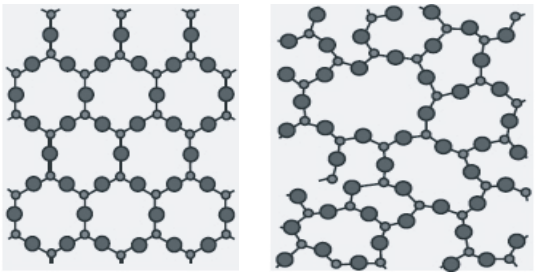
01 Solid State

The solid state :

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

Amorphous and crystalline solids :



(a) **(b)**

Two-dimensional structure of
(a) quartz and (b) quartz glass

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

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

Crystalline solids have a sharp melting point. On the other hand, amorphous solids soften over a range of temperature and can be moulded and blown into various shapes. On heating they may become crystalline

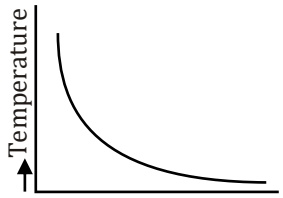
at some temperature. Some glass objects from ancient civilisations are found to become milky in appearance because of some crystallisation. Like liquids, amorphous solids have a tendency to flow, though very slowly. Therefore, sometimes these are called **pseudo solids** or **super cooled liquids.** Glass panes fixed to windows or doors of old buildings are invariably found to be slightly thicker at the bottom than at the top. This is because the glass flows down very slowly and makes the bottom portion slightly thicker.

Differences between crystalline and amorphous solids:

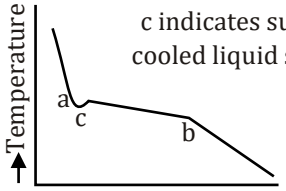
(i) Characteristic Geometry : In the crystalline solids the particles (atoms, ions, or molecules) are definitely and orderly arranged thus these have characteristic geometry while amorphous solids do not have characteristic geometry.

(ii) Melting Points : A crystalline solids has a sharp melting point i.e. it changes into liquid state at a definite temperature. On the contrary an amorphous solid does not has a sharp melting point. For example, when glass is heated, it softens and then starts flowing without undergoing any abrupt or sharp change from solid to liquid state. Therefore, amorphous solids are regarded as "liquids at all temperatures".

(iii) Cooling curve : Amorphous solids show smooth cooling curve while crystalline solids show two breaks in cooling curve. In the case of crystalline solids two breaks points 'a' and 'b' are appear. These points indicate the beginning and the end of the process of crystallization. In this time interval temperature remains constant. This is due to the fact that during crystallisation process energy is liberated which compensates for the loss of heat thus the temperature remains constant.



Cooling curve of an amorphous solid

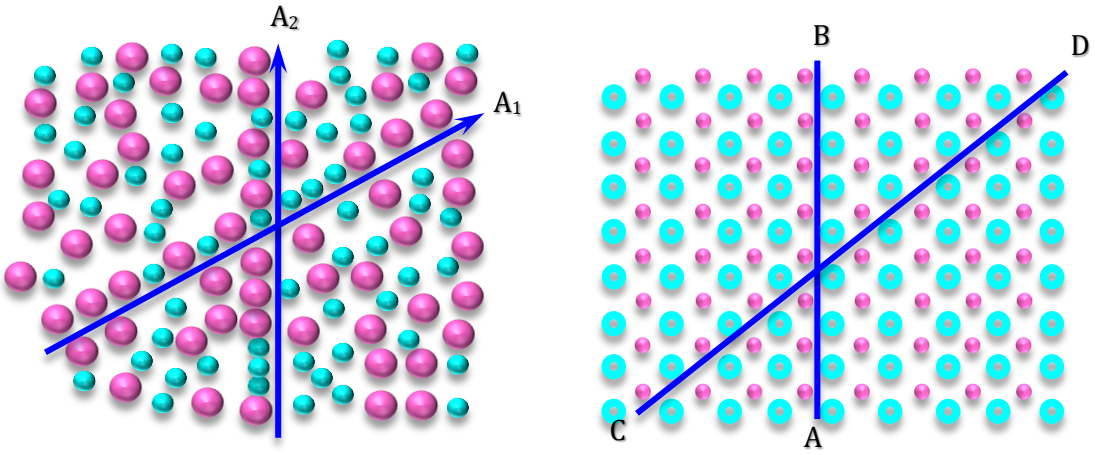


Cooling curve of crystalline solid

(iv) Isotropy and Anisotropy : Amorphous solids differ from crystalline solids and resemble liquids in many respects. The properties of amorphous solids, such as electrical conductivity, thermal conductivity, mechanical strength, refractive index, coefficient of thermal expansion etc. are same in all directions. Such solids are known as isotropic. **Gases and liquids are also isotropic.**

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

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



Isotropy in amorphous solids **Anisotropy in crystallin solids**

(v) Cutting :

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

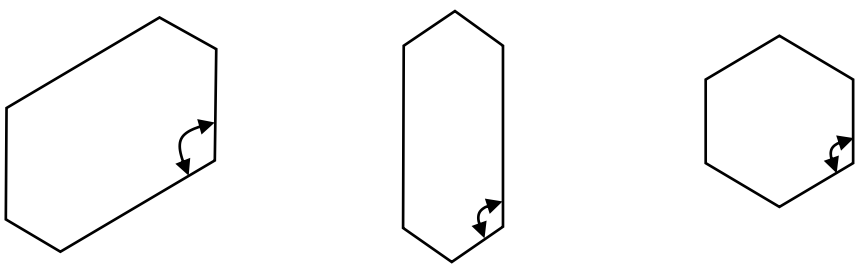
Crystalline state :

"A crystal is a solid composed of atoms (ions or molecules) arranged in an orderly repetitive array".

Most of the naturally occurring solids are found to have definite crystalline shapes which can be recognised easily. These are in large size because these are formed very slowly thus particles get sufficient time to get proper position in the crystal structure. Some crystalline solids are so small that appear to be amorphous. But on examination under a powerful microscope it is also seen to have a definite crystalline shape. Such solids are known as micro crystalline solid. Thus, the crystallinity of a crystal may be defined as "a condition of matter resulting from an orderly, cohesive, three-dimensional arrangement of its component particles (atoms, ions or molecules) in space". This three-dimensional arrangement is called **crystal lattice or space lattice**. The position occupied by the particles in the crystal lattice are called **lattice sites or lattice points**. The lattices are bound by surface that usually planar and known as faces of the crystal.

"The smallest geometrical position of the crystal which can be used as repetitive unit to build up the whole crystal is called a unit cell." The unit cell should have same symmetry elements as the crystal and there should be no gaps between unit cells.

The angle between the two perpendiculars to the two intersecting faces is termed as the interfacial angle which may be same as the angle between the unit cell edges. Goniometer is used to measure the interfacial angle. It is important to note that interfacial angle of a substance remains the same although its shape may be different due to conditions of formation.



Interfacial angles of crystal

This is known as law of constancy of interfacial angle or **law of crystallography.**

These differences are summarised in Table below :

Distinction between Crystalline and Amorphous Solids

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

Illustration 1:

Classify the following as amorphous or crystalline solids :

(a) Polyurethane (b) Naphthalene (c) Benzoic acid (d) Teflon

(e) Potassium nitrate (f) Cellophane (g) Polyvinyl chloride (h) Fibre glass

(i) Copper

Solution:

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

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

Note :

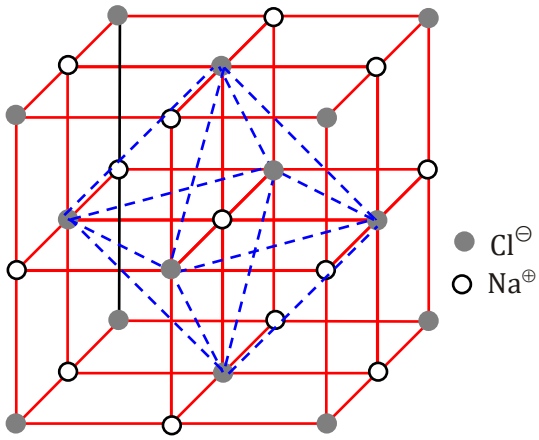
Polymeric substances are generally amorphous.

Types of the crystals :

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

(i) Ionic Crystals :

These are formed by a combination of highly electro-positive ions (cations) and highly electronegative ions (anions). Thus, strong electrostatic force of attraction acts with in the ionic crystals. Therefore, a large amount of energy is required to separate ions from one another. The type of the crystal lattice depends upon (i) The size of the ion (ii) The necessity for the preservation of electrical neutrality. Therefore, alternate cations and anions in equivalent amounts are arranged in the ionic crystal e.g. NaCl, KF, CsCl etc.



Crystal structure of NaCl

(ii) Covalent Crystals :

These are formed by sharing of valence electrons between two atoms resulting in the formation of a covalent bond. The covalent bonds extend in two or three dimensions forming a giant interlocking structure called network. Diamond and graphite are the good examples of this type.

(iii) Molecular Crystals :

In these crystals, molecules occupy the lattice points of the unit cells, except in solidified noble gases in which the units are atoms, where the binding is due to Vander Waal's' forces and dipole-dipole forces. Since Vander Waal's forces are non-directional hence structure of the crystal is determined by geometric consideration only. Solid H_2, N_2, O_2, CO_2, I_2, sugar etc. are well known examples of such crystal in which Vander Waal's forces are acting. Ice is the common example in which dipole-dipole forces of attraction (hydrogen bonding) are active. Many organic and inorganic crystals involve hydrogen bonds. Although these are comparatively weaker but play a very important role in determining the structures of substances e.g. polynucleotides, proteins etc.

(iv) Metallic Crystals :

These are formed by a combination of atoms of electropositive elements. These atoms are bound by metallic bonds. It may be defined as :

The force that binds a metal ion to a number of electrons within its sphere of influences is known as metallic bond OR

A bond which is formed between electropositive elements OR

The attractive force which holds the atoms of two or more metals together in a metal crystal or in an alloy.

We know that the force of attraction between metal ions and valence electrons is very strong. This force of attraction is responsible for a compact solid structure of metal.

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

Some Important Characteristics of Various types of Crystals

S. No.	Characteristics	Ionic Crystals	Covalent Crystals	Molecular Crystals	Metallic Crystals
1.	Units that occupy lattice points	Cations and anions	Atoms	Molecules	Positive ions in a "sea or pond" of electrons.
2.	Binding forces	Electrostatic attraction between ions	Shared electrons	Vander Waals or Dipole-dipole	Electrostatic attraction between positively charged ions and negatively charged electrons.
3.	Hardness	Hard	Very hard (Graphite is soft)	Soft	Hard or soft
4.	Brittleness	Brittle	Intermediate	Low	Low
5.	Melting point	High	Very high	Low	Varying from moderate to high
6.	Electrical Conduction	Semi-conductor due to crystal imperfections, conductor in fused state	Non-conductor (Graphite is good conductor (Exception))	Bad conductor	Good conductors
7.	Solubility in Polar solvents	Soluble	Insoluble	Soluble as well as insoluble	Good conductors
8.	Heat of Vaporisation (kj mol^{-1})	NaCl(s) 170	Graphite 718 very high	NH_3(s) 23.55 Lowest	Cu(s) 304.59 Variable
9.	Heat of fusion (kj mol^{-1})	NaCl 28.45	–	NH_3(s) 5.65	Cu(s) 13.016
10.	Examples	NaCl, KNO_3, CsCl, Na_2SO_4, ZnS	Diamond, graphite, Quartz (SiO_2), SiC	H_2O(s), CO_2(s), Sulphur, Sugar, Iodine, noble gases	Na, Cu, Ag, Fe, Pt, alloys

Types of the crystalline solid :

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

Illustration 2:

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

(a) Potassium sulphate (K_2SO_4) **(b)** Tin (Sn) **(c)** Benzene (C_6H_6) **(d)** Urea (NH_2CONH_2)
(e) Ammonia (NH_3) **(f)** Water (H_2O) **(g)** Zinc sulphide (ZnS) **(h)** Graphite (C)
(i) Rubidium (Rb) **(j)** Argon (Ar) **(k)** Silicon carbide (SiC)
(l) Bronze

Solution :

Ionic solids : (a), (g)
Metallic solids : (b), (i), (*l*)
Molecular solids : (c), (d), (e), (f), (j)
Covalent network solids.: (h), (k)

Isomorphism :

The occurrence of a given substance in more than one solid crystalline forms have different physical properties is known as polymorphism. This property when occurs in elements is known as allotropy.
Sometimes we come across examples of chemically different solids which crystallise in the same crystalline shape. Such substances are said to be Isomorphous (same shape). Their chemical constitutions are very similar and in some cases crystals of one substance may continue to grow when placed in a saturated solution of the other e.g. potash alum and chrome alum crystals have the same shape and can be grown in each other's solutions. Mitscherlich deduced that isomorphous substances have similar chemical formula e.g. phosphates and arsenates are said to be isomorphous with one another viz.

1. $Na_2HPO_4.12H_2O$ and $Na_3AsO_4.12H_2O$
2. K_2SO_4, K_2CrO_4
3. $ZnSO_4.7H_2O$, $MgSO_4.7H_2O$, $FeSO_4.7H_2O$
4. $KMnO_4$, $KClO_4$
5. $K_2SO_4.Al_2(SO_4)_3.24H_2O$, $K_2SO_4.Cr_2(SO_4)_3.24H_2O$. However, the law is not without exceptions.

