observed in NaF, KCl etc.</p> <p>(ii) Frenkel Defect- Smaller cation leaves its normal lattice, occupies the interstitial site. Observed in solids with smaller cations like LiI.</p> <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">  <p>Schottky defect</p> </div> <div style="text-align: center;">  <p>Frenkel defect</p> </div> </div> <p>B) F-center defect-Alkali metal vapours passed on an ionic solid lets out electrons which substitute some anions leading to trapped electrons.</p>

Based on the geometry of unit cells, solids are divided into seven crystal systems as:

System	Parameters	Interaxial angle
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma$
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma \neq \beta \neq 90^\circ$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ \neq \gamma = 120^\circ$
Rhombohedral (or) (Trigonal)	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$

Solved Examples

JEE Main/Boards

Example 1: Both diamond and rhombic (solid) sulphur are covalent solids, however, the latter has very low m.pt. in comparison to diamond. Explain.

Sol: Value of Boiling point and melting point depends on intermolecular force of attraction. By taking into consideration the forces that help the two structure (diamond and sulphur) to hold together, answer the question.

Diamond has three dimensional covalent network and strong intermolecular forces whereas rhombic sulphur has one dimensional covalent network with puckered eight membered ring held together by weak van der Waals' forces.

Example 2: Calculate the number (n) of atoms contained within (a) simple cubic cell (b) a body centred cubic cell (c) a face centred cubic cell.

Sol: (a) The simple cubic unit cell has 8 atoms at eight corners. Each atom is shared by 8 unit cells.

$$\therefore n = 8 \times \frac{1}{8} = 1$$

(b) The body centred cubic cell consists of 8 atoms at the corners and one atom at centre.

$$\therefore n = \left(8 \times \frac{1}{8} \right) + 1 = 2$$

(c) The face centred cubic unit cell consists of 8 atoms at the eight corners and one atom at each of the six faces. This atom at the face is shared by two unit cells.

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

Example 3: An element having atomic mass 60 has face centred cubic unit cells. The edge length of the unit cell is 400 pm. Find out density of the element.

Sol: From the edge length determine the volume of unit cell as, Volume = a^3

Density can be determined using the following expression that relates density with edge length.

$$\rho = \frac{4 \times M_w}{N_A \times a^3 \times 10^{-30}}$$

Edge length of unit cell = 400 pm

$$= 400 \times 10^{-12} \text{ m}$$

$$(1 \text{ pm} = 10^{-12} \text{ m})$$

$$= 400 \times 10^{-10} \text{ cm}$$

Volume of unit cell

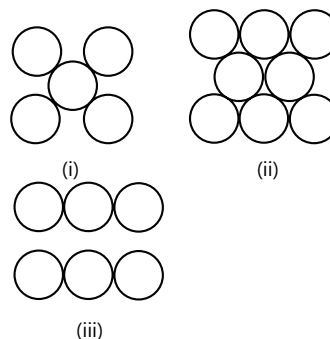
$$= (400 \times 10^{-10} \text{ cm})^3$$

$$= 64 \times 10^{-24} \text{ cm}^3$$

Number of atoms (n) in the fcc unit cell = 4

$$\therefore \text{Density} = \frac{4 \times 60}{6.023 \times 10^{23} \times 64 \times 10^{-24}} \\ = 6.23 \text{ g cm}^{-3}$$

Example 4: The figures given below show the location of atoms in three crystallographic planes in a fcc lattice. Draw the unit cell for the corresponding structure and identify these planes in your diagram.



Sol: (i) Face plane,

(ii) Face diagonal plane and

(iii) Diagonal plane

Example 5: Ferric oxide crystallizes in a hexagonal closed packed array of oxide ions, with two out of every three octahedral holes occupied by ferric ions. Derive the formula of the ferric oxide.

Sol: Hexagonal close packing has an array of oxide ions, where two out of three octahedral holes occupied by Fe^{3+} ions has one octahedral void or holes corresponding to each atom constituting the close packing. In iron oxide only $2/3$ of octahedral holes are occupied by Fe^{3+} ions. It means corresponding to each oxide ion, there are $2/3$ Fe^{3+} ions. Thus, molecular formula of iron oxide is Fe_2O_3 .

Example 6: The structure of CsCl is different from NaCl, though both have the similar formula. Explain.

Sol: CsCl has radius ratio ≥ 0.732 and shows cubic arrangement, whereas radius of NaCl is < 0.732 and has octahedral arrangement.

Example 7: Calculate the wavelength of X-rays, which produces a different angle 2θ equal to 16.80° for a crystal. Assume first order diffraction with inter particle distance in crystal of 0.2 nm.

Sol: using Bragg's equation, $n\lambda = 2d\sin\theta$

Calculate the Wavelength.

Given, $n = 1$, $d = 0.2 \times 10^{-9}$ m,

$$\theta = \frac{16.80}{2} = 8.40^\circ$$

$$\text{Thus, } \lambda = \frac{2 \times 0.2 \times 10^{-9} \sin 8.4}{1} = 5.84 \times 10^{-11} \text{ m}$$

Example 8: Explain, why solids with F-centres are paramagnetic?

Sol: Solids containing F-centres are paramagnetic because the electrons occupying the holes are unpaired.

Example 9: A fcc lattice cube is formed by atoms A and B. If atom A is present at the corner of the cube and the atom B at the faces of the cube. Find out the formula of the compound.

Sol: Contribution of atom 'A' at eight corners of the cube

$$= \frac{1}{8} \times 8 = 1 \text{ atom}$$

Contribution of atom at each face = $\frac{1}{2}$ atom

$$\therefore \text{The atom 'B' at six faces of the cube} \\ = \frac{1}{2} \times 6 = 3 \text{ atom}$$

$$\therefore \text{Formula of the compound} = \mathbf{AB_3}$$

Example 10: A metallic element crystallizes into a lattice containing a sequence of layers of ABABAB Any packing of spheres leaves out voids in the lattice. What percentage by volume of this lattice is empty space?

$$\begin{aligned} \text{Sol: Packing fraction in hcp} &= \frac{6 \times \frac{4}{3} \pi r^3}{\text{Volume}} \\ &= \frac{6 \times 4 \pi r^3}{3 \times \text{Area} \times \text{Height}} \end{aligned}$$

Area (of base) of unit cell in hcp

$$= 6\sqrt{3}r^2 \text{ (Follow text)}$$

Height of unit cell in hcp

$$= 4r \times \sqrt{\frac{2}{3}} \text{ (follow text)}$$

$$\begin{aligned} \therefore \text{Packing fraction} &= \frac{6 \times 4 \pi r^3}{3 \times 6\sqrt{3}r^2 \times 4r \times \sqrt{\frac{2}{3}}} \\ &= \frac{\pi}{3\sqrt{2}} = 0.74 \text{ or } 74\% \end{aligned}$$

Thus, empty space in hcp = $1 - 0.74 = 0.26$ or 26%

JEE Advanced/Boards

Example 1: Metallic gold crystallizes in the face-centred cubic lattice. The length of the cubic unit cell is $a = 4.070 \text{ \AA}$.

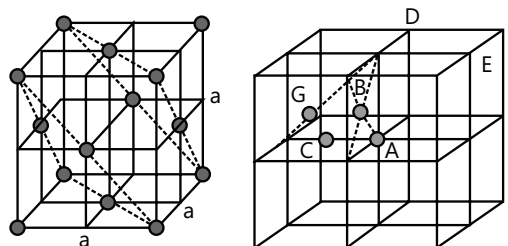
- What is the closest distance between gold atoms?
- How many 'nearest neighbours' does each gold atom have at the distance calculated in (a)?
- What is the density of gold?
- Prove that the packing factor for gold, the fraction of the total volume occupied by the atoms themselves, is 0.74.

Sol: (a) In fcc, $a = 2\sqrt{2}r$

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

$2r$ is closest distance between two atom.

$$\therefore 2r = \frac{4.070}{1.414} = 2.878 \text{ \AA}$$



(b) The problem is to find how many face centers are equidistant from a corner atom. Point A in figure may be taken as the reference corner atom. In that same figure, B is one of the face-center points at the nearest distance to A. In plane ABD in the figure, there are three other points equally close to A: the centers of the squares in the upper right, lower left, and lower right quadrants of the plane, measured around A. Plane ACE,

parallel to the plane of the paper, also has points in the centers of each of the squares in the four quadrants around A. Also, plane ACF, perpendicular to the plane of the paper, has points in the centers of each of the squares in the four quadrants around A. Thus there are 12 nearest neighbors in all, the number expected for a close-packed structure.

The same result would have been obtained by counting the nearest neighbours around B, a face-centered point.

(c) In fcc, $n = 4$, $M = 197 \text{ g mol}^{-1}$

$a = 4.070 \text{ \AA} = 4.070 \times 10^{-10} \text{ cm}$

$$\text{density} = \frac{n \times M}{N_A \cdot a^3} = \frac{4 \times 197}{6.022 \times 10^{23} \times (4.07 \times 10^{-10})^3}$$

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

(d) Since atoms at closest distance are in contact in a close-packed structure, the closest distance between centres calculated in (a), $\frac{a}{\sqrt{2}}$, must equal the sum of the radii of the two spherical atoms, $2r$. Thus, $r = a/2^{3/2}$. From (c), there are 4 gold atoms per unit cell.

Then, Volume of 4 gold atoms $= 4 \left(\frac{4}{3} \pi r^3 \right)$

\therefore Volume of unit cell $= a^3$

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

$$= 16\sqrt{2}r^3$$

\therefore Packing fraction $= \frac{\text{volume of 4 gold atoms}}{\text{volume of unit cell}}$

$$= \frac{\frac{16}{3} \pi r^3}{16\sqrt{2}r^3} = \frac{\pi}{3\sqrt{2}} = 0.74$$

Example 2: A metal crystallizes into two cubic phases, face centred cubic (FCC) and body centred cubic (BCC), whose unit cell lengths are 3.5 and 3.0 Å, respectively. Calculate the ratio of densities of FCC and BCC.

Sol: We know that

$$\rho = \frac{Z \times \text{Formula mass of substance}}{N_0 \times a^3}$$

Since for FCC, $Z = 4$ and for BCC, $Z = 2$

$$d_{\text{FCC}} = \frac{4 \times \text{Formula mass of metal}}{N_0 \times (3.5)^3}$$

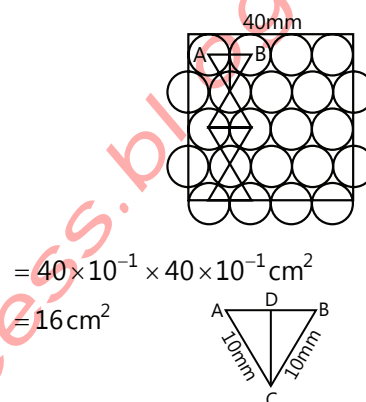
$$\text{and } d_{\text{BCC}} = \frac{2 \times \text{Formula mass of metal}}{N_0 \times (3)^3}$$

Dividing d_{FCC} and d_{BCC}

$$\frac{d_{\text{FCC}}}{d_{\text{BCC}}} = \frac{4}{2} \times \frac{(3)^3}{(3.5)^3} = 2 \times 0.6297 = 1.259$$

Example 3: You are given some marbles with a diameter of 10mm. They are to be placed such that their centres are lying in a square bond by four lines each of length 40 mm. What will be the arrangements of marbles in a plane so that maximum number of marbles can be placed inside the area? Sketch the diagram and derive expression for the number of molecules per unit area.

Sol: Area of square having spherical marbles in it



$$= 40 \times 10^{-1} \times 40 \times 10^{-1} \text{ cm}^2$$

$$= 16 \text{ cm}^2$$

$$CD = 10 \sin 60^\circ = 10 \frac{\sqrt{3}}{2} = 5\sqrt{3}$$

The maximum number of spheres of 10 mm diameter in hcp packing can be seen in figure.

Total length converted by spheres

$$= 5 + 4 \times CD = 5 + 4 \times 10 \sin 60^\circ$$

$$= 5 + 4 \times 5\sqrt{3} = 40 \text{ mm} = 4 \text{ cm}$$

Maximum number of spheres (s)

$$= 14 + 8$$

$$(\text{Full}) \quad (\text{half})$$

$$= 14 + 4 = 18$$

$$\therefore \text{Number of spheres per cm}^2 = \frac{18}{16} = 1.125$$

Example 4: Using the given data find out the type of cubic lattice to which the crystal belong:

	Fe	V	Pd	Al
a in pm	286	301	388	405
ρ in g cm^{-3}	7.86	5.96	12.16	2.70
At. mass in g mol^{-1}	55.85	50.94	106.4	26.98

Sol: We know, $\rho = \frac{n \times \text{At. mass}}{N_0 \times a^3}$

or $n = \frac{\rho \times N_0 \times a^3}{\text{At. mass}}$

For Fe:

$$n = \frac{7.86 \times 6.023 \times 10^{23} \times (286 \times 10^{-10})^3}{55.85} = 2$$

(i.e., cubic lattice of Fe is body centred)

For V:

$$n = \frac{5.96 \times 6.023 \times 10^{23} \times (301 \times 10^{-10})^3}{50.94} = 2$$

(i.e., cubic lattice of V is body centred)

For Pd:

$$n = \frac{12.16 \times 6.023 \times 10^{23} \times (388 \times 10^{-10})^3}{106.4} = 4$$

(i.e., cubic lattice of Pd is face centred)

For Al:

$$n = \frac{2.70 \times 6.023 \times 10^{23} \times (405 \times 10^{-10})^3}{26.98} = 4$$

(i.e., cubic lattice of Al is face centred)

Example 5: The density of a particular crystal of LiF is 2.65 g/cc. X-ray analysis shows that Li^+ and F^- ions are arranged in a cubic array at a spacing of 2.01 Å. From these data calculate the apparent Avogadro constant.