Illustration 3:

Which of the following is a non-crystalline solid ?
(A) CsCl (B) NaCl (C) CaF_2 (D) Glass
Ans. (D)

Illustration 4:

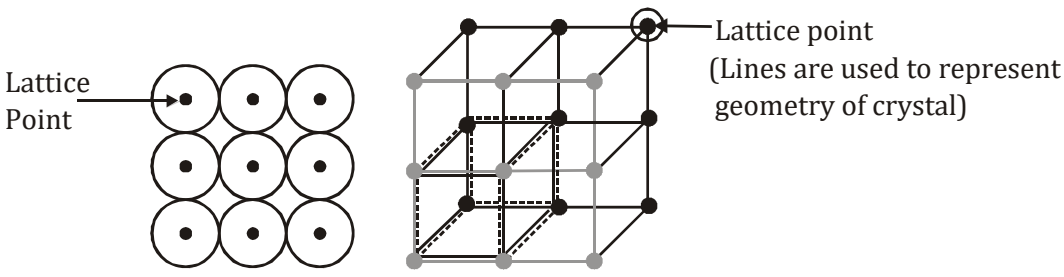
Which of the following statements is incorrect about amorphous solids?
(A) They are anisotropic
(B) They are rigid and incompressible
(C) They melt over a wide range of temperature
(D) There is no orderly arrangement of particles
Ans. (A)

Illustration 5:

Assertion : Crystalline solids are anisotropic.
Reason : The constituent particles are very closely packed.
(A) - Both A and R are true and R is the correct explanation of A.
(B) - Both A and R are true but R is not the correct explanation of A.
(C) - A is true but R is false.
(D) - If both A and R are false.
Ans. (B)

Some basic definition :

Space lattice (Crystal lattice) :



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

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

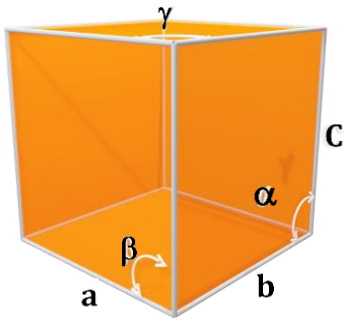
(b) Each point in a crystal lattice represents one constituent particle which may be an atom, a molecule (group of atoms) or an ion.

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

Unit cell :

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

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



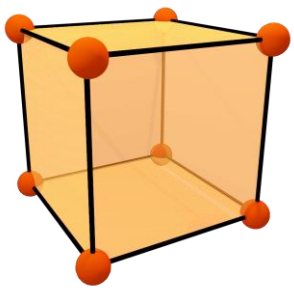
Type of unit cells -

Primitive and Centred Unit cells

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

(a) Primitive Unit Cells (P)

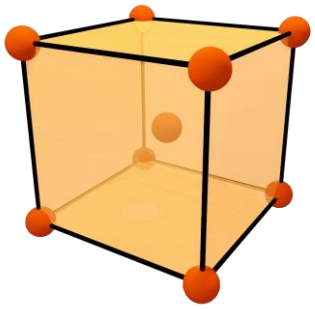
When constituent particles are present only on the corner positions of a unit cell, it is called as **primitive unit cell.**



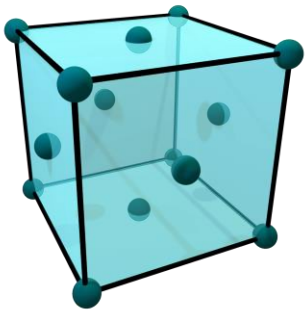
(b) Centred Unit Cells

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

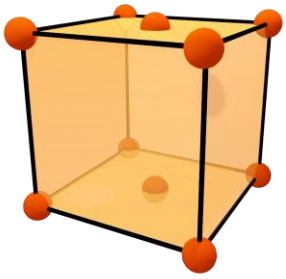
(i) Body-Centred Unit Cells (I) : Such a unit cell contains one constituent particle (atom, molecule or ion) at its body-centre besides the ones that are at its corners.



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



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



The seven crystal systems :

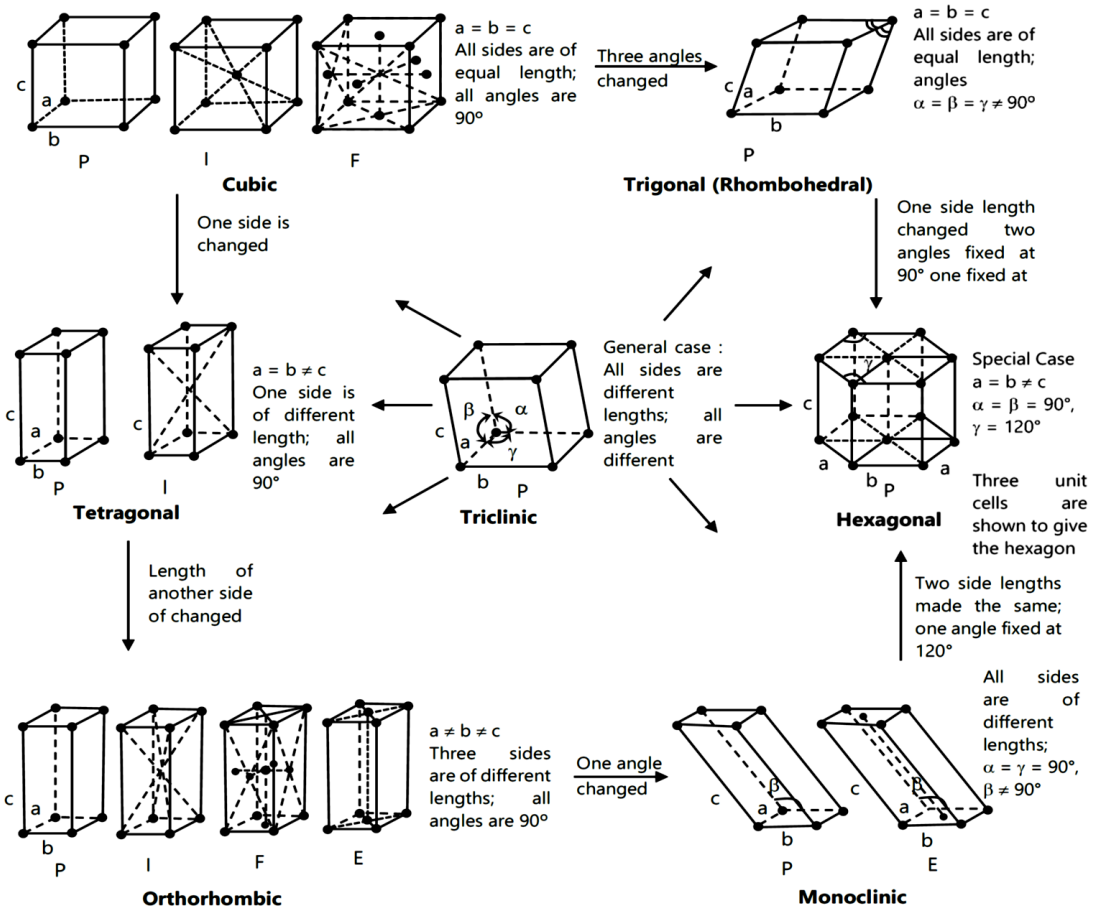
On the basis of the classification of symmetry, the lattice has been divided into seven systems. These can be grouped into 7 crystal systems. These seven systems with the characteristics of their axes (angles and intercepts) along with some examples of each are given in the following table :

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

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

Bravais Lattices :

There are 14 Bravais lattices :



Co-ordination number :

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

Packing fraction or packing density (P.F.) :

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

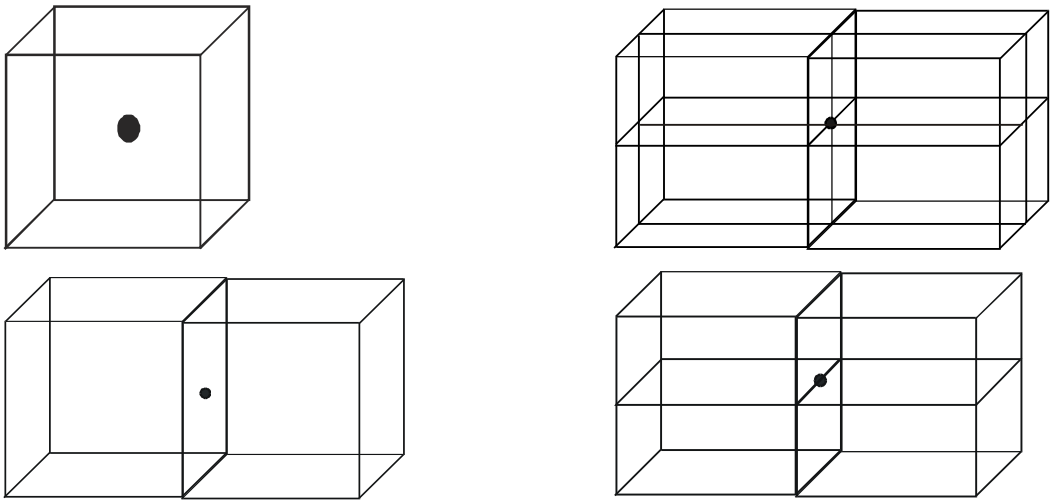
$$\text{P.F.} = \frac{\text{Volume occupied by particles present in a crystal}}{\text{Volume of crystal}}$$

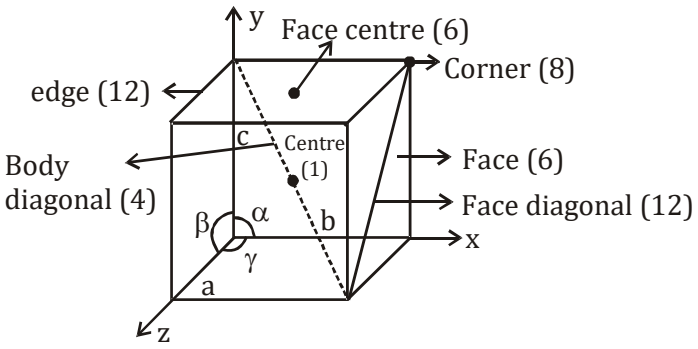
$$\text{P.F.} = \frac{\text{Volume occupied by particles present in unit cell}}{\text{Volume of Unit Cell}}$$

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

In a cube

1. Number of corners = 8
2. Number of faces = 6
3. Number of edges = 12
4. Number of body centre = 1
5. Number of body diagonals = 4
6. Number of face diagonals = 12

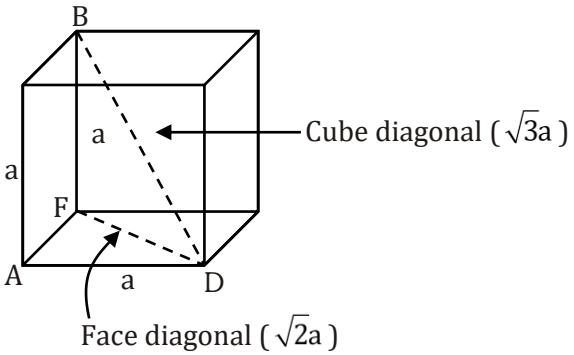


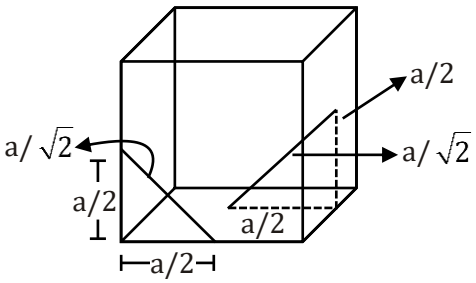


Contribution of an atom at different lattice points of cube :

- A corner of a cube is common in 8 cubes. So $\frac{1}{8}$ th part of an atom is present at this corner of cube.
- A face of a cube is common in 2 cubes. So $\frac{1}{2}$ th part of an atom is present at the face of a cube.
- An edge of a cube is common in four cubes, so $\frac{1}{4}$ th part of the atom is present at the edge of a cube
- A cube centre is not common in any another cube, so one complete atom is present at the cube centre.

Length of face diagonal and cube diagonal :





Distance between 2 adjacent face centres = $\frac{a}{\sqrt{2}} = \frac{a\sqrt{2}}{2}$

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

Consider the triangle AFD (with the help of Pythagoras theorem)

$$FD = \sqrt{AF^2 + AD^2} = \sqrt{a^2 + a^2} = \sqrt{2}a \quad \text{(length of face diagonal.)}$$

Consider the triangle $\angle$BFD (with the help of Pythagoras theorem)

$$BD = \sqrt{BF^2 + FD^2} = \sqrt{a^2 + (\sqrt{2}a)^2} = \sqrt{3}a \quad \text{(length of cube diagonal)}$$

Packing in solid :

Close packing :

It is type of packing with maximum packing fraction & space utilisation.

The constituent particles of a solid are like hard spheres. These spheres can pack in space in various manner to form a packing. To clearly understand the packing of these spheres, the packing can be categorised as :

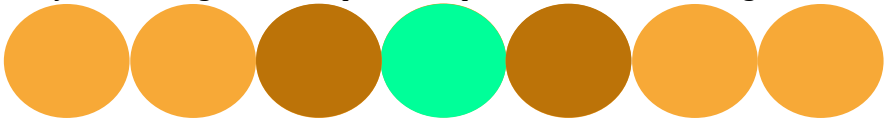
(i) Close packing in one dimension.

(ii) Close packing in two dimensions.

(iii) Close packing in three dimensions.

Close Packing in One Dimension :

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



Close packing of spheres in one dimension

Each sphere is touched by other two spheres; hence coordination numbers of packing is two. To define 1-D lattice only one constant is required minimum repeat distance.

Two-Dimensional packing of spheres:

The spheres in two-dimensional packing form a layer of sphere in two-dimensional space. These layers now placed one on top of other to create a three-dimensional arrangement of spheres in space. To define 2-D lattice completely three constants are required - two edge lengths and one angle between them.

Two possible types of two-dimensional packing are.

(a) Square close packing in two dimensions.

(b) Hexagonal close packing in two dimensions.

(a) Two dimensional square packing of spheres :

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

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

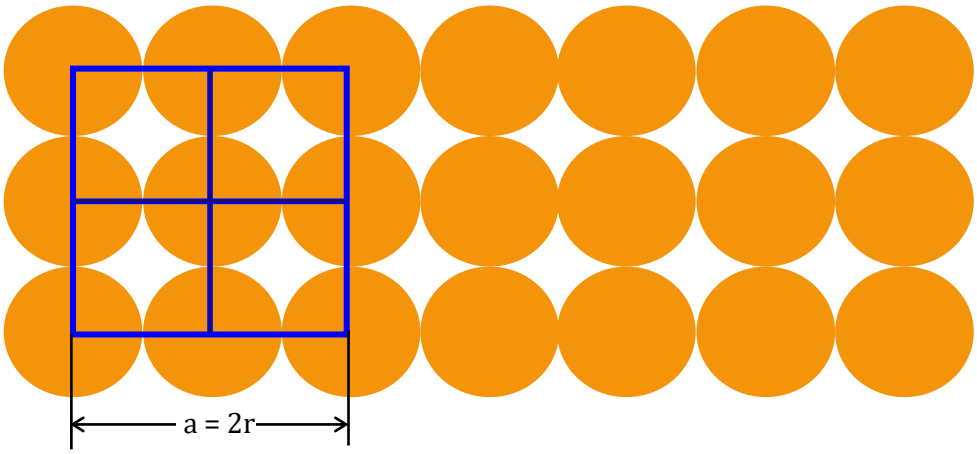
(ii) Each sphere is touched by four others hence coordination number is four.

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

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

(v) Packing fraction in 2-D $= \frac{1\times\pi r^2}{a^2} = \frac{1\times\pi(a/2)^2}{a^2} = \frac{\pi}{4} = 0.74$.

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



(b) Two dimensional hexagonal close packing :

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

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

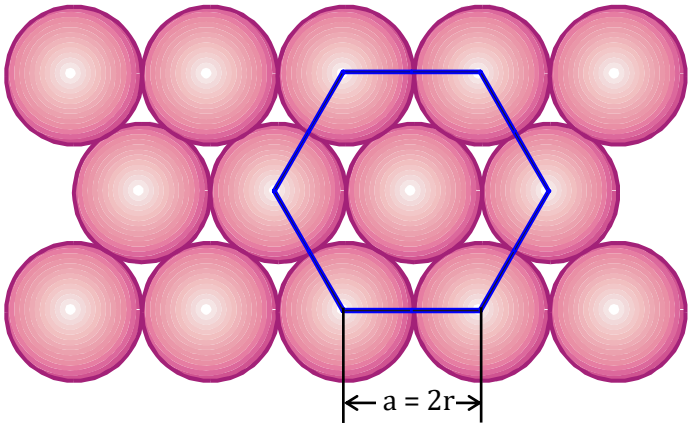
(ii) If centres are joined, hexagonal unit cells are formed. Hence this is called two-dimensional hexagonal close packing.

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

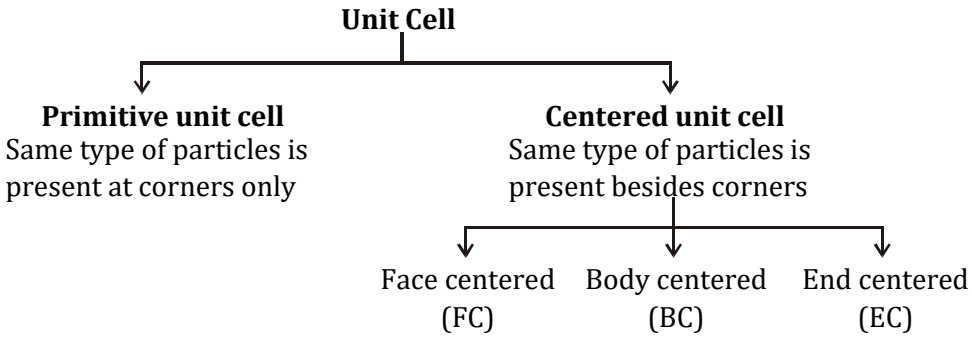
(iv) Each sphere is touched by six others; hence coordination number is six.

(v) Packing fraction in 2-D = $\frac{3\times\pi\left(\frac{a}{2}\right)^2}{\frac{a^3\sqrt{3}}{4}\times 6} = \frac{\pi}{2\sqrt{3}} = 0.91$

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



Classification of unit cell (as per Bravais) :



- In end centred same type of particles are present at corners and any two opposite face centres.
- End centred type of Bravais lattice is present only in orthorhombic and monoclinic type unit cell.

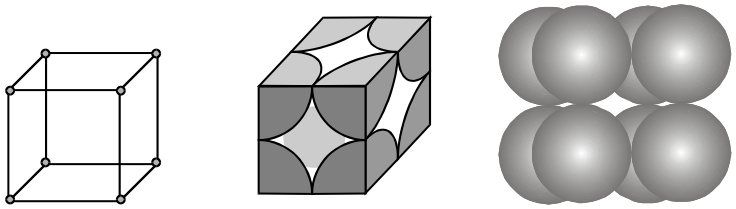
Types of cubic unit cell:

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

(A) Simple/Primitive/Basic Unit cell (Simple cubic, SC) :

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

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

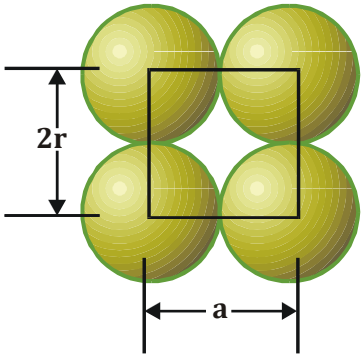


(a) Relationship between Edge length 'a' and Particle radius 'r' :-

i.e.,

$a = 2r$

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



(One face of SC)

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

(c) Packing Fraction (P.F.) :

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

$$= \frac{Z\times\frac{4}{3}\pi r^3}{V} \left[\text{ Volume of atom} = \frac{4}{3}\pi r^3\right]$$

$$P.F. = \frac{1\times\frac{4}{3}\times\pi\times\left(\frac{a}{2}\right)^3}{a^3} = \frac{\pi}{6} = 0.52$$

$[r = \frac{a}{2} \text{ and } V = a^3, Z = 1]$

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

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

(d) Coordination number (CN)

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

Density of the crystal :

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

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

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

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

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

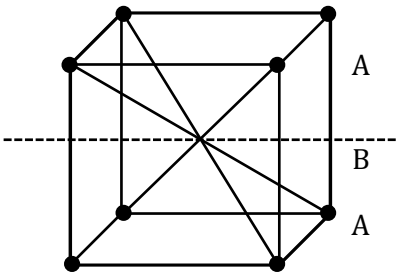
$\therefore$ Density of Crystal, d = Density of a unit cell = $\frac{Z \times M}{V \times N_A}$ g cm^{-3}

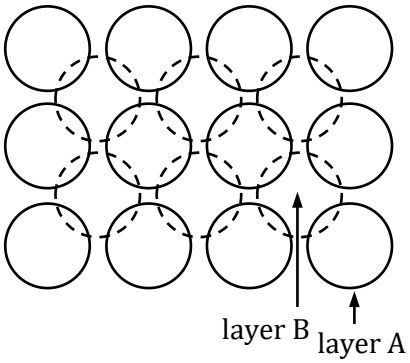
(B) Body Centred Cubic Unit Cell (BCC)

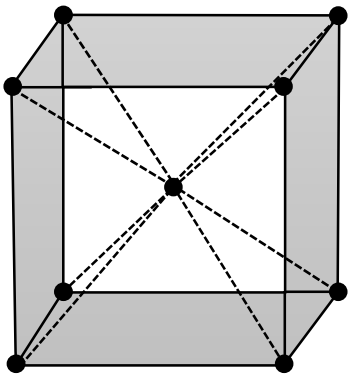
A unit cell having lattice point at the body centre in addition to the lattice point at every corner is called as body centred unit cell : where body diagonal particles are touching particle.

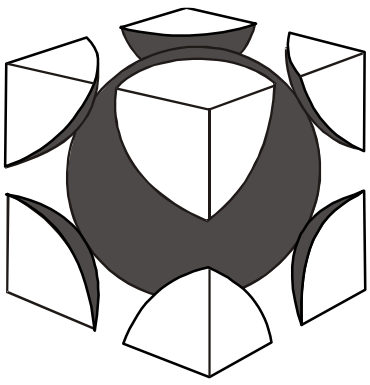
Here the central atom is surrounded by eight equidistant atoms and hence the co-ordination number is eight.

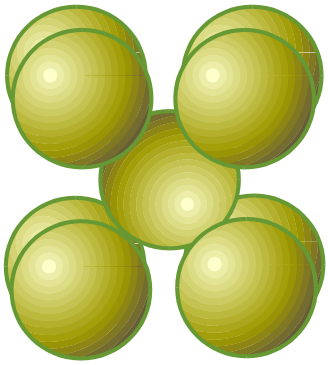
The nearest distance between two atoms will be $\frac{a\sqrt{3}}{2}$







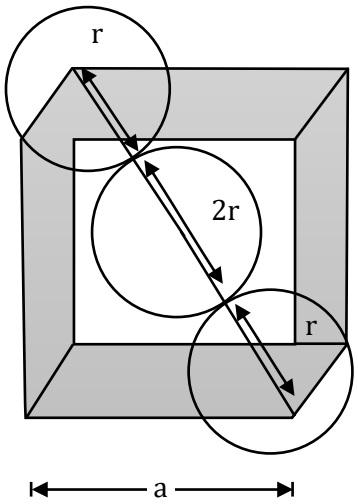




(a) Relationship between edge length 'a' and atomic radius 'r'

In BCC, along cube diagonal all atoms touches each other and the length of cube diagonal is .

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



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

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

(Corner) (Body centre)

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

(c) Packing fraction :

$$P.F. = \frac{Z \times \frac{4}{3}\pi r^3}{V} = \frac{2 \times \frac{4}{3} \times \pi \left(\frac{\sqrt{3}a}{4}\right)^3}{a^3} = \frac{\sqrt{3}\pi}{8} = 0.68$$

[Z = 2, $r = \frac{\sqrt{3}a}{4}$, $V = a^3$]

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

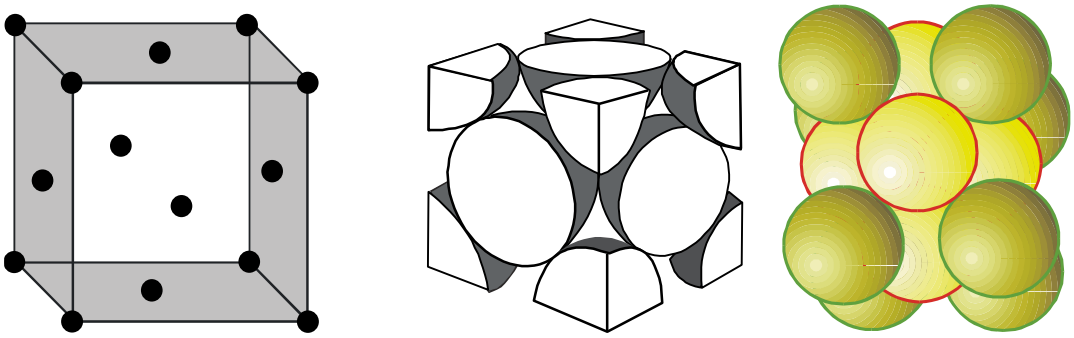
∴ Void space = 100 – 68 = 32 %

(d) Coordination number (CN)

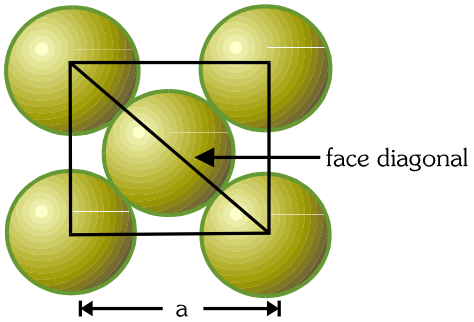
Nearest neighbour	Distance	Number
1	$\sqrt{3}\frac{a}{2}$	8
2	A	6
3	$\sqrt{2}a$	12

(C) Face Centred Cubic unit cell (FCC) :

A unit cell having lattice point at every face centre in addition to the lattice point at every corner called as face centred unit cell. i.e. in this case there are eight atoms at the eight corners of the unit cell and six atoms at the centre of six faces. The co-ordination number will be twelve and the distance between the two nearest atoms will be $\frac{a\sqrt{2}}{2}$



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



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

So $4r = \sqrt{2}a$ i.e. $r = \frac{\sqrt{2}a}{4} = \frac{a}{2\sqrt{2}}$ $\boxed{r = \frac{a}{2\sqrt{2}}}$

(b) Number of atoms per unit cell (z) :

$z = \left(\frac{1}{8}\times 8\right) + \left(6\times\frac{1}{2}\right) = 1 + 3 = 4$ atoms/unit cell

Corner faces

In this case one atom or ion lies at each corner of the cube and one atom or ion lies at the centre of each face of the cube. It may note that only $\frac{1}{2}$ of each face sphere lie within the unit cell and there are six such faces.

The total contribution of 8 corners is $\left(\frac{1}{8}\times 8\right) = 1$, while that of 6 face centred atoms is $\left(\frac{1}{2}\times 6\right) = 3$ in the unit cell. Hence total number of atoms per unit cell is 1 + 3 = 4 atoms (or ions).

(c) Packing Fraction :

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

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

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

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

(d) Coordination number (CN)

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

(D) End Centred Unit Cell:

A unit cell having lattice point at the centres of only one set of opposite faces in addition to the lattice point at every corner called as end centred unit cell.

Note :

This type of Bravais lattice is obtained only in orthorhombic and monoclinic type unit cell.

SUMMARY TABLE

Unit cell	No. of atoms per unit cell	Relation between r & a	Co-ordination Number	Volume occupied by particles (%)
Simple cube	$8 \times \frac{1}{8} = 1$	$r = \frac{a}{2}$	6	$\frac{\pi}{6} \times 100 = 52.4$
Body centred cube (BCC)	$8 \times \frac{1}{8} + 1 = 2$	$r = \frac{a\sqrt{3}}{4}$	8	$\frac{\pi\sqrt{3}}{8} \times 100 = 68$
Face centred cube (FCC)	$8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$	$r = \frac{a\sqrt{2}}{4}$	12	$\frac{\pi}{3\sqrt{2}} \times 100 = 74$

Illustration 6:

A solid crystallises in cubic crystal in which 'X' atoms occupy all the corners and body centres and 'Y' atoms occupy all the face-centres. What is the simplest formula of solid?