[Li = 6.939, F = 18.998 (1 Å = 10^{-8} cm)]

Sol: In this problem, we have to calculate Avogadro constant, i.e., the number of LiF molecules percent in 1 mole of LiF weighs 25.937 g

(LiF = 6.939 + 18.998),

$$\begin{aligned} \text{Volume of 1 mole} &= \frac{\text{wt. of 1 mole}}{\text{wt. per cc (density)}} \\ &= \frac{25.937}{2.65} = 9.78 \text{ cc.} \end{aligned}$$

Since this volume is supposed to be a cube, the length of each edge of the cube

$$= \sqrt[3]{9.78} = 2.138 \text{ cm.}$$

Number of ions present in one edge

$$= \frac{2.138}{2.01 \times 10^{-8}} = 1.063 \times 10^8$$

Number of ions (Li^+ + F^-) present in cube

$$= (1.063 \times 10^8)^3 = 1.201 \times 10^{24}$$

Number of LiF molecules per mole

(i.e., Avogadro constant)

$$= \frac{1.201 \times 10^{24}}{2} = 6.01 \times 10^{23}$$

Example 6: Calculate the glancing angle on the cube (100) of a rock salt ($a = 2.814$ Å) corresponding to second order diffraction maximum for X-rays of wavelength 0.710 Å.

Sol: First determine the distance between lattice plane by using the following expression, $d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$

And then θ angle can be calculated using Bragg's equation

$$2d \sin \theta = n\lambda \quad \dots(i)$$

The distance between consecutive lattice planes is defined by Miller indices (h, k, l) in a cubic lattice by the relation

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} = 2.814 \text{ Å, } h=1, k=0, l=0$$

$$\therefore d_{100} = \frac{2.814 \text{ Å}}{\sqrt{1^2 + 0^2 + 0^2}} = 2.814 \text{ Å} = 2.814 \times 10^{-8} \text{ cm}$$

From equation (i)

$$2 \times 2.814 \times 10^{-8} \sin \theta = 2 \times 0.710 \times 10^{-8}$$

$$\sin \theta = \frac{2 \times 0.710 \times 10^{-8}}{2 \times 2.814 \times 10^{-8}} = 0.2533$$

$$\sin \theta = 0.2533$$

$$\therefore \theta = \sin^{-1}(0.2533)$$

$$\text{or } \theta = 14^\circ 36' 40''$$

Example 7: The edge length of unit cell of a metal having molecular weight 75 g mol⁻¹ is 5 Å which crystallizes in body centred cubic lattice. If density is 2 g cm⁻³, calculate radius of metal atom.

Sol: Density $= \frac{n \times \text{Mol. wt.}}{V \times N_A}$

$$2 = \frac{2 \times 75}{a^3 \times 6.023 \times 10^{23}}$$

($n = 2$ for bcc)

$$\therefore a = 5 \times 10^{-8} \text{ cm}^3$$

$$\therefore r = \frac{\sqrt{3}}{4} \times a = \frac{\sqrt{3}}{4} \times 5 \times 10^{-8}$$

$$= 2.16 \times 10^{-8} \text{ cm} = 216 \text{ pm}$$

Example 8: A solid compound contains X, Y and Z atoms in a cubic lattice with X atoms occupying the corners, Y atoms in the body centred position and Z atom at the centre of the face of the unit cell. What is the empirical formula of the compound?

- (A) XY_2Z_3 (B) XYZ_3
(C) $X_2Y_2Z_3$ (D) X_8YZ_6 (E) XYZ

Sol: (B) Number of atoms of X in a unit cell = $\frac{1}{8} \times 8 = 1$

Number of atoms of Y in a unit cell = 1

Number of atoms of Z in a unit cell = $\frac{1}{2} \times 6 = 3$

Empirical formula of the compound = XYZ_3

Example 9: When an electron in an excited state of Mo atom falls from L to K-shell, an X-ray is emitted. These X-rays are diffracted at angle of 7.75° by planes with a separation of 2.64 \AA . What is the difference in energy between K-shell and L-shell in Mo, assuming a first order diffraction? ($\sin 7.75^\circ = 0.1349$)

Sol: Using Bragg's equation first determine the wavelength and then energy can be calculated as

$$E = \frac{hc}{\lambda}$$

$$n\lambda = 2d\sin\theta$$

$$1 \times \lambda = 2 \times 2.64 \sin 7.75^\circ$$

$$= 2 \times 2.64 \times 0.1349$$

$$\lambda = 0.712 \text{ \AA}$$

Energy difference between K and L-shell of Mo

$$= \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{0.712 \times 10^{-10}} = 2.791 \times 10^{-15} \text{ J}$$

Example 10: The density of crystalline sodium chloride is 2.165 g cm^{-3} . What is the edge length of the unit cell? What would be the dimensions of cube containing one mole of NaCl?

Sol: We know that, $\rho = \frac{N}{a^3} \left(\frac{M}{N_A} \right)$

Where, ρ = density = 2.165 g cm^{-3}

M = molar mass = 58.5

N_A = Avogadro's number = 6.023×10^{23}

N = number of formula unit

per unit cell = 4 (for bcc)

$$a^3 = \frac{N}{\rho} \left(\frac{M}{N_A} \right) = \frac{4}{2.165} \left[\frac{58.5}{6.023 \times 10^{23}} \right] = 1.794 \times 10^{-22}$$

$$a = 5.64 \times 10^{-8} \text{ cm}$$

$$\text{Molar volume} = \frac{\text{Molar mass}}{\text{Density}} = \frac{58.8}{2.165}$$

$$\text{Edge length (a)} = \left[\frac{58.8}{2.165} \right]^{1/3} = 3 \text{ cm}$$

Example 11: In a solid AB having the NaCl structure, A atoms occupy the corners of the cubic unit cell. If all the face centred atoms along one of the axis are removed. what would be the resultant stoichiometry of solid?

Sol: AB has NaCl structure, i.e., 8 corner and 6 face centred atoms. If we remove face centred atoms of one axis, two face centred atoms are removed. Thus, A is at 8 corners and B is at four faces.

$$\therefore \text{Contribution of A} = \frac{8}{8} = 1$$

$$\text{Contribution of B} = \frac{4}{2} = 2$$

$$\therefore \text{Stoichiometry of resultant solid is } AB_2.$$

JEE Main/Boards

Exercise 1

Q.1 Explain each of the following with a suitable example:

- (i) Paramagnetism.
- (ii) Frenkel defect in crystals.

Q.2 State the difference between Schottky and Frenkel defects. Which of the two changes the density of the solid?

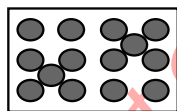
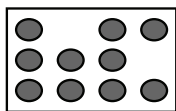
Q.3 (a) What is meant by anisotropy?

(b) Give a sketch of arrangement of particles in a solid which would show anisotropy.

Q.4 (a) Explain with the help of figure square close-packing and hexagonal close-packing of particles in a solid in two dimensions.

(b) What is the coordination number of a particle in the two packings?

Q.5 Some crystal defects are shown in the figures below:



Indicate the types of defect shown by (a) and (b).

Q.6 A compound is formed by two elements M and N. The element N forms ccp and atoms of M occupy $\frac{1}{3}$ rd of tetrahedral voids. What is the formula of the compound?

Q.7 An element with molar mass 2.7×10^{-2} kg mol⁻¹ forms a cubic unit cell with edge length 405 pm. If its density is 2.7×10^3 kg m⁻³, what is the nature of the cubic unit cell?

Q.8 An element occurs in bcc structure with cell edge 300 pm. The density of the element is 5.2 g cm⁻³. How many atoms of the element does 200 g of the element contain?

Q.9 The density of chromium metals is 7.2 g cm⁻³. If the unit cell has edge length of 289 pm, determine the type of unit cell. [Atomic mass of Cr = 52 u; $N_A = 6.02 \times 10^{23}$ mol⁻¹]

Q.10 An element crystallizes in fcc structure. 200 g of this element has 4.12×10^{24} atoms. The density of A is 7.2 g cm⁻³. Calculate the edge length of the unit cell.

Q.11 Lithium metal crystal has body-centred cubic structure. Its density is 0.53 g cm⁻³ and its molecular mass is 6.94 g mol⁻¹. Calculate the volume of a unit cell of lithium metal. [$N_A = 6.023 \times 10^{23}$ mol⁻¹]

Q.12 If NaCl crystals are doped with 2×10^{-3} mol per cent of SrCl₂, calculate the cation vacancies per mole.

Q.13 An element exists in bcc structure with a cell edge of 288 pm. If the density of the element is 7.2 g cm⁻³, what is the atomic mass of the element? [$N_A = 6.023 \times 10^{23}$ mol⁻¹]

Q.14 An element A crystallises in fcc structure, 208 g of this element has 4.283×10^{24} atoms. If edge length of the unit cell of this element is 408 pm, calculate its density.

Q.15 Copper crystallises in face-centred cubic lattice and has a density of 8.930 g cm⁻³ at 239 K. Calculate the radius of Copper atom. [At. mass of Cu = 63.55 u, Avogadro's constant $N_A = 6.02 \times 10^{23}$ mol⁻¹]

Q.16 Metallic gold crystallises in a fcc lattice and has a density of 19.3 g cm⁻³. Calculate the radius of gold atom. [At. mass of gold = 197 u, $N_A = 6.023 \times 10^{23}$ mol⁻¹]

Q.17 A substance forms face-centred cubic crystals. If the edge length of the unit cell is 630 pm and density of the substance is 1.984 g cm⁻³, calculate the molar mass of substance.

Q.18 In a solid AB, having the NaCl structure, B atoms occupy the corners of the cubic unit cell. If all the face centred atoms along one of the axes are removed, then what is the resulting stoichiometry of the solid?

Q.19 Lithium boron hydride crystallizes in an orthorhombic system with 4 molecules per unit cell. The unit cell dimensions are $a = 6.8$ Å, $b = 4.4$ Å and $c = 7.2$ Å. If the molar mass is 21.76, calculate density of crystal.

Q.20 The simple cubic lattice consists of eight identical spheres of radius R in contact, placed at the corners of a cube, what is the volume of the cubical box that will just enclose these eight spheres and what fraction of this volume is actually occupied by the spheres?

Q.21 In an ionic oxide, oxide ions are arranged in hcp array and positive ion occupy two thirds of octahedral void. Suggest the simplest formula assuming metal as M.

Q.22 A compound containing Zn, Al and S crystallises with a closed packed array of sulphide ions. Zinc ions are found in one-eighth of the tetrahedral holes and aluminium ions in one half of the octahedral holes. What is the empirical formula of the compound?

Q.23 What is the percent by mass of titanium in rutile, a mineral that contains Ti and oxygen? If structure can be described as a closest packed array of oxide ions with titanium ions in a one-half of the octahedral holes? What is the oxidation number of titanium? (Ti = 48)

Q.24 Calculate packing efficiency in ccp structure. How does it differ from packing efficiency in hcp structure?

Q.25 A strong current of trivalent gaseous boron passed through a germanium crystal decreases the density of the crystal due to part replacement of germanium by boron and due to interstitial vacancies created by missing Ge atoms. In one such experiment, one gram of germanium is taken and the boron atoms are found to be 150 ppm by weight, when the density of the Ge crystal decreases by 4%. Calculate the percentage of missing vacancies due to germanium, which are filled up by boron atoms. [Atomic wt. Ge = 72.6, B = 11]

Q.26 What is a semiconductor? Describe two main types of semiconductors and explain mechanism for their conduction.

Q.27 (a) The electrical conductivity of a metal decreases with rise in temperature while that of a semiconductor increases. Explain.

(b) The ions of NaF and MgO have the same number of electrons and internuclear distances are about the same [235 pm and 215 pm]. Why are then the melting points of NaF and MgO so different [992°C and 2642°C]?

(c) Why does zinc oxide exhibit enhanced electrical conductivity on heating?

Q.28 Bring out with the help of a sketch the difference between metals insulators and semiconductors in terms of energy gap between valence band and conduction band.

Q.29 Explain with the help of a figure, how an electron (i) moving in an orbital and (ii) spinning in an atom give magnetic properties.

Q.30 How can you show with the help of a diagram that number of octahedral voids is equal to the number of atoms in cubic close packed structure?

Exercise 2

Single Correct Choice Type

Q.1 A solid has a structure in which W atoms are located at the corners of a cubic lattice, O atom at the centre of the edges and Na atom at centre of the cubic. The formula for the compound is:

- (A) NaWO_2 (B) NaWO_3 (C) Na_2WO_3 (D) NaWO_4

Q.2 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

Q.3 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.

Q.4 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^-

Q.5 Which one of the following schemes of ordering closed packed sheets of equal sized spheres do not generates close packed lattice.