Solution:

$Z_X = 8 \times \frac{1}{8} + 1 = 2$

$Z_Y = 6 \times \frac{1}{2} = 3$

$\therefore$ Simplest formula of solid = X_2Y_3

Illustration 7:

A compound formed by elements X and Y has a cubic structure in which X atoms are at the corner of the cube and Y atoms are at the face centres.

a. Calculate : (i) Z_{eff}, (ii) formula of the compound.

b. If all the atoms are removed from a single axis passing through the centre of the cube, calculate
(i) Z_{eff}, (ii) formula of the compound.

Solution:

a. **i.** Number of effective X atoms = 8 corners $\times \frac{1}{8}$ per corner atom share = 1 atom/unit cell

Number of effective Y atoms = 6 face centres $\times \frac{1}{2}$ per face atom share = 3 atom/unit cell

ii. Formula of the compound:

$Z_{eff\,(X)} = 1$, $Z_{eff(Y)} = 3$

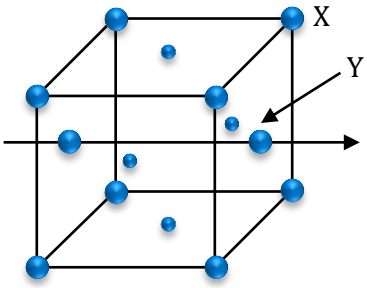
Thus, formula of the compound = XY_3

b. **i.** Two atoms from two face centres are remove by passing an axis as shown in the figure below.

$\therefore$ Face centre atom left = 6 – 2 = 4

$Z_{eff(Y)}$ = 4 face centre atom $\times \frac{1}{2}$ per face atom share = 2 atoms/unit cell

$Z_{eff(X)}$ = 8 corners $\times \frac{1}{8}$ per corner atom share = 1 atom/unit cell



ii. Formula of the compound:

$Z_{eff(X)} = 1$, $Z_{eff(Y)} = 2$

$\therefore$ Formula = XY_2

Illustration 8:

An element (atomic mass = 60) having face centred cubic crystal has a density of 6.23 g cm^{-3}. What is the edge length of the unit cell (Avogadro constant, $N_A = 6.02 \times 10^{23}$ mol^{-1}) :-

Solution:

Since element has FCC structure hence there are 4 atoms in a unit cell (or Z = 4), Atomic mass is 60 (or M = 60), $N_A = 6.02 \times 10^{23}$ and ρ = 6.23 g cm^{-3}.

$\because \quad \rho = \frac{Z \times M}{V \times N_A}$ or $V = \frac{Z \times M}{\rho \times N_A}$

$= \frac{(4)\left(60\,g\,mol^{-1)}\right)}{\left(6.23\,g\,cm^{-3)}\right)\left(6.02\times10^{23}\,mol^{-1}\right)}$

$= \frac{240\times10^{-23}\,cm^{-3}}{37.5046} = 6.4 \times 10^{-23}\,cm^3 = 64 \times 10^{-24}\,cm^3$

Let ℓ be the length of the edge of the unit cell.

$\therefore \quad \ell^3 = V = 64 \times 10^{-24}\,cm^3$

or $\ell = 4.0 \times 10^{-8}\,cm$

Illustration 9:

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 centred cubic structure.

Solution:

Length of the edge of the unit cell = 654 pm = 6.54×10^{-8} cm

$\therefore$ volume (V) of the unit cell = $(6.54 \times 10^{-8}\,cm)^3$

Molecular mass of KBr = 39 + 80

= 119 g mol^{-1}

Density of KBr = 2.75 g cm^{-3}

$\because \quad \rho = \frac{Z \times M}{V \times N_A}$

or $Z = \frac{\rho \times V \times N_A}{M}$

$= \frac{\left(2.75\,g\,cm^{-3}\right)\left(6.54\times10^{-8}\,cm\right)^3\left(6.023\times10^{23}\,mol^{-1}\right)}{119\,g\,mol^{-1}}$

$= \frac{2.75\times(6.54)^3\times(6.023)(10^{-1})}{119}$

$= 3.9 \cong 4$

Since number of atoms (or ions) in a unit cell is four hence the crystal must be face centred cubic.

Illustration 10:

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

Solution:

Length of the edge of the unit cell (ℓ) = 200 pm = 2×10^{-8} cm

$\therefore$ Volume (V) of the unit cell = $(2 \times 10^{-8}\,cm)^3 = 8 \times 10^{-24}\,cm^3$

Mass of the element (M) = 200 g

Number of the atoms (N_0) = 24×10^{23}

the number of atoms per unit cell (FCC) = 4

$\because \quad \rho = \frac{Z \times M}{V \times N_0}$

$= \frac{(4)(200\,g)}{(8\times10^{-24}\,cm^3)(24\times10^{23})} = 41.7\ g\ cm^{-3}$

Illustration 11:

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 diagonals. If volume of this unit cell is 24×10^{-24} cm^3 and density of the element is 7.2 g cm^{-3}. Calculate the number of atoms present in 200 g of the element.

Solution:

Volume (V) of the unit cell = 24×10^{-24} cm^3

Density of (ρ) of the element = 7.2 g cm^{-3}

Mass of the element = 200 g

Number of atoms (Z) per unit cell = [The contribution of the 8 corner is (1/8) × 8=1 and two atoms on one of the diagonals is

2 × 1 = 2] i.e. 1 + 2 = 3 atoms

$\because \quad \rho = \frac{Z \times M}{V \times N_0}$ or $N_0 = \frac{Z \times M}{V \times \rho}$

$N_0 = \frac{(3)(200\,g)}{(24\times10^{-24}\ cm^3)(7.2\,g\,cm^{-3})}$

$N_0 = 3.472 \times 10^{24}$ atoms

Close packing in three dimensions :

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

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

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

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

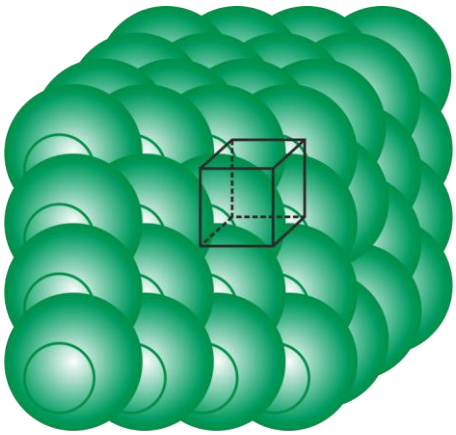
(a) Simple cubic packing in three dimension :

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

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

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

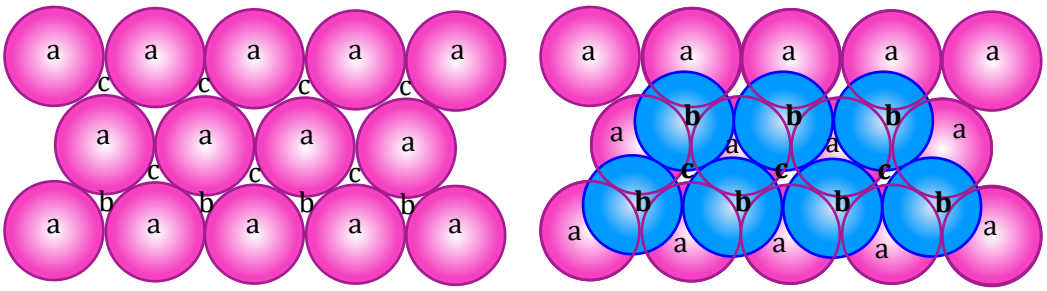
(iii) In this packing, only 52% of available space is occupied by atoms.



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

(b) Three Dimensionally close packing:

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



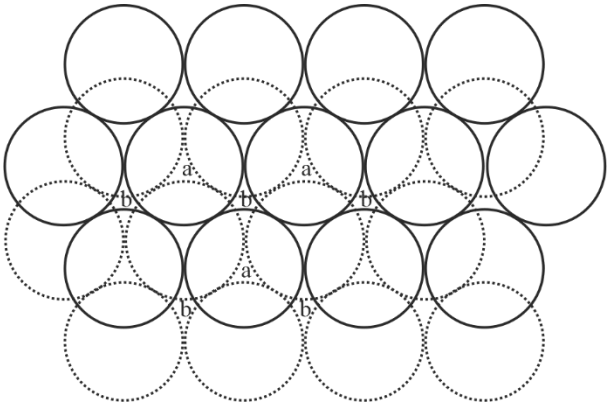
Now we extend the arrangement of spheres in three dimensions by placing second close packed layer (hexagonal close packing) (B) on the first layer (A). The spheres of second layer may placed either on space denoted by 'b' or 'c'. It may be noted that it is not possible to place spheres on both types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

ABC – ABC arrangement (Cubic close packing (FCC)

In second way, the spheres of the third layer (C) lie on the second layer (B) in such a way that they lie over the unoccupied spaces 'C' of the first layer(A). If this arrangement is continuous in the same order this is represented as ABC ABC ABC.... This type of arrangement represents cubic close packed (ccp) structure.

This structure has 3-fold axes of symmetry which pass through the diagonal of the cube. since in this system, there is a sphere at the centre of each face of the unit cell and hence this structure is also known as face-centred cubic (fcc) structure.

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



- IIIrd layer will be different from Ist layer as well as IInd layer.
- It is also known as cubical close packing (CCP), unit cell chosen is face centred unit cell (FCC).

Relation between 'a' and 'R' :

$a \neq 2R$

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

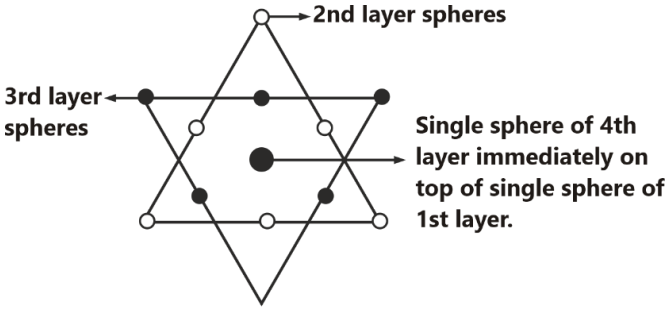
Effective no. of atoms per unit cell (Z) = $Z = \frac{1}{8}\times 8 + \frac{1}{2}\times 6 = 4$

Packing fraction :

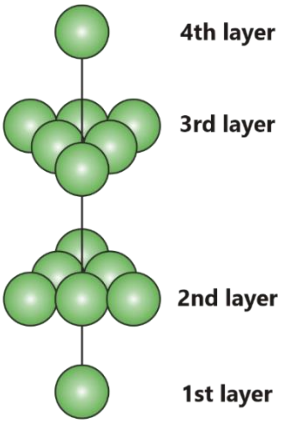
$$\text{P.F.} = \frac{4\times\frac{4}{3}\pi R^3}{a^3} = \frac{4\times\frac{4}{3}\pi R^3}{4\times 4\times 4R^3}\times\sqrt{2}\times 2 = \frac{\pi}{3\sqrt{2}} = 0.74\ (74\%)$$

Coordination number, (CN) = 12

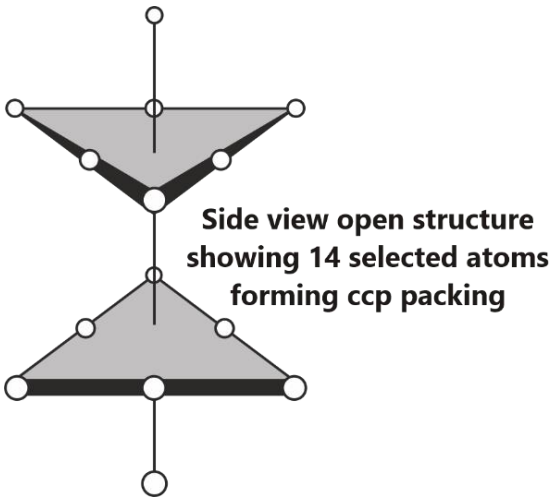
Density (d) = $\frac{Z\times M}{N_A \cdot a^3}$

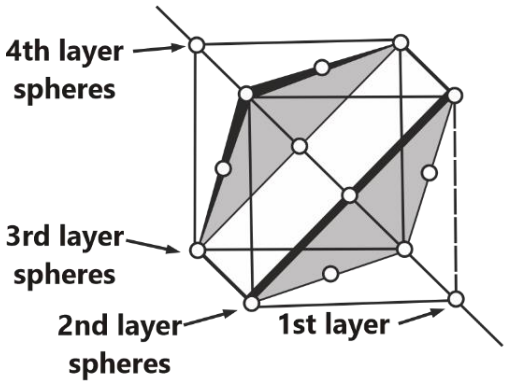


Open structure show top view of 14 Spheres forming ccp packing



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





For unit cell showing 14 spheres

Illustration 12:

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

Solution:

$d = \frac{ZM}{N_A.a^3}$; $6.25 = \frac{4\times60}{6\times10^{23}\times a^3} \Rightarrow a = 4 \times 10^{-8}cm = 4Å.$

Illustration 13:

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 kgm^{-3}, what is the nature of the cubic unit cell?

Solution:

The formula for density is, $d = \frac{Z.M}{N_A.a^3}$

Z = No. of atoms per unit cell.

M = Atomic mass

a = Edge length

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

Putting values we obtain Z = 4.

Hence, it is FCC packing.

Hexagonal close packing (HCP) ABAB ..... Type :

(i) In one way, the spheres of the third layer lie on the spaces of second layer (B) in such a way that they lie directly above those in the first layer(A). In other words, we can say that the third layer becomes identical to the first layer. If this arrangement is continued indefinitely in the same order this represented as ABAB ....

This type of arrangement represents hexagonal close packing (hcp) symmetry (or structure), which means that the whole structure has only one 6-fold axis of symmetry i.e. the crystal has same appearance on rotation through an angle of 60°.

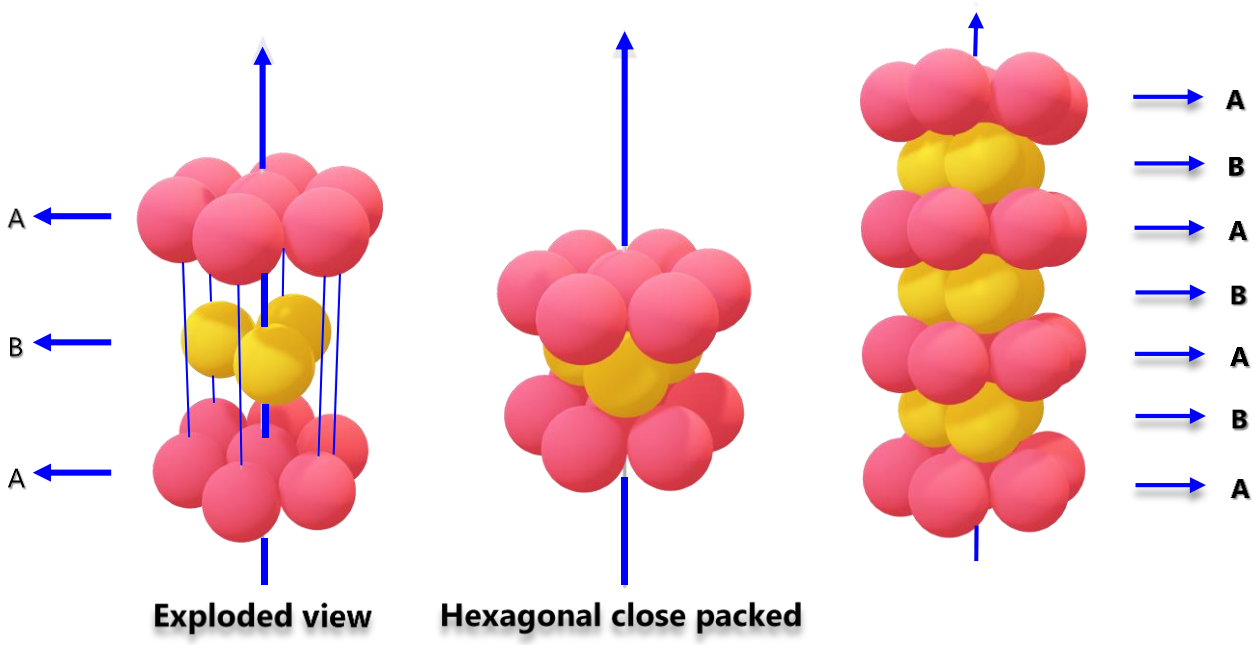
(ii) Every third layer sphere lies on top of first layer sphere. (ABABAB ..... packing)

(iii) Maximum possible space is occupied by spheres.

(iv) Each sphere is touched by 12 other spheres in 3D
(6 is one layer, 3 in top layer and 3 in bottom.)

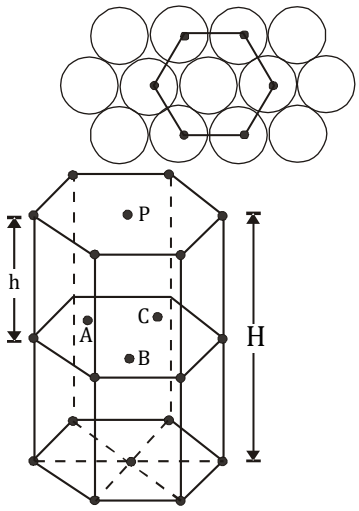
(v) The unit cell for hexagonal close packing is hexagonal unit cell.

(vi) For every atom forming hcp there are effectively two tetra voids and one octa void.
That why this generate ABAB ..... AB pattern. One type of void always remains unoccupied.



Unit cell : $a = b = 2R$; $\gamma = 120°$; $\alpha = \beta = 90°$

(vii) Packing efficiency of HCP units



Applying Pythagoras theorem in ΔCBD : $\left(\frac{a}{2}\right)^2 + CD^2 = a^2$

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

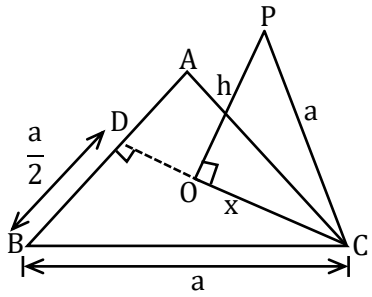
$$\therefore \quad CO = \frac{2}{3} \times CD$$ [$\because$ centroid divides median in the ratio 2 : 1]

$\therefore$ CO = $\frac{1}{\sqrt{3}}a = \frac{2R}{\sqrt{3}}$

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

$h = \sqrt{(2R)^2 - \left(\frac{2R}{\sqrt{3}}\right)^2} = \sqrt{\frac{8}{3}}R = 2\sqrt{\frac{2}{3}}R$

$\therefore$ Total height of hexagon (H) = 2 × h = $4\sqrt{\frac{2}{3}}R$



So, volume of hexagon = area of base × height

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

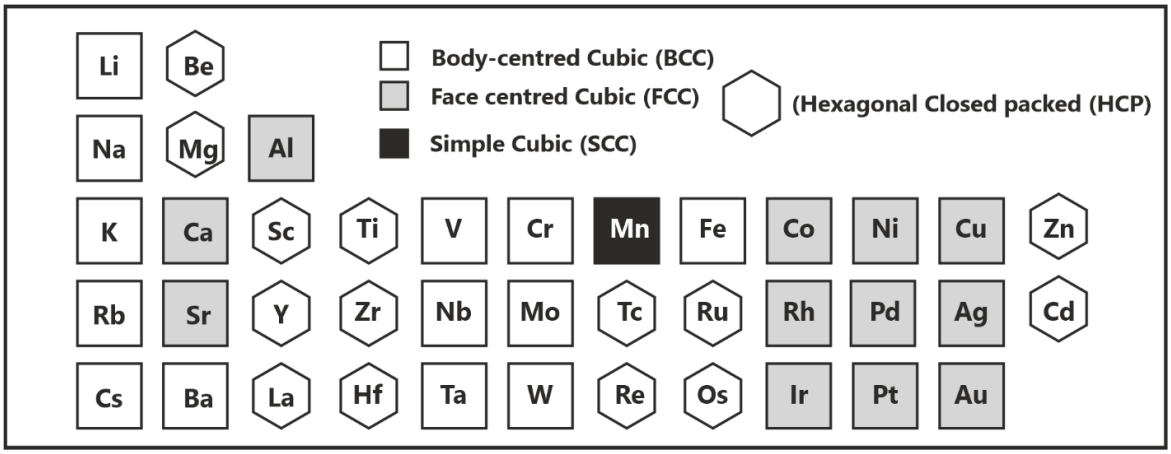
Effective no. of atoms (Z) = $Z = 3 + 2 \times \frac{1}{2} + 12 \times \frac{1}{6}$

$= 3 + 1 + 2 = 6.$

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

Density (d) = $\frac{\text{mass}}{\text{volume}} = \left[\frac{Z \times M}{N_A \times \text{volume}}\right]$ (Z = 6)

Some examples of metals with their lattice types and coordination number are given in the following table.



Three-dimensional close packing

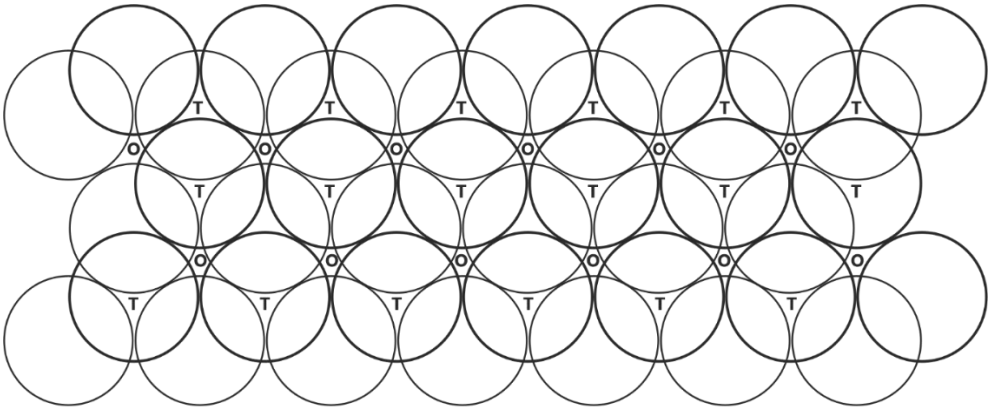
Contents	BCC	CCP/FCC	HCP
Type of packing packing but not close packing	ABAB..... close packing	ABCABC ..... close packing	ABAB .....
No. of atoms	2	4	6
Co-ordination no.	8	12	12
Packing efficiency	68%	74%	74%
Examples V & Cr group Fe	IA, Ba Co group, Ni group, Copper group, all inert gases except helium	Ca, Sr, Al d-block elements Be & Mg	Be & Mg

Note : Only Mn crystallizes in S.C.C.

Interstices or voids or holes in crystals :

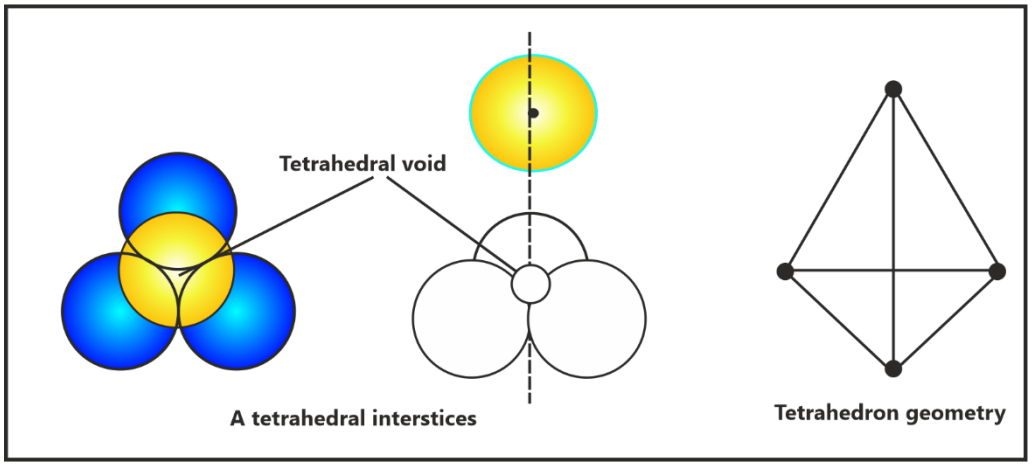
It has been shown that the particles are closely packed in the crystals even than there is some empty space left in between the spheres. This is known as interstices (or interstitial site or hole or empty space or voids). In three dimensional close packing (CCP & HCP) the interstices are of two types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

(i) tetrahedral voids and (ii) octahedral voids.



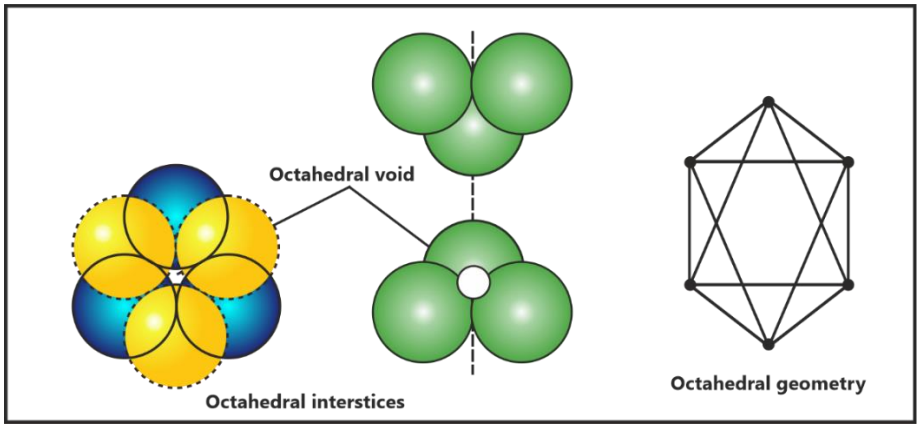
A stack of two layers of close packed spheres and voids generated in them. T = Tetrahedral void; O = Octahedral void

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



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

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



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

Positions of tetrahedral voids in an FCC unit cell :

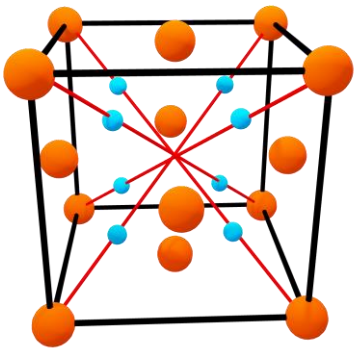
In FCC, one corner and its three-face centred atom of faces meeting at that corner form a tetrahedral void. In FCC, two tetrahedral voids are obtained along one cube diagonal. So, in FCC 8 tetrahedral voids are present.

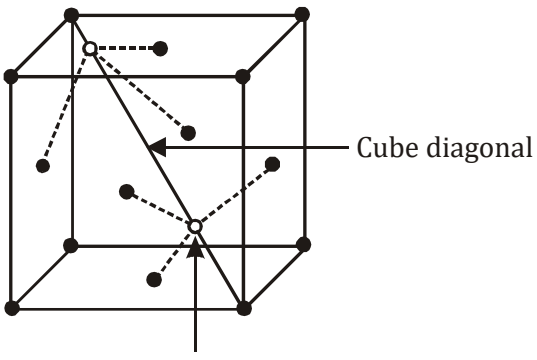
Alternatively, the centre of tetrahedral void is located on the centre of body diagonal of each small cube of volume $\left(\frac{a^3}{8}\right)$.