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

Q.6 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

Q.7 The tetrahedral voids formed by ccp arrangement of Cl^- ions in rock salt structure are

- (A) Occupied by Na^+ ions
(B) Occupied by Cl^- ions
(C) Occupied by either Na^+ or Cl^- ions
(D) Vacant

Q.8 The number of nearest neighbours around each particle in a face-centred cubic lattice is

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

Q.9 If the anions (A) from hexagonal closest packing and cations (C) occupy only $\frac{2}{3}$ 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

Q.10 A solid is formed and it has three types of atoms X, Y, Z. X forms a FCC lattice with Y atoms occupying all the tetrahedral voids and Z atoms occupying half the octahedral voids. The formula of the solid is

- (A) X_2Y_4Z (B) XY_2Z_4 (C) X_4Y_2Z (D) X_4YZ_2

Q.11 The intermetallic compound LiAg crystallizes in cubic lattice in which both lithium and silver have coordination number of eight. The crystal class is

- (A) Simple cubic (B) Body centred cubic
(C) Face centred cubic (D) None of these

Q.12 NH_4Cl crystallizes in a body-centred cubic type lattice with a unit cell edge length of 387 pm. The distance between the oppositely charged ions in the lattice is

- (A) 335.1 pm (B) 83.77 pm
(C) 274.46 pm (D) 137.33 pm

Previous Years' Questions

Q.1 The coordination number of a metal crystallizing in a hexagonal close-packed structure is (1999)

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

Q.2 In a solid 'AB' having the 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 (2001)

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

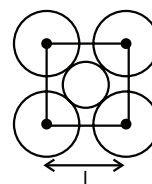
Q.3 A substance A_xB_y crystallizes in a face centred cubic (fcc) lattice in which atoms 'A' occupy each corner of the cube and atom 'B' occupy the centres of each face of the cube. Identify the correct composition of the substance A_xB_y . (2002)

- (A) AB_3 (B) A_4B_3
(C) A_3B (D) Composition cannot be specified

Q.4 Which of the following fcc structure contains cations in alternate tetrahedral voids? (2005)

- (A) NaCl (B) ZnS (C) Na_2O (D) CaF_2

Q.5 The packing efficiency of the two-dimensional square unit cell shown below is (2010)



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

Q.6 Statement-I: In any ionic solid (MX) with Schottky defects, the number of positive and negative ions are same.

Statement-II: Equal number of cation and anion vacancies are present. (2001)

(A) Statement-I is true, statement-II is true, statement-II is the correct explanation of statement-I.

(B) Statement I is true, statement-II is true, statement-II is not the correct explanation of statement-I.

(C) Statement-I is true, statement-II is false.

(D) Statement-I is false, statement-II is true.

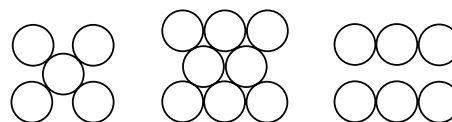
Q.7 Sodium crystallizes in a bcc cubic lattice with the cell edge, $a = 4.29 \text{ \AA}$. What is the radius of sodium atom? (1994)

Q.8 A metallic element crystallizes into a lattice containing a sequence of layers of ABABAB Any packing of layers leaves out voids in the lattice. What percentage by volume of this lattice is empty space? (1996)

Q.9 Chromium metal crystallizes with a body centred cubic lattice. The length of the unit edge is found to be 287 pm. Calculate the atomic radius. What would be the density of chromium in g/cm^3 ? (1997)

Q.10 A metal crystallizes into two cubic phases, face centred cubic (fcc) and body centred cubic (bcc), whose unit cell lengths are 3.5 and 3.0 \AA , respectively. Calculate the ratio of densities of fcc and bcc. (1999)

Q.11 The figures given below show the location of atoms in three crystallographic planes in a fcc lattice. Draw the unit cell for the corresponding structures and identify these planes in your diagram. (2000)



Q.12 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 (2008)

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

Q.13 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 (2010)

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

Q.14 Copper crystallizes in fcc with a unit cell length of 361 pm. What is the radius of copper atom (2009)

- (A) 108 pm (B) 127 pm (C) 157 pm (D) 181 pm

Q.15 Percentage of free space in cubic close packed structure and in body centred packed structure are respectively (2010)

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

Q.16 In a face centred cubic lattice, atom A occupies the corner positions and atom B occupies the face centre positions. If one atom of B is missing from one of the face centred points, the formula of the compound is: (2011)

- (A) AB_2 (B) A_2B_3 (C) A_2B_5 (D) A_2B

Q.17 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: (2012)

- (A) 75 pm (B) 300 pm (C) 240 pm (D) 152 pm

Q.18 CsCl crystallises in body centred cubic lattice. If 'a' is its edge length then which of the following expressions is correct? (2014)

- (A) $r_{Cs^+} + r_{Cl^-} = 3a$ (B) $r_{Cs^+} + r_{Cl^-} = \frac{3a}{2}$
(C) $r_{Cs^+} + r_{Cl^-} = \frac{\sqrt{3}}{2}a$ (D) $r_{Cs^+} + r_{Cl^-} = \sqrt{3}a$

Q.19 Sodium metal crystallizes in a body centred cubic lattice with a unit cell edge of 4.29 Å. The radius of sodium atom is approximately: (2015)

- (A) 1.86 Å (B) 3.22 Å (C) 5.72 Å (D) 0.93 Å

JEE Advanced/Boards

Exercise 1

Q.1 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?

Q.2 A compound alloy of gold and copper crystallizes in a cubic lattice in which gold occupies the lattice points at the corners of the cube and copper atom occupies the centres of each of the cube faces. What is the formula of this compound?

Q.3 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?

Q.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 close packed array of oxide ions, with titanium in one half of the octahedral holes. What is the oxidation number of titanium?

Q.5 Spinel is a important class of oxides consisting of two types of metal ions with the oxide ions arranged in ccp pattern. The normal spinel has one-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 Zn^{2+} , Al^{3+} and O^{2-} , with Zn^{2+} in the tetrahedral holes. Give the formulae of the spinel.

Q.6 KF crystallizes in the NaCl type structure. If the radius of K^+ ions 132 pm and that of F^- ion is 135 pm, what is the shortest K- F distance? What is the edge length of the unit cell? What is the closet K-K distance?

Q.7 A closed packed structure of uniform spheres has the edge length of 534 pm. Calculate the radius of sphere, if it exist in

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

Q.8 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 3.569 Å.

Q.9 An element crystallizes into a structure which may be described by a cubic type of unit cell having one atom on each corner of the cube and two 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 g cm^{-3} , calculate the number of atoms present in 200 g of element.

Q.10 Silver has an atomic radius of 144 pm and the density of silver is 10.6 g cm^{-3} . To which type of cubic crystal, silver belongs?

Q.11 AgCl has the same structure as that of NaCl. The edge length of unit cell of AgCl is found to be 555 pm and the density of AgCl is 5.561 g cm^{-3} . Find the percentage of sites that are unoccupied.

Q.12 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?

Q.13 The two ions A^+ and B^- have radii 88 and 200 pm respectively. In the closed packed crystal of compound AB, predict the co-ordination number of A^+ .

Q.14 CsCl has the bcc arrangement and its unit cell edge length is 400 pm. Calculate the interionic distance in CsCl.

Q.15 Gold crystallizes in a face centered cubic lattice. If the length of the edge of the unit cell is 407 pm, calculate the density of gold as well as its atomic radius assuming it to be spherical.

Atomic mass of gold = 197 amu.

Q.16 The density of KBr is 2.75 g cm^{-3} . The length of the edge of the unit cell is 654 pm. Show that KBr has face centered cubic structure.

($N = 6.023 \times 10^{23} \text{ mol}^{-1}$, At. mass: K = 39, Br = 80)

Q.17 An element crystallizes in a structure having FCC unit cell of an edge 200 pm. Calculate the density, if 200 g of this element contains 24×10^{23} atoms.

Q.18 The effective radius of the iron atom is 1.42 Å. It has FCC structure. Calculate its density. (Fe = 56 amu)

Q.19 A crystal of lead(II) sulphide has NaCl structure. In this crystal the shortest distance between Pb^{+2} ion and S^{2-} ion is 297 pm. What is the length of the edge of the unit cell in lead sulphide? Also calculate the unit cell volume.

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

Q.21 Iron has body centered cubic lattice structure. The edge length of the unit cell is found to be 286 pm. What is the radius of an iron atom?

Q.22 Cesium chloride forms a body centered cubic lattice. Cesium and chloride ions are in contact along the body diagonal of the unit cell. The length of the side of the unit cell is 412 pm and Cl^- ion has a radius of 181 pm. Calculate the radius of Cs^+ ion.

Q.23 In a cubic closed packed structure of mixed oxides the lattice is made up of oxide ions, one eighth of tetrahedral voids are occupied by divalent ions (A^{2+}) while one half of the octahedral voids occupied trivalent ions (B^{3+}). What is the formula of the oxide?

Q.24 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^- ? Give reasons for your answer.

Q.25 Calculate the value of Avogadro's number from the following data:

Density of NaCl = 2.165 cm^{-3}

Distance between Na^+ and Cl^- in

NaCl = 281 pm.

Q.26 If the radius of Mg^{2+} ion, Cs^+ ion, O^{2-} ion, S^{2-} ion and Cl^- ion are 0.65 Å, 1.69 Å, 1.40 Å, 1.84 Å, and 1.81 Å respectively. Calculate the co-ordination numbers of the cations in the crystals of MgS, MgO and CsCl.

Q.27 Iron occurs as bcc as well as fcc unit cell. If the effective radius of an atom of iron is 124 pm. Compute the density of iron in both these structures.

Q.28 KCl crystallizes in the same type of lattice as does

NaCl. Given that $\frac{r_{Na^+}}{r_{Cl^-}} = 0.5$ and $\frac{r_{Na^+}}{r_{K^+}} = 0.7$ Calculate:

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

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

Q.29 An element A (Atomic weight = 100) having bcc structure has unit cell edge length 400 pm. Calculate the density of A and number of unit cells and number of atoms in 10 gm of A.

Exercise 2

Single Correct Choice Type

Q.1 The density of the CaF_2 (fluorite structure) is 3.18 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

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

- (A) Coordination number of cation is four whereas that of anion is six.
(B) Coordination number of cation is six whereas that of anion is four.
(C) Coordination number of each cation and anion is four.
(D) Coordination number of each cation and anion is six.

Q.3 A compound XY crystallizes in BCC lattice with unit cell edge length of 480 pm. If the radius of Y^- is 225 pm, then the radius of X^+ is

- (A) 127.5 pm (B) 190.68 pm
(C) 225 pm (D) 255 pm

Q.4 In the closest packing of atoms A (radius: r_a), the radius of atom B that can be fitted into tetrahedral voids is

- (A) $0.155 r_a$ (B) $0.225 r_a$
(C) $0.414 r_a$ (D) $0.732 r_a$

Q.5 In diamond, carbon atom occupies FCC lattice points as well as alternate tetrahedral voids. If edge length of the unit cell is 356 pm, then radius of carbon atom is

- (A) 77.07 pm (B) 154.14 pm
(C) 251.7 pm (D) 89 pm

Q.6 Which of the following will show schottky defect

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

Q.7 Copper metal crystallizes in FCC lattice. Edge length of unit cell is 362 pm. The radius of largest atom that can fit into the voids of copper lattice without disturbing it.

- (A) 53 pm (B) 45 pm (C) 93 pm (D) 60 pm

Q.8 In FCC unit cell, what fraction of edge is not covered by atoms?

- (A) 0.134 (B) 0.24
(C) 0.293 (D) None of these

Multiple Correct Choice Type

Q.9 80.0 gm salt of weak base & strong acid XY is dissolved in water and formed 2 litre of aqueous solution. The pH of the resultant solution was found to be 5 at 298 K. If XY forms CsCl type crystal having

r_{X^+} (radius of X^+) = 1.6 \AA

and r_{Y^-} (radius of Y^-) = 1.864 \AA

then select write statement(s).

(Given: $K_b(\text{XOH}) = 4 \times 10^{-5}$; $N_A = 6 \times 10^{23}$)

- (A) Molar mass of salt is 100 g/mol.
(B) % Degree of dissociation of salt is 0.25.
(C) Edge length of AB is 4 \AA .
(D) Density of solid salt XY is 2 in gm/cc.

Q.10 Select correct statement(s)

- (A) 8 Cs^+ ions occupy the second nearest neighbour location of a Cs^+ ion
(B) Each sphere is surrounded by six voids in two dimensional hexagonal close packed layer
(C) If the radius of cations and anions are 0.3 \AA and 0.4 \AA then coordination number of cation in the crystal is 6.
(D) In AgCl , the silver ion is displaced from its lattice position to an interstitial position such a defect is called a frenkel defect.

Q.11 Which of the following statements is/are correct?

- (A) The coordination number of each type of ion in CsCl is 8.
(B) A metal that crystallises in BCC structure has a coordination ion number 12.
(C) A unit cell of an ionic crystal shares some of its ions with other unit cells.
(D) The length of the unit cell in NaCl is 552 pm.
 $[r_{\text{Na}^+} = 95 \text{ pm}; r_{\text{Cl}^-} = 181 \text{ pm}]$

Q.12 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) If the radius of cations and anions are 0.2 \AA and 0.95 \AA the coordination number of cation in the crystal is 4.
- (C) An atom/ion is transferred from a lattice site to an interstitial position in Frenkel defect.
- (D) Density of crystal always increases due to substitutional impurity defect.

Assertion Reasoning Type

Q.13 Statement-I: Distance between nearest lattice points in BCC is greater than the same in FCC of the atoms of comparable size.

Statement-II: FCC has greater packing efficiency than BCC.

- (A) Statement-I is true, statement-II is true, statement-II is the correct explanation of statement-I.
- (B) Statement-I is true, statement-II is true, statement-II is not the correct explanation of statement-I.
- (C) Statement-I is true, statement-II is false.
- (D) Statement-I is false, statement-II is true.

Q.14 Statement-I: Increasing temperature increases the density of point defects.

Statement-II: The process of formation of point defects in solids is endothermic and has $\Delta S > 0$.