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

Total number of tetrahedral void = 8

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

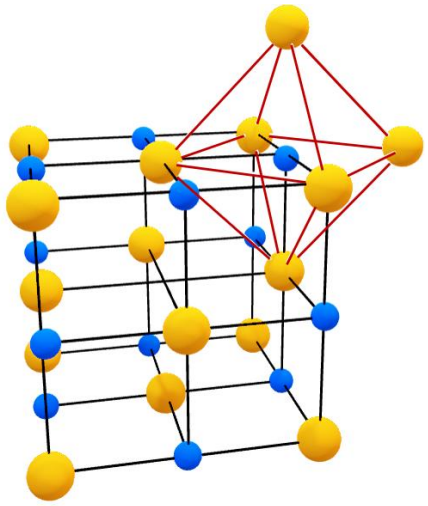




- Tetrahedral void
- Atom Forming FCC Packing

Position of octahedral void in FCC unit cell :

Position of octahedral void is at mid-point of each edge (total 12 edges in a cube) and at the centre of cube. Each octahedral void located at mid-point of edge contributes 1/4 to the unit cell. The octahedral void situated at the centre contributes 1.



Tetrahedral void
Atom Forming FCC Packing

In FCC, total number of octahedral voids are

$$(1 \times 1) \quad + \quad (12 \times \frac{1}{4}) = 1 + 3 = 4$$

(Cube centre) (edge)

In FCC, number of particles = 4

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

Position of tetrahedral and octahedral void in HCP:

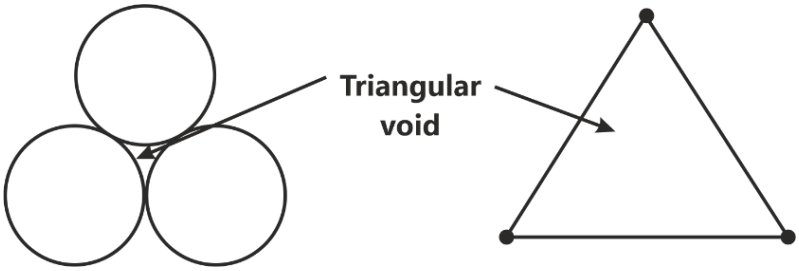
(i) Above & below each sphere, there is a tetrahedral void, hence number of tetrahedral void per unit cell = 12

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

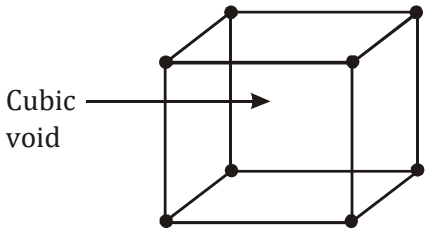
Note : In any closed packing of maximum efficiency, there are two TV & one OV per particle

Triangular and cubic voids:

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

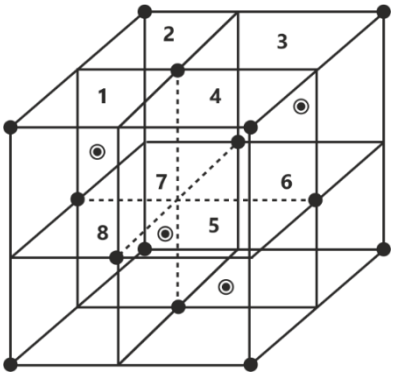


(ii) Cubic void : It is formed in simple cubic unit cell by eight spheres at the corners of cube.



Crystal of diamond:

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



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

Illustration 14:

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

Solution:

$z_P = 4$

$\Rightarrow \quad = \frac{25}{100} \times 8 = 2$

$\therefore$ Simplest formula of solid = $P_4Q_2 = P_2Q$

Illustration 15:

A compound made of particles A, B, and C forms CCP lattice.

In the lattice, ions A occupy the lattice points and ions B and C occupy the alternate TVs. If all the ions along one of the body diagonals are removed, then formula of the compound is

(A) $A_{3.75}B_3C_3$ (B) $A_{3.75}B_3C_4$ (C) $A_3B_{3.75}C_3$ (D) $A_3B_3C_{3.75}$

Ans. (A)

Solution:

Since the lattice is CCP (Z_{eff} = 4).

$\therefore$ Number of A ions = 4

(corner + face centre = 1 + 3 = 4

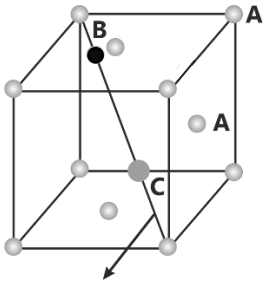
Number of B ions = Number of alternate TV = 4

Number of C ions = Number of alternate TV = 4

Number of A ions removed = $2 \times \frac{1}{8}(\text{corner share}) = \frac{1}{4}$

Other diagonals are not shown in the figure

Number of B ions removed = 1



Number of C ions removed = 1

(Since body diagonal ions are inside the cube so they do not share with other ions).

Number of A ions left = $4-\frac{1}{4}=3.75$

Number of B ions left = 4 – 1 = 3

Number of C ions left = 4 – 1 = 3

Thus, formula is : $A_{3.75}B_3C_3$

Illustration 16:

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

Solution:

In one unit cell of CCP, no. of N = 4; total no. of tetrahedral void = 8; occupied tetrahedral void by M = 8/3; Empirical formula : $N_4M_{8/3} = N_3M_2$.

Illustration 17:

A compound is formed by two elements X and Y. Atoms of the element Y (as anions) make CCP and those of the element X (as cations) occupy all the octahedral voids. What is the formula of the compound?

Solution:

Number of Y anions = $\frac{1}{8}\times 8+\frac{1}{2}\times 6=4$

Number of X cation = number of tetrahedral voids = 4

Formula of compound = $X_4Y_4 = XY$

Illustration 18:

Atoms of element B form hcp lattice and those of the element A occupy 2/3rd of tetrahedral voids. What is the formula of the compound formed by the elements A and B?

Solution:

Number of B = $\frac{1}{6}\times 12+\frac{1}{2}\times 2+3=6$

Number of A = $\frac{2}{3}\times 12=8$

Formula of compound = $A_8B_6 = A_4B_3$

Illustration 19:

What is the two-dimensional coordination number of a molecule in square close-packed layer?

Solution:

In square close packing, each atom touches four others, hence CN = 4.

Illustration 20:

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

Solution:

Since, for every atom forming hcp structure there are two tetrahedral voids and one octahedral void.

Total voids = 3 × 0.5 = 1.5 mol, total tetrahedral void = 2 × 0.5 = 1 mol.

Illustration 21:

Which of the following lattices has the highest packing efficiency (i) Simple cubic (ii) Body-centred cubic and (iii) Hexagonal close-packed lattice?

Solution:

Hexagonal close-packing has highest packing efficiency (74%).

Packing in ionic solid :

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

(ii) Oppositely charged particles should lie closer and similarly charged particles should lie away from each other.

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

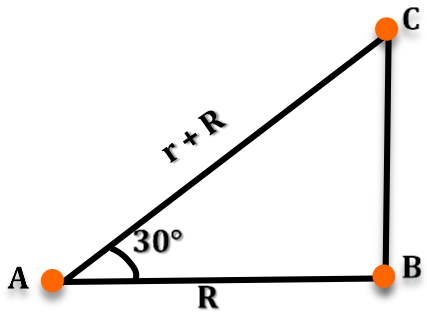
Point (ii) and (iii) contradict each other because on increase the CN, the repulsion between like charges will also increases. Hence, in all the ionic solids, there must be a balance with the help of relative size of ions to ensure maximum CN and minimum repulsion between like charges.

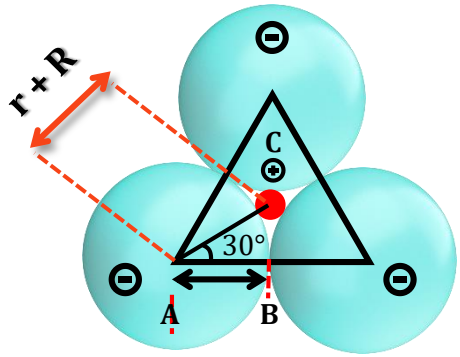
Limiting radius ratios :

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

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

(i) Triangular : All anions touches each other and co-ordination number is 3





R = Radius of Anion
r = Radius of cation

AC = R + r

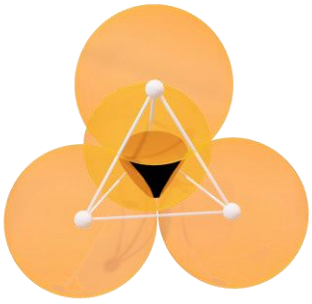
AB = R

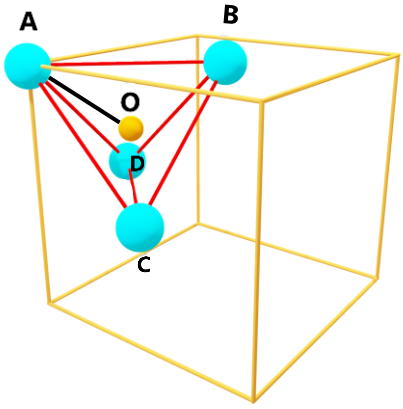
$\angle BAC = 30°$

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

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

(ii) Tetrahedral void : All anions touches each other and co-ordination number of cation is 4.





R = Radius of Anion
r = Radius of cation

$AB = \frac{\sqrt{2}a}{2} = 2R$

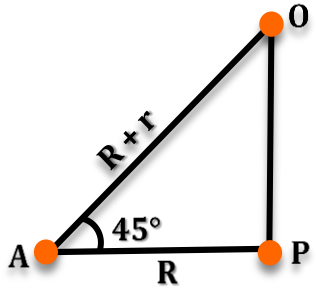
$AO = \frac{\sqrt{3}a}{4} = R + r$

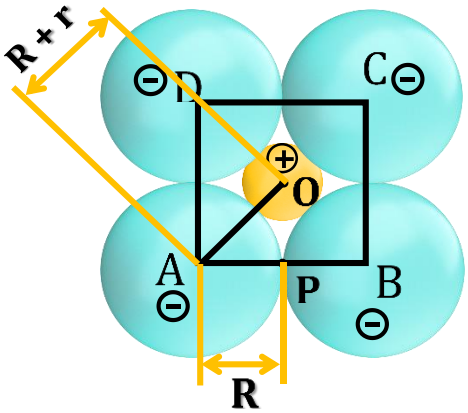
Now, $\frac{(R+r)}{R} = \frac{\sqrt{3}}{\sqrt{2}}$

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

Radius Ratio $\left(\frac{r}{R}\right) = 0.225$

(iii) Octahedral void : All the anions are touch each other and co-ordination number is 6.





R =Radius of Anion
r = Radius of cation

AO = R + r

AP = R

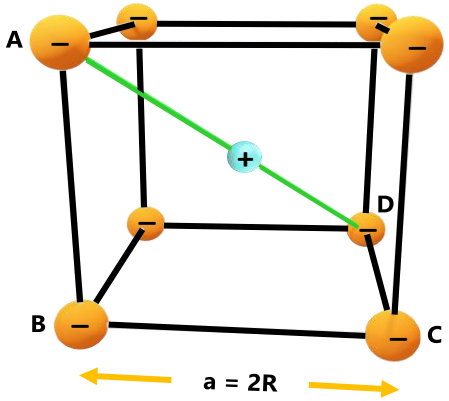
$\angle$ OAP= 45°

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

$r = (\sqrt{2} - 1)R$

r = 0.414 R

(iv) Cubic void : All the anions are touch each other and co-ordination number is 8.



R =Radius of Anion
r = Radius of cation

AB = a = 2R

AD = $\sqrt{3}a = 2(R + r)$

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

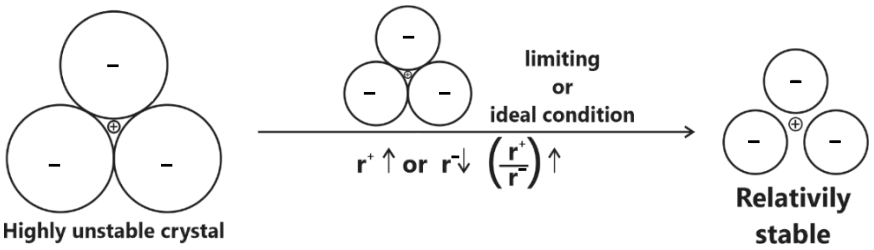
$\therefore \quad r = (\sqrt{3}-1)R = 0.732R$

Radius Ratio (R.R.) = 0.732

The preferred direction of the structure with increase in the radius ratio is as follows :

Plane triangular $\xrightarrow{0.225}$ Tetrahedral $\xrightarrow{0.414}$ octahedral $\xrightarrow{0.732}$ Cubic

Limiting or ideal radius ration $\left(\frac{r^{\oplus}}{r^{\ominus}}\right)$:



The minimum $\frac{r^{\oplus}}{r^{\ominus}}$ values for the existence of a cation in a particular void is called **limiting radius ratio** for that void. With the increase in radius ratio, space between anion will increase & hence the cation may tend for higher coordination number.

Limiting radius ratio for various types of sites

Limiting radius ratio = r/R	Coordination Number of cation	Structural Arrangement (Geometry of voids)	Example
0.155 - 0.225	3	Plane Trigonal	Boron Oxide
0.225 - 0.414	4	Tetrahedral	ZnS, SiO_2
0.414 - 0.732	4	Square planar	–
0.414 - 0.732	6	Octahedral	NaCl, MgO_2
0.732 - 1.000	8	Cubic	CsCl

Illustration 22:

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

Solution:

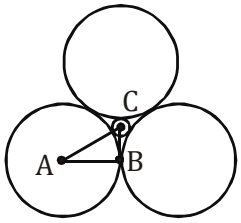
(i) AB = R

AC = R + r

$\angle BAC = 30°$

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

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

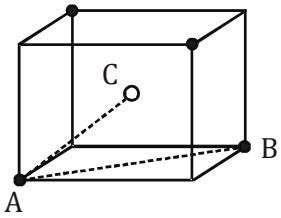


(ii) $AB = \sqrt{2}a = 2R$

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

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

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



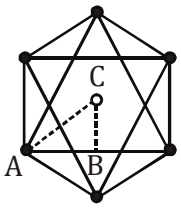
(iii) AB = R

AC = R + r

$\angle BAC = 45°$

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

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



(iv) AB = a = 2R

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

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

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

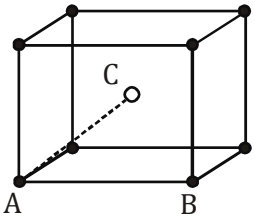


Illustration 23:

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

Solution:

In $Na^{\oplus}Cl^{\ominus}$ crystal each $Na^{\oplus}$ ion is surrounded by 6 $Cl^{\oplus}$ ions and vice versa. Thus $Na^{\oplus}$ ion is placed in octahedral hole.

The limiting radius ratio for octahedral site = 0.414

or $\frac{A^{\oplus}}{B^{\ominus}} = \frac{r}{R} = 0.414$

Given that radius of anion ($B^{\ominus}$) R = 250 pm

i.e. radius of cation ($A^{\oplus}$) r = 0.414 R = 0.414 × 250 pm

or r = 103.5 pm

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

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

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

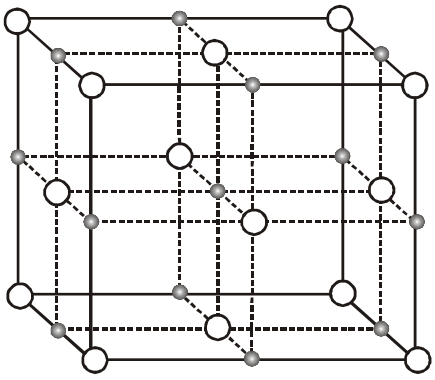
or r = 0.225 × R = 0.225 × 250 = 56.25 pm

Thus, ideal radius for cation is 56.25 pm for tetrahedral hole. But the radius of $C^{\oplus}$ is 180 pm. It is much larger than ideal radius i.e. 56.25 pm. Therefore, we cannot slip cation $C^{\oplus}$ into the tetrahedral site.

Structure of ionic solids :

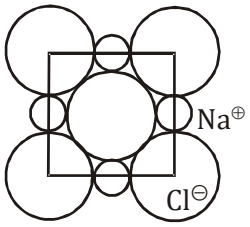
(a) Structure of NaCl :

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



$Cl^{\ominus}$ forming FCC packing

$Na^{\oplus}$ ion in octahedra void



Structure of a face

(i) Each $Na^{\oplus}$ is surrounded by six $Cl^{\ominus}$ and each $Cl^{\ominus}$ is surrounded by six $Na^{\oplus}$ ion. [6:6 coordination]

(ii) Total number of $Na^{\oplus}$ and $Cl^{\ominus}$ in each unit cell is 4.

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

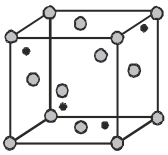
(iv) The density of NaCl crystal is given by $d = \left(\frac{4 \times M_{NaCl}}{N_A \times a^3}\right)$

N_A = Avogadro's number; a = Edge length

- The edge length of NaCl unit cell is given by $(2r^{\oplus +} + 2r^{\ominus}) \Rightarrow \boxed{\frac{a}{2} = r^{\oplus} + r^{\ominus}}$ (FCC & Octa void)

(b) Zinc blende (sphalerite) structure:

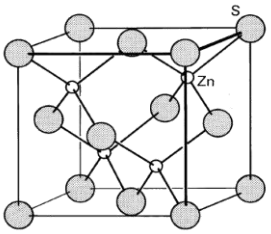
Larger anions form ccp arrangement and smaller cations filling half of alternate tetrahedral voids.



$\bigcirc \longrightarrow S^{2\ominus}$

$\bullet \longrightarrow Zn^{2\oplus}$

Zinc blende structure



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

(ii) Formula units of ZnS per unit cell = 4.

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

(iv) $r_{Zn^{2\oplus}} + r_{S^{2\ominus}} = \dfrac{a\sqrt{3}}{4}$

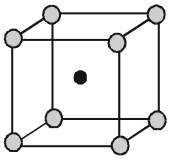
(c) Cesium halide structure: (CsCl) $Cl^{\ominus}$ at the corners of cube and $Cs^{\oplus}$ in the center.

(i) C.N. of $Cs^{\oplus}$ = 8 ; C.N. of $Cl^{\ominus}$ = 8 [8 : 8 coordination]

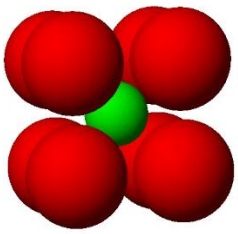
(ii) Formula units of CsCl per cube = 1

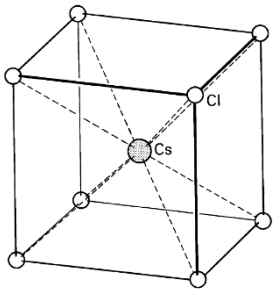
(iii) $d_{CsCl} = \dfrac{M_{CsCl}}{N_A \times a^3}$

(iv) $r_{Cs^{\oplus}} + r_{Cl^{\ominus}} = \dfrac{a\sqrt{3}}{2}$



Cesium chloride structure





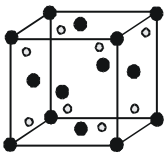
(d) Fluorite structure : (CaF_2) $Ca^{2\oplus}$ forming CCP arrangement and $F^{\ominus}$ filling all tetrahedral voids.

(i) C.N. of $F^{\ominus}$ = 4 ; C.N. of $Ca^{2\oplus}$ = 8 [8 : 4 coordination]

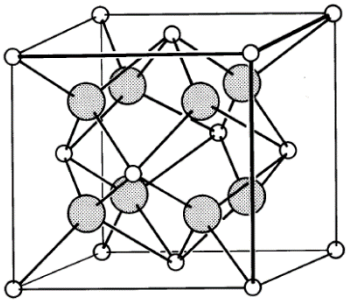
(ii) Formula units of CaF_2 per unit cell = 4

(iii) $d_{CaF_2} = \dfrac{4 \times M_{CaF_2}}{N_A \times a^3}$

(iv) $r_{Ca^{2\oplus}} + r_{F^{\ominus}} = \dfrac{a\sqrt{3}}{4}$



Fluorite structure



(e) Antifluorite structure : (Li_2O, Na_2O) $O^{2\ominus}$ ion forming CCP and $Li^{\oplus}$ taking all tetrahedral voids.

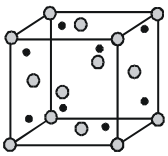
(i) C.N. of $Li^{\oplus}$ = 4

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

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

(iii) $d_{H_2O} = \frac{4 \times M_{H_2O}}{N_A \times a^3}$

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

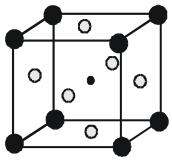


Antifluorite structure

(f) Corundum Structure : (Al_2O_3) $O^{2\ominus}$ forming hcp and $Al^{3\oplus}$ filling 2/3 octahedral voids.

(g) Rutile structure: (TiO_2) $O^{2\ominus}$ forming hcp while $Ti^{4\oplus}$ ions occupy half of the octahedral voids.

(h) Perovskite structure : ($CaTiO_3$) $Ca^{2\oplus}$ in the corner of cube $O^{2\ominus}$ at the face center and $Ti^{4\oplus}$ at the centre of cube.



Perovskite structure

(i) Spinel and inverse spinel structure ($MgAl_2O_4$) :

O^{2-} forming fcc, $Mg^{2\oplus}$ filling 1/8 of tetrahedral voids and $Al^{3\oplus}$ taking half of octahedral voids. In an inverse spinel structure, $O^{2\ominus}$ ion form FCC lattice, divalent cations occupy 1/8 of the tetrahedral voids and trivalent cation occupies 1/8 of the tetrahedral voids and 1/4 of the octahedral voids.

Imperfections in solids:

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

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

Types of Point Defects :

Point defect can be classified into three types:

(i) Stoichiometric defects

(ii) Non-stoichiometric defects

(iii) Impurity added defect

(i) Stoichiometric Defect

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

(a) Vacancy Defect :

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

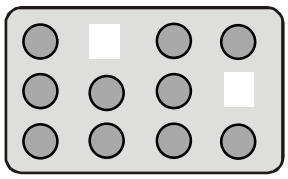


Fig. : Vacancy defects

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

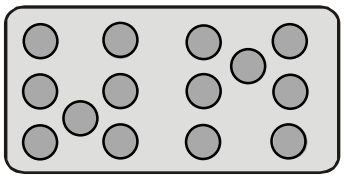
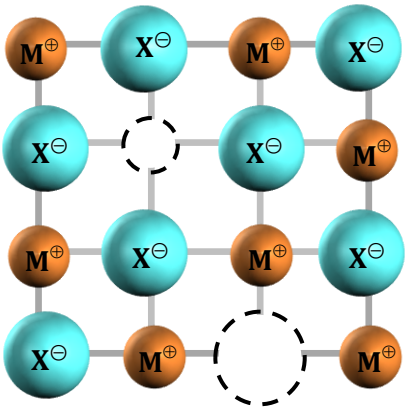


Fig. : Interstitial defects

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

Schottky Defect : It is basically a vacancy defect in ionic solids. In order to maintain electrical neutrality, the number of missing cations and anions are equal (in stoichiometric ratio) Like simple vacancy defect, Schottky defect also decreases the density of the substance. Number of such defects in ionic solids is quite significant. For example, in NaCl there are approximately, 10^6 Schottky pairs per cm^3 at room temperature. In 1 cm^3 there are about 10^{22} ions. Thus, there is one Schottky defect per 10^{16} ions. Schottky defect is shown by ionic substances in which the cation and anion are of almost similar sizes. For example, NaCl, KCl, CsCl and AgBr. It may be noted that AgBr shows both, Frenkel as well as Schottky defects.



Schottky defect

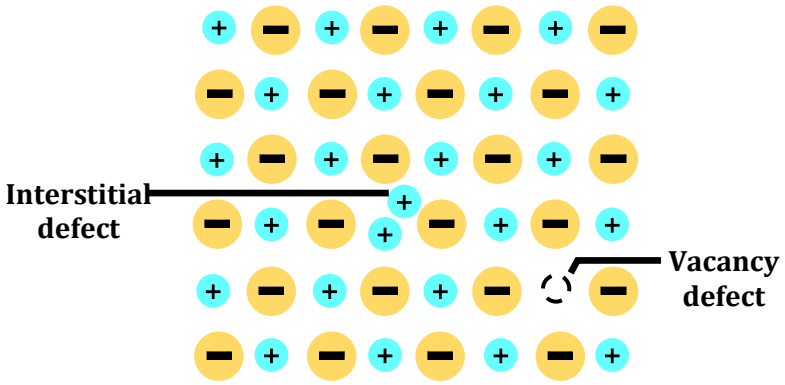
Influence : The presence of large number of schottky defects in crystal results in significant decrease in its density.

Frenkel Defect : This defect is shown by ionic solids.

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

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

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



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

(ii) Non-Stoichiometric Defects

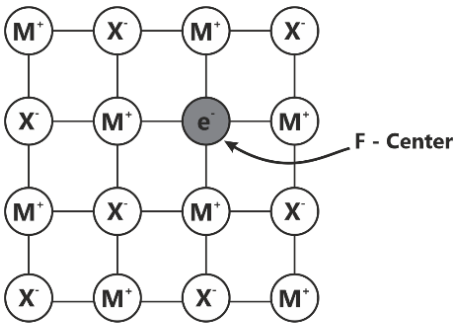
The defects discussed so far do not disturbs the stoichiometry of the crystalline substance. However, a large number of non-stoichiometric inorganic solids are known which contain the constituent elements in non-stoichiometric ratio due to defects in their crystal structures. These defects are of two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

(a) Metal excess defect.

(b) Metal deficiency defect.

(a) Metal Excess Defect

(I) Metal excess defect due to anionic vacancies :



Medal excess defects due to anion vacanices

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

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

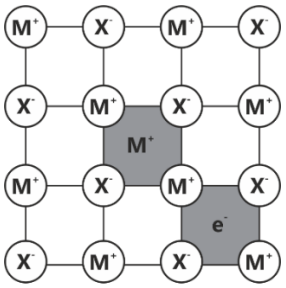
They impart yellow colour to the crystals of NaCl. The colour results by excitation of these electrons when they absorb energy from the visible light falling on the crystals. Similarly, excess of lithium makes LiCl crystals pink and excess of potassium makes KCl crystals violet (or lilac).

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

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

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

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



Medal excess defects due to interstitial cation

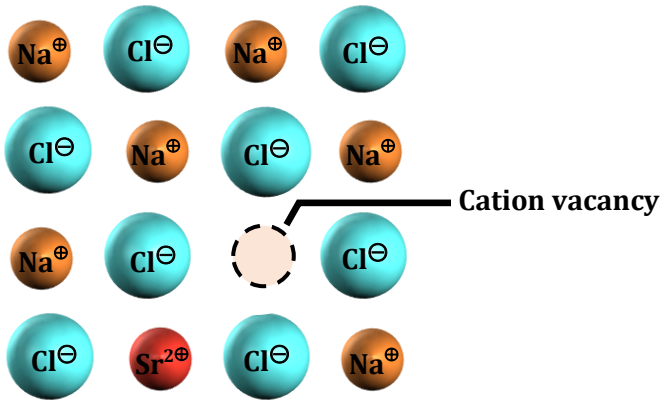
(b) Metal Deficiency Defect

There are many solids which are difficult to prepare in the stoichiometric composition and contain less amount of the metal as compared to the stoichiometric proportion. A typical example of this type is FeO which is mostly found with a composition of $Fe_{0.95}O$.

It may actually range from $FeO_{0.93}O$ to $Fe_{0.96}O$. In crystals of FeO, some $Fe^{2\oplus}$ cations are missing and the loss of positive charge is made up by the presence of required number of $Fe^{3\oplus}$ ions.

(iii) Impurity Defects

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



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

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

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

$\therefore$ More spontaneous at higher temperatures.

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

Illustration 24:

What are different possible type of metal excess defects in ionic solids ? Give examples of each.

Solution:

The metal excess defect can be created by two ways :

(i) Metal ion addition from outside. Ex. Na vapours diffused in NaCl crystal.

(ii) Anion leaving lattice site to give metal excess.

Illustration 25:

Explain what happens when NaCl is heated in atmosphere of Na vapours.