- (A) Statement-I is true, statement-II is true, statement-II is the correct explanation of statement-I.
- (B) Statement-I is true, statement-II is true, statement-II is not the correct explanation of statement-I.
- (C) Statement-I is true, statement-II is false.
- (D) Statement-I is false, statement-II is true.

Q.15 Statement-I: Increase in dielectric constant is observed in Frenkel defect.

Statement-II: Anions come in interstitial space in case of Frenkel defect.

- (A) Statement-I is true, statement-II is true, and statement-II is the correct explanation of statement-I.
- (B) Statement-I is true, statement-II is true, and statement-II is not the correct explanation of statement-I.
- (C) Statement-I is true, statement-II is false.
- (D) Statement-I is false, statement-II is true.

Q.16 Statement-I: KCl is more likely to show Schottky defect, while LiI is more likely to show Frenkel defect.

Statement-II: Schottky defect is more likely in ionic solids in which cations and anions are of comparable size while Frenkel defect is more likely in which cations and anions have large differences in their ionic sizes.

- (A) Statement-I is true, statement-II is true, statement-II is the correct explanation of statement-I.
- (B) Statement-I is true, statement-II is true, statement-II is not the correct explanation of statement-I.
- (C) Statement-I is true, statement-II is false.
- (D) Statement-I is false, statement-II is true.

Comprehension Type

Paragraph 1: Calcium crystallizes in a cubic unit cell with density 3.2 g/cc . Edge-length of the unit cell is 437 pm .

Q.17 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 melt?

- (A) 31% (B) 36% (C) 28% (D) 49%

Paragraph 2: Silicon carbide (SiC) and diamond are covalent solid which crystallize in cubic structures. In SiC, carbon atoms occupy points of the face centred cubic lattice (FCC positions) and silicon atoms occupy half of the tetrahedral voids available. In diamonds, same position of the tetrahedral voids are occupied by other carbon atoms.

Also the density of SiC and diamond are 3.2 and 3.6 g/cc respectively. Answer the following four questions based on the above information: (M: Si = 28)

Q.18 The radius of silicon atom is

- (A) 0.76 \AA (B) 1.12 \AA (C) 3.54 \AA (D) 4.75 \AA

Q.19 Which of the following will not change the density of SiC solid?

- (A) Substitution of some Si atoms by some carbon atoms
- (B) Schottky defects
- (C) Interchange of some Si atom by some C atom
- (D) Decreasing the temperature of solid

Paragraph 3: Calcium crystallizes in a cubic unit cell with density 3.2 g/cc. Edge-length of the unit cell is 437 picometer (pm).

Q.20 The type of unit cell is

- (A) Simple cubic (B) BCC
(C) FCC (D) Edge-centred

Q.21 The nearest neighbour distance is

- (A) 154.5 pm (B) 309 pm (C) 218.5 pm (D) 260 pm

Match the Columns

Q.22

Column I	Column II
(A) Rock salt structure	(p) Co-ordination number of cation is 4
(B) Zinc Blende	(q) $\frac{\sqrt{3}}{4}d = r_+ + r_-$
(C) Fluorite structure	(r) Co-ordination number of cation and anion are same
	(s) Distance between two nearest anion is $\frac{a}{\sqrt{2}}$

Q.23 [Distance in terms of Edge length of cube (a)]

Column I	Column II
(A) 0.866 a	(p) Shortest distance between cation and anion in CsCl structure.
(B) 0.707 a	(q) Shortest distance between two cations in CaF_2 structure
(C) 0.433 a	(r) Shortest distance between carbon atom in diamond
	(s) Shortest distance between two cation in rock salt structure

Previous Years' Questions

Q.1 Which of the following statement(s) is(are) correct? (1998)

- (A) The coordination number of each type of ion in CsCl crystal is 8.
(B) A metal that crystallizes in bcc structure has a coordination number of 12.
(C) A unit cell of an ionic crystal shares some of its ions with other unit cells.
(D) The length of the unit cell in NaCl is 552 pm.

($r_{\text{Na}^+} = 95 \text{ pm}$; $r_{\text{Cl}^-} = 181 \text{ pm}$)

Q.2 The correct statement(s) regarding defects in solids is(are). (1999)

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

Paragraph 1: 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 hexagon 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'. (2008)

Q.3 The number of atoms in one of this hcp unit cell is

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

Q.4 The volume of this hcp unit cell is

- (A) $24\sqrt{2}r^3$ (B) $16\sqrt{2}r^3$ (C) $12\sqrt{2}r^3$ (D) $\frac{26r^3}{3\sqrt{3}}$

Q.5 The empty space in this hcp unit cell is

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

6. Match the crystal system/unit cells mentioned in column I with their characteristic features mentioned in column II. (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 system
(C) Cubic and tetragonal	(r) have only two crystallographic angles of 90°
(D) Hexagonal and monoclinic	(s) belongs to same crystal system

Q.7 Silver (atomic weight = 108 g mol^{-1}) has a density of 10.5 g cm^{-3} . The number of silver atoms on a surface of area 10^{-12} m^2 can be expressed in scientific notation as $y \times 10^x$. The value of x is. (2010)

Q.8 The number of hexagonal faces that are present in a truncated octahedron is. (2011)

Q.9 Marbles of diameter 10 mm are to be put in a square area of side 40 mm so that their centers are within this area. Find the maximum number of marbles per unit area and deduce an expression for calculating it. (2003)

Q.10 The crystal AB (rock salt structure) has molecular weight $6.023y \text{ u}$, where, y is an arbitrary number in u. If the minimum distance between cation and anion is $y^{1/3} \text{ nm}$ and the observed density is 20 kg/m^3 . Find the (a) density in kg/m^3 and (b) type of defect. (2004)

Q.11 An element crystallizes in fcc lattice having edge length 400 pm. Calculate the maximum diameter of atom which can be placed in interstitial site without distorting the structure. (2005)

Q.12 The edge length of unit cell of a metal having molecular weight 75 g/mol is 5 \AA 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. (2006)

Q.13 Match the crystal system/unit cells mentioned in column I with their characteristic features mentioned in column II. Indicate your answer by darkening the appropriate bubbles of the 4×4 matrix given in the ORS. (2007)

Column I	Column II
(A) Simple cubic and face-centred cubic	(p) Have these cell parameters $a = b = c, \alpha = \beta = \gamma = 90^\circ$
(B) Cubic and rhombohedra	(q) Are two crystal systems
(C) Cubic and tetragonal	(r) Have only two crystallography
(D) Hexagonal and monoclinic	(s) Belong to same crystal system

Paragraph 2: 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 '.

Q.14 The number of atoms on this HCP unit cell is (2008)

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

Q.15 The volume of this HCP unit cell is (2008)

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

Q.16 The empty space in this HCP unit cell is (2008)

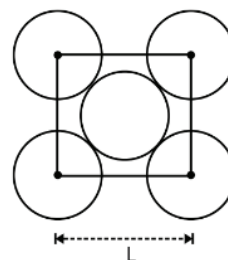
- (A) 75% (B) 47.6% (C) 32% (D) 26%

Q.17 The correct statement (s) regarding defects in solids is (are) (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

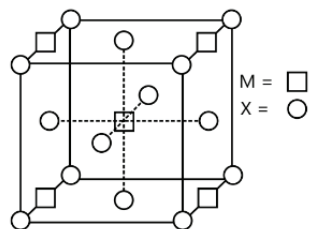
Q.18 The coordination number of Al in the crystalline state of AlCl_3 is (2009)

Q.19 The packing efficiency of the two-dimensional square unit cell shown below is (2010)



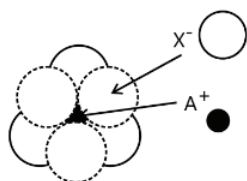
- (A) 39.27% (B) 68.02%
(C) 74.05% (D) 78.54%

Q.20 A compound M_pX_q has cubic close packing (ccp) arrangement of arrangement of X. Its unit cell structure is shown below. (2012)



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

Q.21 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 (2013)



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

Q.22 If the unit cell of a mineral has cubic close packed (ccp) array of oxygen atoms with m fraction of octahedral holes occupied by aluminium ions and n fraction of tetrahedral holes occupied by magnesium ions, m and n, respectively, are (2015)

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

Q.23 The **CORRECT** statement(s) for cubic close packed (ccp) three dimensional structure is(are) (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

PlancEssential Questions

JEE Main/Boards

Exercise 1

Q.18 Q.25 Q.29

Exercise 2

Q.5 Q.10

Previous Years' Questions

Q.5 Q.7 Q.10

JEE Advanced/Boards

Exercise 1

Q.5 Q.11 Q.15 Q.24

Exercise 2

Q.7 Q.10 Q.11 Q.22

Previous Years' Questions

Q.7 Q.9 Q.12

Answer Key

JEE Main/Boards

Exercise 1

Q.6 M_2N_3 Q.8 2.85×10^{24} atoms

Q.10 299.8 pm

Q.12 $1.2046 \times 10^{19} \text{ mol}^{-1}$ Q.14 2.86 g cm^{-3}

Q.16 144.2 pm

Q.18 A_4B_3

Q.20 0.523

Q.22 $ZnAl_2S_4$

Q.24 74%

Q.30 4

Q.7 face-centred cubic

Q.9 2

Q.11 $4.348 \times 10^{-23} \text{ cm}^3$

Q.13 52 u

Q.15 127.7 pm

Q.17 74.70 g mol^{-1} or 74.70 uQ.19 0.6709 g cm^{-3} Q.21 M_4O_6 or M_2O_3

Q.23 60%; 4

Q.25 4.7 %

Exercise 2

Q.1 B

Q.2 C

Q.3 C

Q.4 A

Q.5 C

Q.6 B

Q.7 D

Q.8 D

Q.9 C

Q.10 A

Q.11 B

Q.12 A

Previous Years' Questions

Q.1 A

Q.2 D

Q.3 A

Q.4 B

Q.5 D

Q.6 A

Q.7 1.86 \AA

Q.8 26%

Q.9 7.3 g/cc

Q.10 432:343

Q.12 A

Q.13 D

Q.14 B

Q.15 B

Q.16 C

Q.17 D

Q.18 C

Q.19 A

JEE Advanced/Boards

Exercise 1

Q.1 A-B

Q.3 $A_4B_2C_2$ Q.5 $ZnAl_2O_4$

Q.7 267 pm, 231.2 pm, 188.8 pm

Q.9 3.472×10^{24} atomsQ.2 $AuCu_3$

Q.4 59.95%, +4

Q.6 267 pm, 534 pm, 378 pm

Q.8 3.5 g cm^{-3}

Q.10 FCC

- Q.11 0.24%
 Q.13 6
 Q.15 19.4 g/cm^3 , 143.9 pm
 Q.17 41.67 cm^{-3}
 Q.19 $a = 5.94 \times 10^{-8} \text{ cm}$, $V = 2.096 \times 10^{-22} \text{ cm}^{-3}$
 Q.21 123.84 pm
 Q.23 AB_2O_4
 Q.25 6.01×10^{23}
 Q.27 7.887 g/cc , 8.59 gm/cm^3
 Q.29 5.188 gm/cm^3 , 6.023×10^{22} atoms of A, 3.0115×10^{22} unit cells
 Q.12 438.5 pm , 219.25 pm
 Q.14 346.4 pm
 Q.16 FCC
 Q.18 5.74 g cm^{-3}
 Q.20 1.81 \AA
 Q.22 175.8 pm
 Q.24 103.4 pm , No
 Q.26 4, 6, 8
 Q.28 (a) 1.143, (b) 1.172

Exercise 2

Single Correct Choice Type

- Q.1 C Q.2 D Q.3 B Q.4 B Q.5 A Q.6 D
 Q.7 A Q.8 C

Multiple Correct Choice Type

- Q.9 A, C Q.10 B, D Q.11 A, C, D Q.12 A, C

Assertion Reasoning Type

- Q.13 A Q.14 A Q.15 C Q.16 A

Comprehension Type

- Q.17 A Q.18 B Q.19 C Q.20 C Q.21 D

Match the Columns

- Q.22 $A \rightarrow r, s; B \rightarrow p, q, r, s; C \rightarrow q$ Q.23 $A \rightarrow p; B \rightarrow q, s; C \rightarrow r$

Previous Years' Questions

- Q.1 A, C, D Q.2 B, C Q.3 B Q.4 A Q.5 D
 Q.6 $A \rightarrow p, s; B \rightarrow p, q; C \rightarrow q; D \rightarrow q, r$ Q.7 7 Q.8 8 Q.9 25
 Q.10 (a) 5 kg/m^3 (b) Metal excess defect Q.11 117 pm Q.12 217 pm
 Q.13 $A \rightarrow p, s; B \rightarrow p, q; C \rightarrow q; D \rightarrow q, r$ Q.14 B Q.15 A Q.16 D
 Q.17 B, C Q.18 6 Q.19 D Q.20 B Q.21 A
 Q.22 A Q.23 B, C, D

Solutions

JEE Main/Boards

Exercise 1

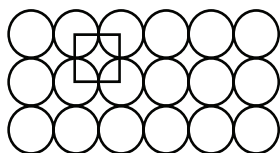
Sol 1: (i) See theory on page no. 19.20

(ii) See theory on page no. 19.22

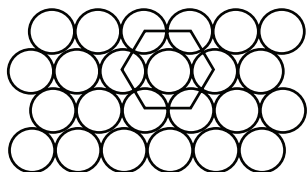
Sol 2: See theory on page no. 19.21

Sol 3: (a) When same property is measured in different direction in solid gives different value is called Anisotropy.

Sol 4: (a) Square close packing



Hexagonal close packing



(b) Coordination number of square close packing is 4.
Coordination number of hexagonal close packing is 6.

Sol 5: (a) Schottky defect

(b) Frenkel defect

Sol 6: Effective number of atom in

$$\text{ccp} = \text{fcc} = 6 \times \frac{1}{2} + 8 \times \frac{1}{8}$$

$$= 4 = \text{N-atom}$$

Tetrahedral void = 8 (in fcc)

$$\text{Number of M-atom} = \frac{8}{3}$$

$$\text{So empirical formula} = \text{M}_8\text{N}_4 = \text{M}_2\text{N}_3$$

Sol 7: molar mass = $2.7 \times 10^{-2} \text{ kg/mol} = 27 \text{ gm/mol}$

Let's say in one cubic unit, there is Z-effective atoms

$$\frac{(z) \times \text{mass of one atom}}{\text{Volume of cell}} = \text{density}$$

$$\frac{(z) \times \frac{27}{6 \times 10^{23}} \times 10^{-3}}{(405 \times 10^{-12})^3} = 2.7 \times 10^{23}$$

$$Z = 4$$

So cubic unit would be fcc

Sol 8: Effective Atom = 2

$$\frac{2 \times (\text{mass of one atom})}{(300 \times 10^{-12})^3} = 5.200 \text{ kgm/m}^3$$

$$\text{Mass of one atom} = \frac{5.2 \times 10^6 \times 27 \times 10^{-30}}{2} \text{ gm}$$

$$= 70.2 \times 10^{-24} \text{ gm}$$

$$\text{Atoms in } 200 \text{ gm} = \frac{200}{70.2 \times 10^{-24}} = 2.84 \times 10^{24} \text{ atoms}$$

Sol 9: Like question number 7, we suppose it has z-effective atoms in one unit cell

$$Z = \frac{(52 \times 1.66 \times 10^{-24})}{(298 \times 10^{-12})^3} = 7.2 \times 10^6 \text{ gm/m}^3$$

$$z = 2$$

So the unit would be bcc

Sol 10: $4.12 \times 10^{24} \text{ atom} = 200 \text{ gm}$

$$\text{Mass of one atom} = \frac{200}{4.12 \times 10^{24}} = 4.85 \times 10^{-23} \text{ gm}$$

Effectively number in fcc = 4

$$\frac{4 \times (4.85 \times 10^{-23})}{r^3} = 7.2 \text{ g/cm}^3$$

$$r = 300$$

Sol 11: $Z_{\text{eff.}} = 2$

$$\frac{2 \times \left(\frac{6.94}{6.023 \times 10^{23}} \right)}{V} = 0.53 \text{ gm/cm}^3$$

$$V = 4.348 \times 10^{-23} \text{ cm}^3$$

Sol 12: One Sr^{2+} will replace 2 Na^+

So incoming of one Sr^{2+} will result into one cation vacancy

Let's say 100 moles are total

$$\text{In one mole, } \text{Sr}^{2+} = 6.023 \times 10^{23} \times \frac{2 \times 10^{-3}}{100}$$

$$\text{Cation vacancy} = 12.04 \times 10^{+18} = 1.204 \times 10^{19}$$

$$\text{Sol 13: } \frac{2 \times (\text{atomic mass})}{(2.88 \times 10^{-10})^3} = 7.2 \times 10^6 \text{ gm/m}^6$$

$$\text{Atomic mass} = 8.6 \times 10^{-23} \text{ gm}$$

$$\text{Atomic mass} \approx 52 \text{ amu}$$

$$\text{Sol 14: Density} = \frac{Z_{\text{eff}} (\text{mass of one atom})}{r^3}$$

$$= \frac{4 \times \left(\frac{208}{4.283 \times 10^{24}} \right)}{(4.08 \times 10^{-10})^3} = 2.86 \text{ gm/cm}^3$$

$$\text{Sol 15: } 8.930 \times 10^6 \text{ gm/m}^3 = \frac{4 \times \left(\frac{63.55}{6.023 \times 10^{23}} \right)}{a^3}$$

$$a^3 = \frac{4 \times 63.55}{8.93 \times 6.023} \times 10^{-29}$$

$$a = 3.6161 \text{ \AA}$$

$$\sqrt{2} a = 4r \text{ (in fcc structure, analyze diagonal of a face)}$$

$$r = 127.8 \text{ pm}$$

$$\text{Sol 16: } 19.3 \times 10^6 = \frac{4 \times \left(\frac{197}{6.023 \times 10^{23}} \right)}{a^3}$$

$$\text{Similarly } a = 407.74 \text{ pm}$$

$$\sqrt{2} a = 4r \text{ (in fcc structure)}$$

$$r = 144.15 \text{ pm}$$

$$\text{Sol 17: } 1.984 \times 10^6 = \frac{4 \times \left(\frac{M}{6.023 \times 10^{23}} \right)}{(6.3 \times 10^{-10})^3}$$

$$M = 74.69 \text{ gm}$$

Sol 18: In NaCl (fcc structure)

$$\text{Cl}^- \text{ at centre of face} = 6 \times \left(\frac{1}{2} \right) = 3$$

$$\text{Cl}^- \text{ at corners} = 8 \times \left(\frac{1}{8} \right) = 1$$

$$\text{Na}^+ \text{ at centre of edge} = 12 \times \left(\frac{1}{4} \right) = 3$$

$$\text{Na}^+ \text{ at centre of cube} = 1$$

If face centred, that is Cl^- is removed, along one axis.

$$\text{Then } \text{Cl}^- = 4 \times \left(\frac{1}{2} \right) + 8 \times \left(\frac{1}{8} \right) = 3$$

$$\text{Na}^+ = 3 + 1 = 4$$



Similarly A_4B_3

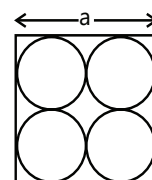
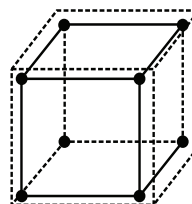
$$\text{Sol 19: Density} = \frac{4 \times (\text{mass of a molecule})}{abc}$$

$$= \frac{4 \times \left(\frac{21.76}{6.023 \times 10^{23}} \right)}{6.8 \times 4.4 \times 7.8 \times 10^{-30}} \text{ gm/m}^6$$

$$= 0.6709 \text{ gm/cm}^3$$

Sol 20 Let's say radius of sphere = r

Side of cube that just encloses the sphere = 4r



$$\text{Volume} = (4R)^3 = 64 R^3$$

$$\text{Volume of sphere} = 8 \times \frac{4}{3} \pi R^3$$

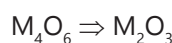
$$\text{Fraction} = \frac{8 \times \frac{4}{3} \pi}{64} = 52.35\%$$

Sol 21: Analyzing hcp structure

$$\text{O}^{2-} \text{ (in hcp array)} = 6$$

$$\text{Octahedral void (in hcp)} = 6$$

$$\text{M occupies } \frac{2}{3} \text{ rd of octahedral voids} = \frac{2}{3} \times 6 = 4$$



Sol 22: Closest packed array = fcc

$$\text{Zinc} = \frac{1}{8} \times (\text{Number pf tetrahedral void})$$

$$= \frac{1}{8} \times 8 = 1$$

$$\text{Aluminium} = \frac{1}{2} \times (\text{Number of octahedral void})$$

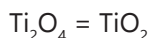
$$= \frac{1}{2} \times 4 = 2$$

$$S (\text{in fcc}) = 4$$



Sol 23: O (in fcc) = 4

$$\text{Ti} = \frac{1}{2} \times (\text{Number of Octahedral void}) = \frac{1}{2} \times 4 = 2$$



$$\% \text{ by mass of Ti} = \frac{48}{48 + 32} = 60 \%$$

$$\text{Ti oxidation state} = +4$$

Sol 24: Packing efficiency of hcp

$$Z_{\text{eff}} = 6$$

$$a = 2r (\text{side of hexagon})$$

$$b = (\text{height of hexagon}) = \frac{2\sqrt{3}}{\sqrt{3}} r$$

$$\text{So packing eff.} = \frac{6 \times \frac{4}{3} \pi (r)^3}{6 \times \frac{\sqrt{3}}{2} \times (2r)^2 \times \frac{2\sqrt{3}}{\sqrt{3}} r} = 74\%$$

Packing eff. For fcc

$$Z_{\text{eff}} = 4$$

$$a = \frac{4}{\sqrt{2}} r (\text{side of cubic})$$

$$\text{So packing eff.} = \frac{4 \times \left(\frac{4}{3} \pi r^3 \right)}{16\sqrt{2}r^3} = 74\%$$

Sol 25: Let's suppose weight of Ge crystal is W

$$d_i = \text{initial density} = \frac{W}{V}$$

$$d_f = 0.96 d_i = 0.96 \frac{W}{V}$$

Volume is fixed so it implied boron decreases weight 4%

$$m_f = \text{mass final} = 0.96 W$$

$$xW + (1-x) \frac{W}{72.6} \times 11 = 0.96 W$$

$$x = 95.3\%$$

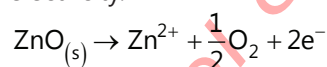
$$\% \text{ of vacancy} = 4.7\%$$

Sol 26: Refer theory.

Sol 27: (a) In metal on increasing temp, the alignment of electron get disturb due to excitation of electron due to which conductivity decrease while in case of semiconductor on increasing temp. electrons absorb energy and get excited to conduction band hence conductivity increases.

(b) Due to difference in size of atoms.

(c) On heating ZnO , O^{2-} ion is replaced by e^- due to which lattice contain free electrons to conduct electricity.



Sol 28: Refer theory

Sol 29: Refer theory

Sol 30: In ccp structure = fcc structure

Number of octahedral void

$$= \text{one at center of cube} + \left(\frac{1}{4} \right)^{1/2}$$

$$\text{At very edge centre, there is} \left(\frac{1}{4} \right)$$

octahedral void = $1 + 12 \left(\frac{1}{4} \right) = 4$

Number of effective atom

$$= \text{at every corner, there is} \left(\frac{1}{8} \right)^{\text{th}} \text{ part of an atom} + \text{at}$$

$$\text{every center of face, there is} \left(\frac{1}{2} \right)^{\text{nd}} \text{ part of an atom}$$

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

Exercise 2

$$\text{Sol 1: (B)} W = 8 \left(\frac{1}{8} \right) = 1, 0 = 12 \left(\frac{1}{4} \right) = 3$$

$$\text{Na} = 1$$



Sol 2: (C) $\text{CaF}_2 \Rightarrow \text{Ca}^{2+} (\text{in fcc}) + \text{F}^-$

(at octahedral void)



(at every corner)

Cordination number $\Rightarrow 8 : 4$ (CaF_2)

$8 : 8$ (CsCl)

Sol 3: (C) Correct

Sol 4: (A) $\text{CsCl} \Rightarrow \text{BCC} \Rightarrow \text{Cs}^+$ (at center) + Cl^- (at every corner)

$$1\text{Cs}^+ + \left(8 \times \frac{1}{8}\right)\text{Cl}^- = 1\text{Cs}^+ + 1\text{Cl}^-$$

Sol 5: (C) For close packing two same sheets cannot be together.

Sol 6: (B) $\text{ZnS} \Rightarrow \text{S}^{2-}$ (fcc) + Zn^{2+} (occupies alternate tetrahedral void)

For occupation of tetrahedral void $\frac{r_{\text{Zn}^{2+}}}{r_{\text{S}^{2-}}} = 0.225$

$$r_{\text{S}^{2-}} = 100 \text{ pm}$$

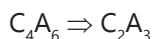
Sol 7: (D) $\text{NaCl} \Rightarrow \text{Na}^+$ (at octahedral voids) + Cl^- (fcc structure).

Sol 8: (D) fcc \Rightarrow number of nearest neighbour around each particle = 12

Sol 9: (C) A \Rightarrow hcp effective number of atoms = 6

Octahedral void = 6

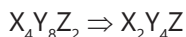
$$C = 6 \left(\frac{2}{3} \right) = 4$$



Sol 10: (A) Z_{eff} . For X $\Rightarrow 8 \left(\frac{1}{8} \right) + 6 \left(\frac{1}{2} \right) = 4$

$$Z_{\text{eff}} \text{ For Y} \Rightarrow 8$$

$$Z_{\text{eff}} \text{ For Z} \Rightarrow \frac{1}{2} (4) = 2$$



Sol 11: (B) Co-ordination number = 8 = BCC

Sol 12: (A) Oppositely charged ions will be nearest atom.

Analyzing body (cubic) diagonal of BCC structure

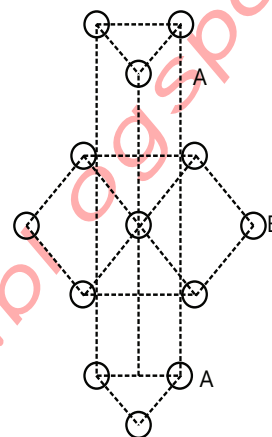
$$(r_{\text{NH}_4^+} + 2r_{\text{Cl}^-} + r_{\text{NH}_4^+}) = \sqrt{3} \quad (387)$$

$$2(r_{\text{NH}_4^+} + r_{\text{Cl}^-}) = 670.30 \text{ pm}$$

$$r_{\text{NH}_4^+} + r_{\text{Cl}^-} = 335.15 \text{ pm}$$

Previous Years' Questions

Sol 1: (A) Three consecutive layers of atoms in hexagonal close packed lattice is shown below:



Atom X is in contact of 12 like atoms, 6 from layer B and 3 from top and bottom layers A each.

Sol 2: (D) In NaCl , Na^+ occupies body centre and edge centres while Cl^- occupies corners and face centres, giving four Na^+ and four Cl^- per unit cell. In the present case, A represent Cl^- and B represents Na^+ . Two face centres lies on one axis.

$$\Rightarrow \text{Number of A removed} = 2 \times \frac{1}{2} = 1$$

Number of B is removed because it is not present on face centres.

$$\Rightarrow \text{A remaining} = 4 - 1 = 3$$

$$\text{B remaining} = 4$$

$$\Rightarrow \text{Formula} = \text{A}_3\text{B}_4$$

Sol 3: (A) In cubic system, a corner contribute $\frac{1}{8}$ th part of atom to one unit cell and a face centre contribute $\frac{1}{2}$ part of atom to one unit cell. Therefore,

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

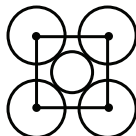
$$\text{Number of B per unit cell} = \frac{1}{2} \times 6 = 3$$

$$\Rightarrow \text{Formula} = \text{AB}_3$$

Sol 4: (B) In ZnS, S^{2-} (sulphide ions) are present at fcc position giving four sulphide ions per unit cell. To comply with 1 : 1 stoichiometry, four Zn^{2+} ions must be present in four alternate tetrahedral voids out of eight tetrahedral voids present.

In NaCl, Na^+ ions are present in octahedral voids while in Na_2O , Na^+ ions are present in all its tetrahedral voids giving the desired 2 : 1 stoichiometry. In CaF_2 , Ca^{2+} ions occupies fcc positions and all the tetrahedral voids are occupied by fluoride ions.

Sol 5: (D)



Contribution of circle from corner of square = $\frac{1}{4}$

⇒ Effective number of circle per square

$$= \frac{1}{4} \times 4 + 1(\text{at centre}) = 2$$

⇒ Area occupied by circle = $2\pi r^2$;

r = radius.

Also, diagonal of square $4r = \sqrt{2}L$,

where L = side of square.

⇒ Packing fraction

$$= \frac{\text{Area occupied by circle}}{\text{Area of square}}$$

$$= \frac{2\pi r^2}{L^2} = \frac{2\pi r^2}{8r^2} = \frac{\pi}{4} = 0.7854$$

⇒ % packing efficiency = 78.54%

Sol 6: (A) In ionic solid MX (1 : 1 solid), same number of M^{n+} and X^{n-} ions are lost in Schottky defect to maintain electro-neutrality of solid.

Sol 7: In bcc arrangement of atoms: $4r = \sqrt{3}a$, atoms on body diagonal remain in contact

$$\Rightarrow r = \frac{\sqrt{3}a}{4} = \frac{\sqrt{3} \times 4.29}{4} = 1.86 \text{ \AA}$$

Sol 8: The given arrangement: ABABAB..... represents hexagonal close-packed unit cell in which there are six atoms per unit cell. Also, volume of unit cell = $24\sqrt{2}r^3$.

⇒ Packing fraction

$$= \frac{\text{Volume occupied by atoms}}{\text{Volume of unit cell}}$$

$$= 6 \times \frac{4}{3} \pi r^3 \times \frac{1}{24\sqrt{2}r^3} = 0.74$$

⇒ Percent empty space

$$= 100(1 - 0.74) = 26\%$$

Sol 9: In bcc unit cell $4r = \sqrt{3}a$

$$\Rightarrow r(\text{Cr}) = \frac{\sqrt{3}}{4}a = \frac{\sqrt{3}}{4} \times 287 \text{ pm} = 124.3 \text{ pm}$$

$$\text{Density of solid} = \frac{NM}{N_A \cdot a^3}$$

N = Number of atoms per unit cell

M = Molar mass

a^3 = Volume of cubic unit cell

N_A = Avogadro's number

$$= \frac{2 \times 52 \text{ g}}{6.023 \times 10^{23}} \times \left(\frac{1}{2.87 \times 10^{-8} \text{ cm}} \right)^3 = 7.3 \text{ g/cm}^3$$

Sol 10: We have, F.C.C unit cell length = 3.5 Å,

B.C.C unit cell length = 3.0 Å

Now no. of atoms for F.C.C(n_1) = 4;

$$V_1 = a^3 = (3.5 \times 10^{-8})^3$$

Now no. of atoms for B.C.C(n_2) = 2

$$V_2 = a^3 = (3.0 \times 10^{-8})^3$$

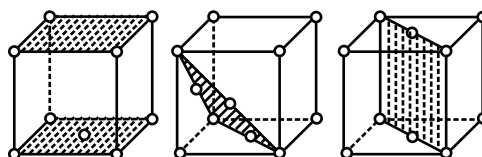
$$\text{Density in F.C.C} = \frac{(n_1 \times \text{At. wt})}{(V_1 \times \text{Av. No})}$$

$$\text{Density in B.C.C} = \frac{(n_2 \times \text{At. wt})}{(V_2 \times \text{Av. No})}$$

Therefore,

$$\begin{aligned} \frac{D_{\text{F.C.C}}}{D_{\text{B.C.C}}} &= (n_1 / n_2) \times (V_1 / V_2) \\ &= (4 / 2) \times (3.0 \times 10^{-8})^3 / (3.5 \times 10^{-8})^3 \\ &= 432 : 343 \end{aligned}$$

Sol 11:



Sol 12: (A) No. of atoms of Y = 4

$$\text{No. of atoms of X} = \frac{2}{3} \times 8$$

Formula of compound will be X_4Y_3

Sol 13: (D) For an ionic substance in FCC arrangement,

$$2(r^+ + r^-) = \text{edge length}$$

$$2(110 + r^-) = 508$$

$$r^- = 144 \text{ pm}$$

Sol 14: (B) For F.C.C

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

$$r = \frac{\sqrt{2}a}{4} = \frac{\sqrt{2} \times 361}{4} = 127 \text{ pm}$$

Sol 15: (B) Packing fraction of cubic close packing and body centred packing are 0.74 and 0.68 respectively.

$$\text{Sol 16: (C)} \text{ Effective no. of A atoms} = \frac{1}{8} \times 8 = 1$$

$$\text{Effective no. of B atoms} = \frac{1}{2} \times 5 \text{ (One is missing)} = \frac{5}{2}$$

$$\text{Therefore formula is } A_1B_{\frac{5}{2}} = A_2B_5$$

Sol 17: (D) For BCC, $\sqrt{3}a = 4r$

$$r = \frac{\sqrt{3} \times 351}{4} = 152 \text{ pm}$$

$$\text{Sol 18: (C)} \quad 2r_{\text{Cl}^-} + 2r_{\text{Cs}^+} = \sqrt{3}a$$

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

$$\text{Sol 19: (A)} \quad R = \frac{\sqrt{3}}{4}a = 1.86 \text{ \AA}$$

JEE Advanced/Boards

Exercise 1

Sol 1: AB = (CsCl type structure)

$$\text{Sol 2: Gold (Au)} = 8 \times \frac{1}{8} = 1$$

$$\text{Copper (Cu)} = \left(\frac{1}{2}\right) \times 6 = 3$$

$$\text{AuCu}_3$$

$$\left. \begin{array}{l} \text{Sol 3: A = ccp = fcc} = 4 \\ B = \frac{1}{4}(8) = 2 \\ C = \frac{1}{2}(4) = 2 \end{array} \right\} Z_{\text{eff.}} = \text{effective number of atoms}$$



$$\left. \begin{array}{l} \text{Sol 4: O}^{2-} = \text{ccp} = 4 \\ \text{Ti} = \frac{1}{2}(4) = 2 \end{array} \right\} Z_{\text{eff.}} = \text{effective number of atoms}$$



↓

+4

$$\left. \begin{array}{l} \text{Sol 5: O}^{2-} = \text{ccp} = 4 \\ A = \frac{1}{8} \times (8) = 1 = \text{Zn}^{2+} \\ B = \frac{1}{2}(4) = 2 = \text{Al}^{3+} \end{array} \right\} Z_{\text{eff.}} = \text{effective number of atoms}$$



Sol 6: Analyzing one edge of FCC (KF) structure

$$2(r_+ + r_-) = a$$

$$r_+ + r_- = \text{shortest KF - distance} = 132 + 135 = 267 \text{ pm}$$

$$a = 534 \text{ pm}$$

$$\text{Closest K - K distance} = \frac{\sqrt{2}a}{2} = 377.6 \text{ pm}$$

Sol 7: (a) $2r = a$

$$r = 267 \text{ pm}$$

$$(b) \sqrt{3}a = 4r$$

$$r = 231.22 \text{ pm}$$

(c) FCC

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

$$R = 188.8 \text{ pm}$$

$$\text{Sol 8: density} = \frac{8 \left(\frac{12}{6.023 \times 10^{23}} \right)}{(3.569 \times 10^{-10})^3}$$

$$(Z_{\text{eff.}} = 8 \text{ for fcc of diamond}) = 3.5 \text{ gm/cm}^3$$

Sol 9: Mass of unit cell = $7.2 \times 24 \times 10^{-24}$

$$= 17.28 \times 10^{-23} \text{ gm}$$

Number of unit cell in 200 gm

$$= \frac{200}{17.28 \times 10^{-23}} = 11.57 \times 10^{23}$$

$$\text{Number of atoms in one unit cell} = 8 \times \left(\frac{1}{8}\right) + 2 = 3$$

So, Number of atoms in 200 gm of solid = $3 \times 11.57 \times 10^{23}$

$$= 3.472 \times 10^{24} \text{ atom}$$

Sol 10: $r_{\text{Ag}} = 144 \text{ pm}$

$$\text{Density} = \frac{Z_{\text{eff.}} \times \left(\frac{108}{6.023 \times 10^{23}}\right)}{a^3} = 1.6 \times 10^6$$

$$\frac{a^3}{Z_{\text{eff.}}} = 16.91 \times 10^{-30}$$

$$\Rightarrow a = (Z_{\text{eff.}} \times 16.91 \times 10^6)^{1/3} \text{ pm}$$

Case I: Simple cubic

$$Z_{\text{eff.}} = 1$$

$$a = 2r$$

Which does not satisfies

Case II : BCC

$$Z_{\text{eff.}} = 2$$

$$a = 323.38 \text{ pm}$$

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

$$r = 140 \text{ pm}$$

Which does not satisfy

Case III : FCC

$$Z_{\text{eff.}} = 4$$

$$a = 407.44 \text{ pm}$$

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

$$r = 144 \text{ pm}$$

So, the structure will be FCC

Sol 11: $a = 555 \text{ pm}$



$$5.561 \times 10^6 = \frac{\text{Mass of unit cell}}{(5.55 \times 10^{-10})^3}$$

$$95 \times 10^{-23} = \text{mass of unit cell}$$

$$95.06 \times 10^{-23} = \text{mass of unit cell}$$

Mass of unit cell (theoretical)

$$= 4 \times \left(\frac{108 + 35.5}{6.023 \times 10^{23}}\right) = 95.301 \times 10^{-23} \text{ gm}$$

$$\% \text{ of sites} = \frac{95.30 - 95.06}{95.30} \times 100 = 0.24 \%$$

$$\text{Sol 12: Nearest height distance} = \frac{\sqrt{2}a}{2} = 2r$$

$$= 438.40 \text{ pm}$$

$$r = 219.2 \text{ pm}$$

$$\text{Sol 13: } \frac{r_{\text{A}^+}}{r_{\text{B}^-}} = \frac{88}{200} = 0.44 > 0.414$$

So it will occupy octahedral void

So coordination number would be = 6

$$\text{Sol 14: } \sqrt{3}a = 2(r_+ + r_-)$$

$$(r_+ + r_-) = \frac{\sqrt{3} \times 400}{2}$$

$$r_+ + r_- = 346.41 \text{ pm}$$

$$\text{Sol 15: } a = 407 \text{ pm}$$

$$\text{Density} = \frac{4 \times \left(\frac{197}{6.02 \times 10^{23}}\right)}{(4.07 \times 10^{-10})^3} = 19.40 \text{ gm/cm}^3$$

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

$$R = 143.9 \text{ pm}$$

$$\text{Sol 16: } 2.75 \times 10^6 = \frac{Z_{\text{eff.}} \left(\frac{39 + 80}{6.023 \times 10^{23}}\right)}{(6.54 \times 10^{-10})^3}$$

$$Z_{\text{eff}} \sim 4$$

FCC structure

$$\text{Sol 17: Density} = \frac{\text{mass}}{\text{volume}} = \frac{200}{\text{volume of 200gm}}$$

$$4 \text{ atoms then volume} = (2.00 \times 10^{-10})^3 \text{ m}^3$$

$$24 \times 10^{23} \text{ atom then volume} = \frac{8 \times 10^{-30}}{4} \times 24 \times 10^{23} \text{ m}^3$$

$$\text{Density} = \frac{200 \times 4}{28 \times 10^{-30} \times 24 \times 10^{23}} \text{ gm/m}^3 = 41.67 \text{ gm/m}^3$$

$$\text{Sol 18: } \sqrt{2}a = 4r$$

$$a = 2\sqrt{2}r = 4.016 \text{ \AA}$$

$$\text{Density} = \frac{4 \times \left(\frac{56}{6.023 \times 10^{23}} \right)}{10^{-30} \times (4.016)^3} \text{ gm/m}^6 = 5.74 \text{ gm/m}^6$$

Sol 19: $(r_{\text{Pb}^{2+}} + r_{\text{S}^{2-}}) = 297 \text{ pm}$

$\text{PbS} \Rightarrow \text{NaCl}$ type structure

Analyzing edge in Rock Salt Structure

$$a = 2(r_{\text{Pb}^{2+}} + r_{\text{S}^{2-}}) = 594 \text{ pm}$$

$$V = a^3 = 209.5 \times 10^{-30} \text{ m}^3$$

Sol 20: $\sqrt{3} a = 2(r_{\text{Cs}^+} + r_{\text{Cl}^-}) = 7 \text{ \AA}$

$$\sqrt{3} = 2(1.69 + r_{\text{Cl}^-}) = 7 \text{ \AA}$$

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

Sol 21: $\sqrt{3} a = 4r_{\text{Fe}}$

$$r_{\text{Fe}} = 123.8 \text{ pm}$$

Sol 22: $\sqrt{3} a = 2(r_{\text{Cs}^+} + r_{\text{Cl}^-})$

$$\sqrt{3} (412) = 2(r_{\text{Cs}^+} + 181)$$

$$r_{\text{Cs}^+} = 175.8 \text{ pm}$$

Sol 23: ccp = fcc

Tetrahedral void = 8 ;

Octahedral void = 4

$$Z_{\text{eff}} = \text{effective number of atoms} = 4 = 8 \times \left(\frac{1}{8} \right) + 6 \times \left(\frac{1}{2} \right)$$

$$A^{2+} = \frac{1}{8} (8) = 1$$

$$B^{3+} = \frac{1}{2} (4) = 2$$

$$\text{O}^{2-} (\text{fcc}) = 4$$



Sol 24: In NaCl structure, Na^+ occupies tetrahedral

voids, so radius of cation $\frac{r_+}{r_-} = (\sqrt{2} - 1)$

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

It $r_+ = 180 \text{ pm}$ then $\frac{r_+}{r_-} = 0.72$

No, it can not be slipped into tetrahedral void

Because for tetrahedral voids

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

Sol 25: $\text{Density} = \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}}$

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

$$a = 2 \times 281 = 562 \text{ pm}$$

$$2.165 \times 10^6 = \frac{4 \times (\text{mass of a molecule})}{(5.62 \times 10^{-10})^3}$$

Mass of a molecule

$$= \frac{23 + 35.5}{\text{Avogadro's number}} = 96.07 \times 10^{-24}$$

$$N_A = \text{Avogadro's number} = 6.089 \times 10^{23}$$

Sol 26: MgS

$$\frac{r_+}{r_-} = \frac{0.65}{1.84} = 0.35$$

$$0.225 < \frac{r_+}{r_-} < 0.414 \text{ (Tetrahedral void)}$$

Mg^{2+} will occupy tetrahedral void (alternate)

So the coordination number = 4

MgO

$$\frac{r_+}{r_-} = \frac{0.65}{1.40} = 0.464$$

$$0.414 < \frac{r_+}{r_-} < 0.732$$

So Mg^{2+} will occupy octahedral void

Coordination number = 4

CsCl

$$\frac{r_+}{r_-} = \frac{1.69}{1.81} = 0.933$$

$$0.732 < \frac{r_+}{r_-} < 1$$

So Cs^+ will occupy center position in BCC structure

Coordination number = 8

Sol 27: BCC

$$r = 124 \text{ pm}$$

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

$$a = 286.3 \text{ pm}$$

$$\text{density} = \frac{2 \times \left(\frac{56}{6.02 \times 10^{23}} \right)}{(2.863 \times 10^{-10})^3} = 7.924 \text{ gm/cm}^3$$

FCC

$$r = 124 \text{ pm}$$

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

$$a = 350.72 \text{ pm}$$

$$\text{density} = \frac{4 \times \left(\frac{56}{6.023 \times 10^{23}} \right)}{(3.5072 \times 10^{-10})^3} = 8.620 \text{ gm/cm}^3$$

Sol 28: $r_{K^+} = \frac{r_{Na^+}}{0.7}$

$$\frac{r_{K^+}}{r_{Cl^-}} = \frac{r_{Na^+}}{(0.7)r_{Cl^-}} = \frac{5}{7} = 0.714$$

(a) Sides of KCl = $2(r_{K^+} + r_{Cl^-}) = 2 \left(\frac{5}{7} + 1 \right) r_{Cl^-}$

Sides of NaCl = $2(r_{Na^+} + r_{Cl^-}) = 2(1.5) r_{Cl^-}$

$$\text{Ratio} = \frac{12}{7 \times 1.5} = \frac{8}{7} = 1.143$$

(b) Ratio density = $\frac{d_1}{d_2} = \frac{4 \times \frac{M_{NaCl}}{(r_{NaCl})^3}}{4 \times \frac{M_{KCl}}{(r_{KCl})^3}}$

$$= \frac{M_{NaCl}}{M_{KCl}} \left(\frac{r_{KCl}}{r_{NaCl}} \right)^3$$

$$= \frac{58.5}{74.5} \left(\frac{8}{7} \right)^3 = 1.1725$$

Sol 29: BCC structure

Effective number of atoms = 2

$$\text{Density} = \frac{2 \times \left(\frac{100}{6.023 \times 10^{23}} \right)}{(4 \times 10^{-10})^3} = 5.188 \text{ gm/cm}^3$$

$$\text{Volume of 10 gm} = \frac{10}{5.188} = 1.927 \text{ cm}^3$$

$$= 1.927 \times 10^{-6} \text{ cm}^3$$

$$\text{Volume of one unit} = (4 \times 10^{-10})^3 = 64 \times 10^{-30} \text{ cm}^3$$

$$\text{Number of unit cells} = \frac{1.927 \times 10^{-6}}{64 \times 10^{-30}} = 0.301 \times 10^{23}$$

$$\text{Number of atoms} = 6.023 \times 10^{22} \text{ atoms}$$

Exercise 2

Single Correct Choice Type

Sol 1: (C) $\text{CaF}_2 = \text{Ca}^{2+}$ (in fcc structure) + F^- (at tetrahedral void)

$$= 4 + 8 = 12 \text{ atoms} = 4 \text{ molecules}$$

$$3.18 \times 10^6 = \frac{4 \times \left(\frac{78}{6.023 \times 10^{23}} \right)}{a^3} \Rightarrow a = 546 \text{ pm}$$

Sol 2: (D)

(a) False each has co-ordination number = 6

(b) False

(c) False

(d) True

Both should have equal co-ordination number

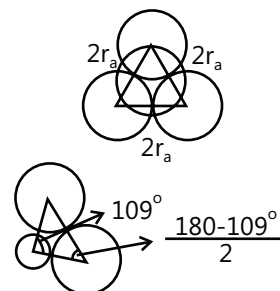
Sol 3: (B) Analyzing cubic diagonal in three dimension

$$\left(\frac{r_{y^-} + 2r_{x^+} + r_{y^-}}{\sqrt{3}} \right) = 480 \text{ pm}$$

$$r_{x^+} + 225 = 240 \sqrt{3}$$

$$r_{x^+} = 190 \text{ pm}$$

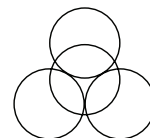
Sol 4: (B) Closest packing \Rightarrow fcc



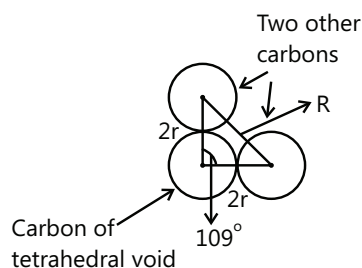
$$\frac{2r_a}{\sin 109^\circ} = \frac{r_a + r_b}{\sin(35.5^\circ)}$$

$$r_b = 0.225r_a$$

Sol 5: (A) Analyzing unit of tetrahedral void



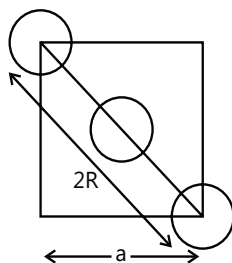
In the shown fig. of four carbon atoms, there is one more carbon atom which is in tetrahedral void of the group. It is in touch with all other carbon atoms. None of the 4 carbon-atoms touches each other.



$$\frac{R}{\sin 109^\circ} = \frac{2r}{\sin\left(\frac{180-109^\circ}{2}\right)}$$

$$R = 3.256 r_c$$

Face of cubic



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

$$R = \frac{a}{\sqrt{2}}$$

$$3.256 r_c = \frac{356}{\sqrt{2}}$$

$$r_c = 77.0 \text{ pm}$$

Sol 6: (D) Schottky defect appears in molecules which have same size of ions & have high co-ordination. Thus, CsCl will show this defect.

Sol 7: (A) Edge length = $a = 362 \text{ pm}$

In fcc unit, analyzing face diagonal

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

radius of copper

$$r = \frac{356}{2\sqrt{2}} = 128 \text{ pm}$$

fcc has two types of void

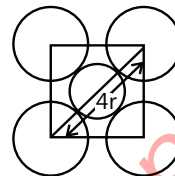
\Rightarrow tetrahedral, octahedral

Octahedral void will allow for largest radius of atom without any disturbance

$$\frac{r_A}{r_{Cu}} = 0.414$$

$$\Rightarrow r_A = 53 \text{ pm}$$

Sol 8: (C) Face of FCC unit cell:



$$\text{Edge length} = \frac{4r}{\sqrt{2}} = 2\sqrt{2} r$$

$$\text{Covered length} = 2r$$

$$\text{Fraction cover} = \frac{2r}{2\sqrt{2}r} = 70\%$$

$$\text{Fraction not covered} = 100 - 70.7 = 29.3\%$$

Multiple Correct Choice Type

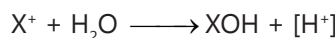
Sol 9: (A, C) XY has CsCl type structure

$$\text{So } 2(r_{x^+} + r_{y^-}) = \sqrt{3} a$$

$$A = 4\text{\AA}$$

Let's suppose molecular weight of XY = M

$$\text{So } [XY] = \frac{80}{2 \times M} = C$$



c

$$c(1-\alpha) \quad c\alpha \quad c\alpha$$

$$\frac{K_w}{K_b} = \frac{[XOH][H^+]}{[X^+]}$$

$$[H^+] = 10^{-5}$$

$$\frac{10^{-14}}{4 \times 10^{-5}} = \frac{c\alpha}{c(1-\alpha)} \times 10^{-5}$$

$$\alpha \sim \frac{1}{4} \times 10^{-4}$$

$$[H^+] = c\alpha = 10^{-5}$$

$$C = \frac{10^{-5}}{(1/4) \times 10^{-4}}$$

$$C = 0.4$$

$$\frac{80}{2M} = 0.4$$

$$M = 100 \text{ gm/mole}$$

$$\text{Density} = \frac{1 \times \left(\frac{100}{6.02 \times 10^{23}} \right)}{(4 \times 10^{-10})^3} = 2.6 \text{ gm/cm}^3$$

Sol 10: (B, D)

- (A) Wrong. Analyzing CsCl structure
- (B) Voids on center of edge so six void
- (C) Co-ordination will not be affected.
- (D) Correct

Sol 11: (A, C, D)

- (A) Correct
- (B) No, co-ordination in BCC structure = 8
- (C) Yes

$$(D) \frac{r_{\text{Na}^+}}{r_{\text{Cl}^-}} = \frac{95}{181} = 0.524 > 0.414$$

$$\text{So length of edge} = 2(r_{\text{Na}^+} + r_{\text{Cl}^-}) = 552 \text{ pm}$$

Sol 12: (A, C)

- (A) Correct
- (B) $\frac{r_+}{r_-} = \frac{0.2}{0.95} = 0.210 < 0.225$
 $\frac{r_+}{r_-} > 0.155$
 It will occupy trigonal void
 Co-ordination number = 3
- (C) Correct
- (D) No, It depends on other atom that is coming

Assertion Reasoning Type

Sol 13: (A) Statement-II correct

$$\text{Statement-I BCC} \Rightarrow 4r = \sqrt{3} a$$

$$a = \frac{4r}{\sqrt{3}}$$

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

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

BCC > FCC (distance between nearest lattice points)

Sol 14: (A) Statement-II $\Delta G = \Delta H - T\Delta S$

ΔH for formation of point defect > 0

$$\Delta S > 0$$

So hence increasing T leads to decrease in G

So increasing temperature, we will get more point defect.

Statement-II is explaining statement-I

Sol 15: (C) Statement-II is wrong. Because cations comes in interstitial space because of small size.

Sol 16: (A) Both are correct, statement-II is explaining statement-I

Comprehension Type

Sol 17: (A) In fcc packing efficiency = 74%

Let's say total volume of the solid = V

$$\text{Mass} = (3.2) V$$

Now, after melting, mass would be same.

$$3 = \frac{(3.2)V}{V_f}$$

$$V_f = 1.066 V$$

$$\text{So, final packing efficiency} = \frac{(0.74)V}{(1.066V)} = 69.3\%$$

Hence empty space ~ 31%

Sol 18: (B) SiC \Rightarrow C = fcc

Si = at half of tetrahedral voids

Molecular weight = 28

Diamond \Rightarrow C = fcc

C = at tetrahedral void

For SiC

$$10^6 \times 3.2 = \frac{(Z_{\text{eff}}) \left(\frac{28 + 12}{6.023 \times 10^{23}} \right)}{a^3}$$

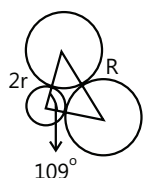
$$Z_{\text{eff.}} = 4$$

$$a = 436.23 \text{ pm}$$

For diamond

$$10^6 \times 3.6 = \frac{8 \times \left(\frac{12}{6.023 \times 10^{23}} \right)}{a^3}$$

$$b = 353.76 \text{ pm}$$



$$\frac{R}{\sin 109^\circ} = \frac{2r_c}{\sin\left(\frac{180-109}{2}\right)}$$

$$R = 3.256 r_c$$

$$2R = \sqrt{2} b$$

$$r_c = 76.81 \text{ pm}$$

Analysis by ratio of densities

$$\frac{d_1}{d_2} = \frac{3.2}{3.6} = \frac{M_{\text{SiC}} / V}{M_{\text{C}_2} / V}$$

$$\frac{8}{9} = \frac{(2r_c)^3}{(r_{\text{Si}} + r_c)^3} \times \frac{(28+12)}{24}$$

$$\frac{r_{\text{Si}}}{r_c} = 1.46$$

$$r_{\text{Si}} = 1.12 \text{ \AA}$$

Sol 19: (C)

(A) It will change density

(B) Changes always

(C) It will not change as the mass & the volume both are constant.

(D) Decreasing temperature \longrightarrow Decreases distance \longrightarrow increases density

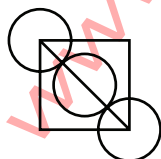
$$\text{Sol 20: (C) Density} = \frac{2 \times (\text{Atomic mass})}{\text{Volume}}$$

$$3.2 \times 10^6 = \frac{Z \times \left(\frac{40}{6.023 \times 10^{23}} \right)}{(4.37 \times 10^{-10})^3}$$

$$Z \sim 4$$

FCC unit

Sol 21: (D) Face



$$4r = \sqrt{2} (437 \text{ pm})$$

$$r = 154.5 \text{ pm}$$

Distance between nearest neighbour = 309 pm

Match the Columns

Sol 22: (A \rightarrow r, s; B \rightarrow p, q, r, s; C \rightarrow q)

(A) Rock salt structure

Co-ordination number = 6

$$A = 2 (r_+ + r_-)$$

Co-ordination number of cation and anions are same

$$\text{Distance between nearest anion} = \frac{\sqrt{2}a}{2} = \frac{a}{\sqrt{2}}$$

(B) Zinc blende structure

Co-ordination number of cation = 4

$$\frac{\sqrt{3}a}{4} = r_+ + r_-$$

Co-ordination number of cation and anions are same

(C) Fluorite structure

(p) Incorrect

(q) Correct

(r) Incorrect

(s) Incorrect

Sol 23: A \rightarrow p; B \rightarrow q, s; C \rightarrow r

Solve matrix reverse

$$(p) \text{ Shortest distance} = (r_+ + r_-) = \frac{\sqrt{3}a}{2}$$

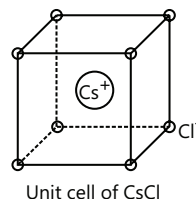
$$(q) = \text{Shortest distance between two cations} = \frac{a}{\sqrt{2}}$$

$$(r) 0.433a = 2r$$

$$(s) = \frac{\sqrt{2}a}{2} = 0.707 a$$

Previous Years' Questions

Sol 1: (A, C, D) The unit cell of CsCl has bcc arrangement of ions in which each ion has eight oppositely charged ions around it in the nearest neighbours as shown below :



Unit cell of CsCl

(B) In bcc, coordination number of atom is 8.

(C) In a unit cell, a corner is shared in eight unit cells and a face centre is shared between two adjacent unit cells.

(D) In NaCl unit cell; $2(r_{\text{Na}^+} + r_{\text{Cl}^-}) = a$

$$\Rightarrow a = 2(95 + 181) = 552 \text{ pm}$$

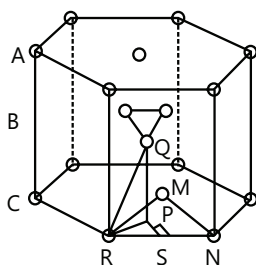
Sol 2: (B, C) (A) Incorrect statement. A small difference in sizes of cation and anion favour Schottky defect while Frenkel defect is favoured by large difference in sizes of cation and anion.

(B) Correct statement. In Frenkel defect, the smaller atom or ion gets dislocated from its normal lattice positions and occupies the interstitial space.

(C) In F-centre defect, some anions leave the lattice and the vacant sites hold the electrons trapped in it maintaining the overall electro-neutrality of solid.

(D) Incorrect Statement. In Schottky defect, some of the atoms or ions remaining absent from their normal lattice points without distorting the original unit cell dimension. This lowers the density of solid.

Sol 3: (B)



An hcp unit cell

$$\text{Contribution of atoms from corner} = \frac{1}{6}$$

$$\text{Contribution from face centre} = \frac{1}{2}$$

\Rightarrow Total number of atoms per unit cell

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

Sol 4: (A) In close packed arrangement, side of the base = $2r$

$$\Rightarrow RS = r$$

Also MNR is equilateral triangle, $\angle PRS = 30^\circ$

$$\text{In triangle PRS, } \cos 30^\circ = \frac{RS}{PR} = \frac{\sqrt{3}}{2}$$

$$\Rightarrow PR = \frac{2}{\sqrt{3}} RS = \frac{2}{\sqrt{3}} r$$

In right angle triangle PQR,

$$PQ = \sqrt{QR^2 - PR^2}$$

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

$$\Rightarrow \text{Height of hexagon} = 2PQ = 4\sqrt{\frac{2}{3}} r$$

\Rightarrow Volume = Area of base \times height

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

Sol 5: (D) Packing fraction

$$= \frac{\text{Volume occupied by atoms}}{\text{Volume of unit cell}}$$

$$= 6 \times \frac{4}{3} \pi r^3 \times \frac{1}{24\sqrt{2} r^3} = 0.74$$

\Rightarrow Fraction of empty space

$$= 1 - 0.74 = 0.26 = 26\%$$

Sol 6: (A \rightarrow p,s; B \rightarrow p,q) (A) Simple cubic and face centred cubic both have cell parameters $a = b = c$ and $\alpha = \beta = \gamma = 90^\circ$. Also both of them belongs to same, cubic, crystal system.

(B) Both cubic and rhombohedral crystal systems have their cell parameters $a = b = c$ and $\alpha = \beta = \gamma$ but they belongs to different crystal systems.

(C) Cubic and tetragonal are two different type of crystal systems having different cell parameters.

(D) Hexagonal and monoclinic are two different crystal systems and both have two of their crystallographic angle of 90° .

Sol 7: Ag crystallises in FCC unit cell with 4 atoms per unit cell.

$$\rho = \frac{4 \times 108}{6.023 \times 10^{23} \times a^3} = 10.5 \text{ g cm}^{-3}$$

$\Rightarrow a^3$ (Volume of unit cell)

$$= 6.83 \times 10^{-23} \text{ cm}^3$$

$$\Rightarrow a = 4 \times 10^{-8} \text{ cm} = 4 \times 10^{-10} \text{ m}$$

\Rightarrow Surface area of unit cell

$$= a^2 = 1.6 \times 10^{-19} \text{ m}^2$$

\Rightarrow Number of unit cells on 10^{-12} m^2 surface

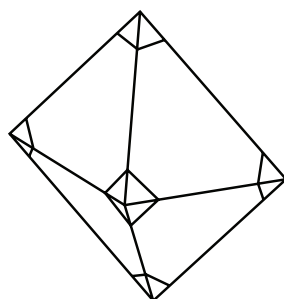
$$= \frac{10^{-12}}{1.6 \times 10^{-19}} = 6.25 \times 10^6$$

∴ There are two atoms (effectively) on one face of unit cell

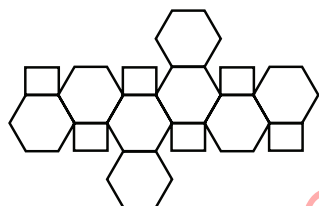
Number of atoms on 10^{-12} m^2 surface = $2 \times$ number of unit cell = 1.25×10^7 .

$$\Rightarrow x = 7$$

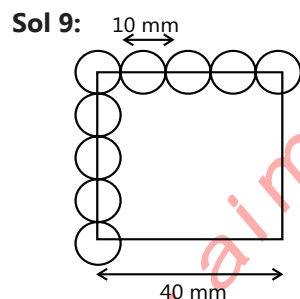
Sol 8: The truncated octahedron is the 14-faced Archimedean solid, with 14 total faces : 6 squares and 8 regular hexagons. The truncated octahedron is formed by removing the six right square pyramids one from each point of a regular octahedron as :



Truncated octahedron



Truncated octahedron unfolded in two dimension



(a) Side of square = 40 mm

Distance of marble = 10 mm

Number of marbles spheres along an edge of square with their centres within the square = 5 (shown in diagram)

Maximum number of marbles per unit are = $5 \times 5 = 25$

(b) If x mm is the side of square and d is diameter of marble then maximum number of marbles on square are with centres within square area can be known by the following general formula :

$$N = \left(\frac{x}{d} + 1 \right)^2$$

Sol 10: (a) In rock-salt like crystal AB, there are four AB units per unit cell. Therefore, density (d) is

$$d = \frac{4 \times 6.023y}{6.023 \times 10^{23} \times 8y \times 10^{-27}}$$

$$[\because a = 2y^{1/3} \text{ mm} = 2y^{1/3} \times 10^{-9} \text{ m}]$$

$$= 5 \times 10^3 \text{ g/m}^3 = 5 \text{ kg/m}^3$$

(b) Since, observed density is greater than expected, theoretical density, there must be some excess metal occupying interstitial spaces. This type of defect is known as metal excess defect.

Sol 11: In a cubic crystal system, there are two types of voids known as octahedral and tetrahedral voids. If r_1 is the radius of void and r_2 is the radius of atom creating these voids then

$$\left(\frac{r_1}{r_2} \right)_{\text{octa}} = 0.414 \text{ and } \left(\frac{r_1}{r_2} \right)_{\text{tetra}} = 0.225$$

The above radius ratio values indicate that octahedral void has larger radius hence for maximum diameter of atom to be present in interstitial space:

$$r_1 = 0.414 r_2$$

Also in fcc,

$$4r_2 = \sqrt{2} a$$

\Rightarrow Diameter required

$$\begin{aligned} (2r_1) &= (2r_2) \times 0.414 = \frac{a}{\sqrt{2}} \times 0.414 \\ &= \frac{400 \times 0.414}{\sqrt{2}} = 117 \text{ pm} \end{aligned}$$

Sol 12: From the given information, the number of atoms per unit cell and therefore, type of unit cell can be known as

$$\begin{aligned} \rho &= \frac{NM}{N_A a^3} \Rightarrow N = \frac{\rho N_A a^3}{M} \\ &= \frac{2 \times 6 \times 10^{23} \times (5 \times 10^{-8} \text{ cm})^3}{75} = 2 \text{ (bcc)} \end{aligned}$$

\Rightarrow In bcc,

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

$$\Rightarrow r = \frac{\sqrt{3}}{4}a$$

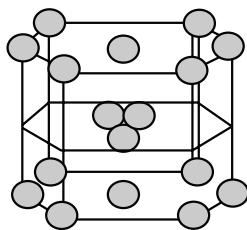
$$= \frac{\sqrt{3}}{4} 5 \times 10^{-10} \text{ m}$$

$$= 2.17 \times 10^{-10} \text{ m} = 217 \text{ pm}$$

Sol 13: A \rightarrow p,s; B \rightarrow p,q; C \rightarrow q; D \rightarrow q,r

Crystals class	Axial distances	Angles
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$
Trigonal and rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$
Monoclinic	$a \neq b \neq c$	$\alpha = \beta = 90^\circ$ $\gamma \neq 90^\circ$
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$

Sol 14: (B)



$$\text{Total effective number of atoms} = 12 \times \frac{1}{6} + 2 \times \frac{1}{2} + 3 = 6$$

Sol 15: (A) Height of unit cell $= 4r\sqrt{\frac{2}{3}}$

$$\text{Base area} = 6 \times \frac{\sqrt{3}}{4} (2r)^2$$

$$\text{Volume} = \text{height} \times \text{base area} = 24\sqrt{2}r^3$$

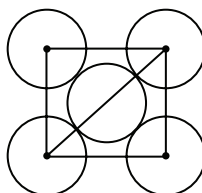
Sol 16: (D) Packing fraction = 74%

Empty space = 26%

Sol 17: (B, C) Conceptual Fact.

Sol 18: Coordination number of Al is 6. It exists in ccp lattice with 6 coordinate layer structure.

Sol 19: (D)



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

$$\text{Packing Efficiency} = \frac{2 \times \pi r^2}{(2\sqrt{2}r)^2} = \frac{2\pi r^2}{8r^2} = \frac{\pi}{4}$$

Sol 20: (B) $X = 8 \times \frac{1}{8} \times 6 \times \frac{1}{2} = 4$

$$M = 4 \times \frac{1}{4} + 1 = 2$$

So, unit cell formula of the compound is M_2X_4 and the empirical formula of the compound is MX_2

Sol 21: (A) According to the given A^+ is present in the octahedral void of X^- . The limiting radius in octahedral void is related to the radius of sphere as

$$r_{\text{void}} = 0.414r_{\text{sphere}}$$

$$r_{A^+} = 0.414r_{X^-} = 0.414 \times 250 \text{ pm} = 103.5 = 104 \text{ pm}$$

Sol 22: (A) In ccp lattice:

Number of O atoms $\rightarrow 4$

Number of Octahedral voids $\rightarrow 4$

Number of tetrahedral voids $\rightarrow 4$

Number of $Al^{3+} = 4 \times m$

Number of $Mg^{2+} = 8 \times m$

Due to charge neutrality

$$4(-2) + 4m(+3) + 8n(+2) = 0$$

$$\therefore m = \frac{1}{2} \text{ and } n = \frac{1}{8}$$

Sol 23: (B, C, D) Conceptual facts.

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