Solution:

Upon heating NaCl in atmosphere of Na, the $Cl^{\ominus}$ diffuse out and react with sodium to form NaCl.

$$Na + Cl^{\ominus} \longrightarrow Na^{\oplus} + Cl^{\ominus} + e^{\ominus}$$

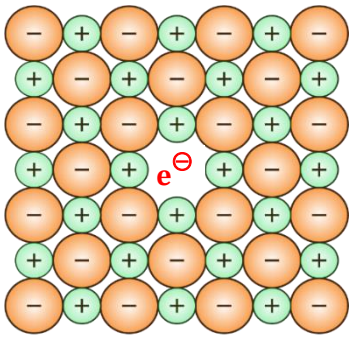
Now the electron diffuses into crystal and occupy a position in interstitial site. The net result is that, formula of NaCl changes to $Na_{(1+x)}Cl$ due to slight excess of NaCl.

The electron trapped in the interstitial site constitute F-centre (colour centre). These centres are responsible for changing properties of crystals :

(i) Crystal may become coloured

(ii) Increasing of electric & thermal conductance (N-type semi-conductor)

(iii) Increase of paramagnetism.



An F-centre in a rystal

Illustration 26:

What happens when Zinc oxide is heated ?

Solution:

Upon heating ZnO, the crystal of ZnO turn yellow due to creation of F centres in ZnO crystal.

$$\left(Zn^{2\oplus} + O^{2\ominus}\right) \rightarrow Zn^{2\oplus} + \frac{1}{2}O_2 + 2e^{\ominus}$$

The O^{2-} ion is oxidised to form O_2 gas which escapes from crystal and the liberated electrons occupy interstitial sites creating F-centres.

The kind of defect is metal excess defect.

Illustration 27:

Explain the kind of defect present in solid $Fe_{0.9}O$.

Solution:

The $Fe_{0.9}$ shows metal deficiency defect. The normal FeO is oxidised by O_2 and to supply extra electron some $Fe^{2\oplus}$ ions get oxidised to $Fe^{3\oplus}$.

$$\frac{1}{2}O_2 + 2e^{\ominus} \rightarrow O^{2\ominus}$$

$$2Fe^{2\oplus} \rightarrow 2Fe^{3\oplus} + 2e^{\ominus}$$

For every O_2, 4 $Fe^{2\oplus}$ get oxidised to $Fe^{3\oplus}$. In the process the formula become FeO_{1+x} or $Fe_{\left(\frac{1}{1+x}\right)}O$.

This is example of metal deficiency defect. Due to this defect electrical conductance increases.

[p-type semi-conductor]

Illustration 28:

What type of defect can arise when a solid is heated? Which physical property is affected by it and in what way?

Solution:

Vacancy defect arises when a solid is heated. Density of substance decreases.

Illustration 29:

What type of stoichiometric defect is shown by :

(i) ZnS **(ii)** AgBr

Solution:

(i) ZnS shows Frenkel defect.

(ii) AgBr shows Frenkel as well as Schottky defects. (Exception as radius ratio is not too large or too small.)

Illustration 30:

Ionic solids, which have anionic vacancies due to metal excess defect, develop colour. Explain with the help of a suitable example?

Solution:

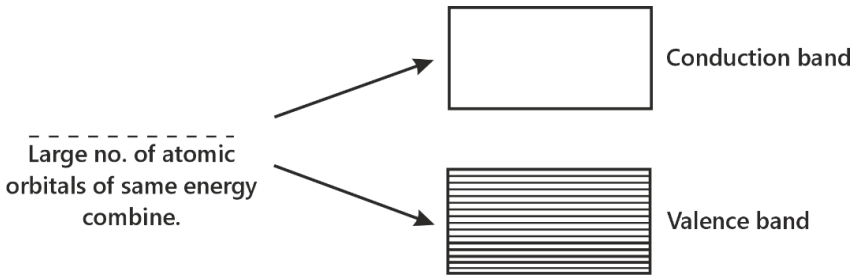
The colour results by excitation of electrons, when they absorb energy from visible light falling on crystal.

Example : Excess lithium makes LiCl pink.

Electrical properties:

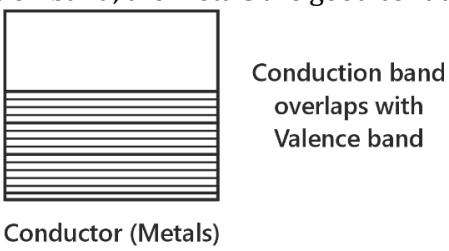
Energy band :

The outermost atomic orbital containing valence electrons of large number of atoms in solid superimpose together to form large number of molecular orbitals (bonding and antibonding). The energy gap between these bonding and antibonding M.O.'s are so small that they appear like a band. The bonding M.O.'s together form valence band while antibonding M.O.'s form conduction band. The energy of conduction band is higher than valence band.



Conductor :

A conductor is a substance in which the valence band overlaps with conduction band. Due to large number of electrons in conduction band, the metals are good conductors.



Insulator and Semiconductor :

In insulator the energy gap between filled valance band and conduction band is large. While in semiconductor, the energy gap is moderate. Now on increasing temperature of a semiconductor, the electron jumps from valence band to conduction band, thus increasing conductance. The semiconductor show increase in conductance while insulator show no change in conduction on heating.

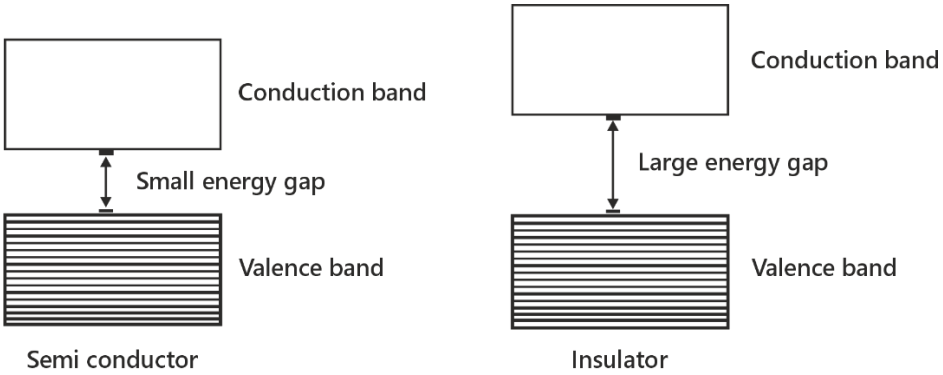


Illustration 31:

Differentiate between conductors, insulators and semiconductors.

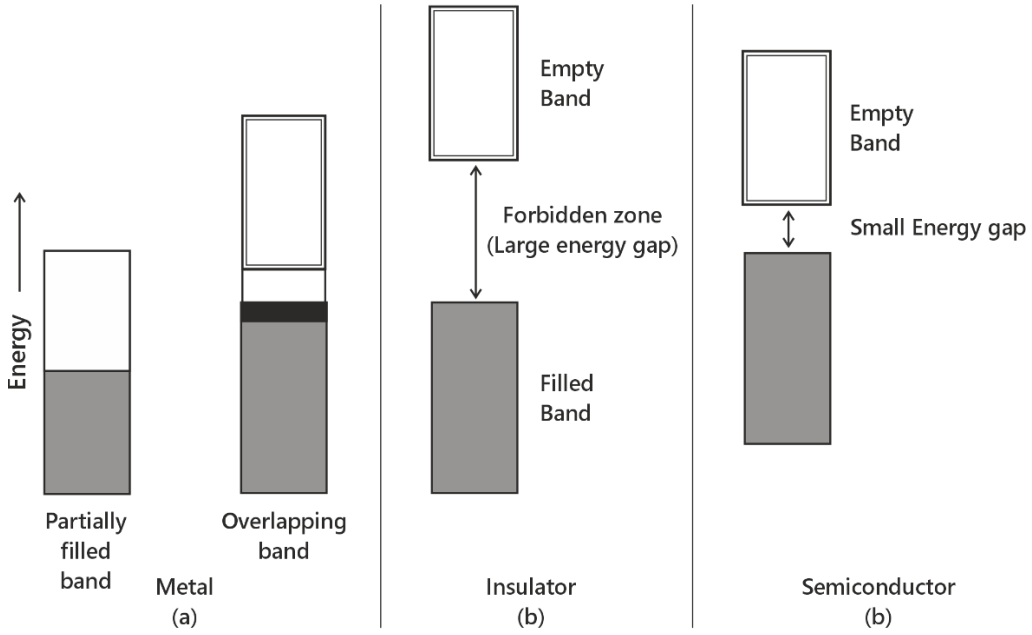
Solution:

The conductivity ($\Omega^{-1}\,m^{-1}$) values can be used to define conductor, insulator and semiconductor.

Substance	Range of conductivity ($\Omega^{-1}\,m^{-1}$)	Effect of temperature
Conductor	10^4 — 10^7	Conductance decreases
Insulator	10^{-20} — 10^{-10}	No effect
Semiconductors	10^{-6} to — 10^4 ohm^{-1} cm^{-1}	Conductance increases

Conduction of electricity in semi-conductor :

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



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

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

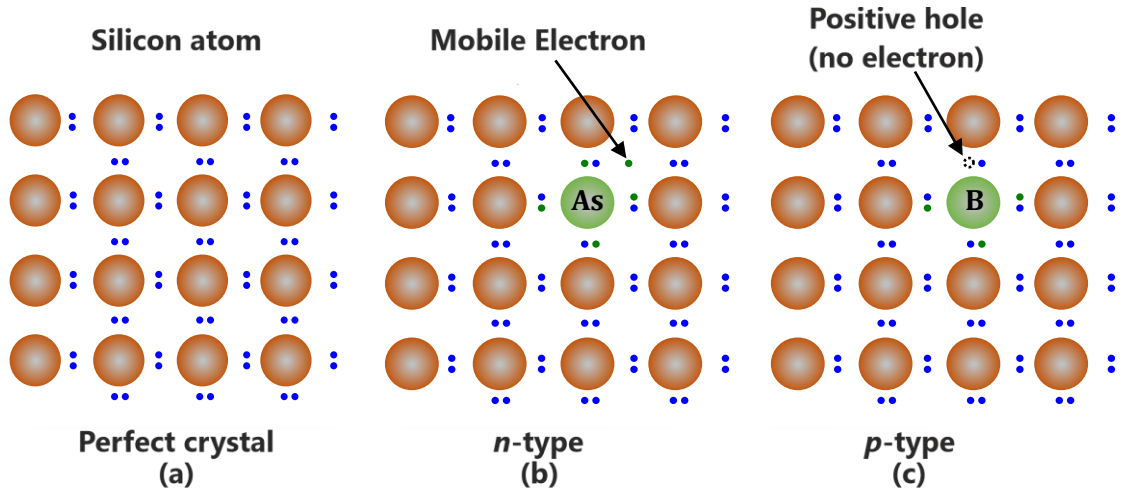
(a) Electron – rich impurities

Silicon and germanium belong to group 14 of the periodic table and have four valence electrons each. In their crystals each atom forms four covalent bonds with its neighbours. When doped with a group 15 element like P or As, which contains five valence electrons, they occupy some of the lattice sites in silicon or germanium crystal. Four out of five electrons are used in the formation of four covalent bonds with the four neighbouring silicon atoms.

The fifth electron is extra and becomes delocalised. These delocalised electrons increase the conductivity of doped silicon (or germanium). Here the increase in conductivity is due to the negatively charged electron, hence silicon doped with electron-rich impurity is called ***n-type semiconductor***.

(b) Electron – deficit impurities

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



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

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

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

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

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

Illustration 32:

A group 14 element is to be converted into n-type semiconductor by doping it with a suitable impurity. To which group should this impurity belong?

Solution:

The impurity should belong to group 15.

Example : Phosphorus , Arsenic.

Magnetic properties :

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

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

(i) paramagnetic (ii) diamagnetic (iii) ferromagnetic (iv) antiferromagnetic and (v) ferrimagnetic.

(i) Paramagnetism :

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

(ii) Diamagnetism :

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

(iii) Ferromagnetism :

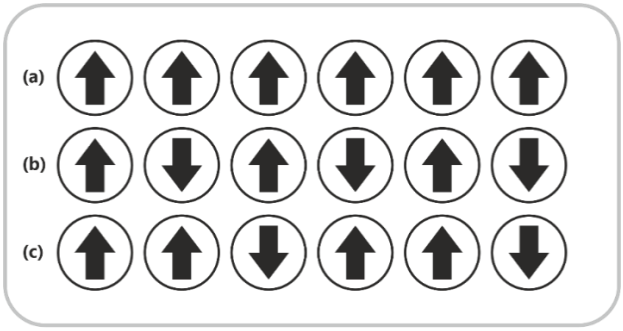
A few substances like iron, cobalt, nickel, gadolinium and CrO_2 are attracted very strongly by a magnetic field. Such substances are called ferromagnetic substances. Besides strong attractions, these substances can be permanently magnetised. In solid state, the metal ions of ferromagnetic substances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

(iv) Anti-ferromagnetism :

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

(v) Ferrimagnetism :

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



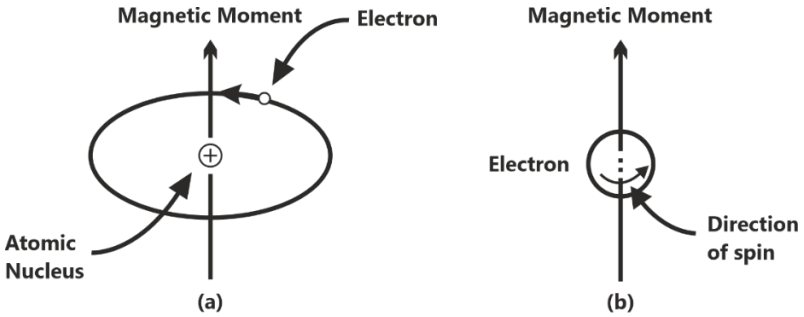
Schematic alignment of magnetic moments in (a) ferromagnetic (b) antiferromagnetic (c) ferrimagnetic

Illustration 33:

On what factors do magnetic properties of a substance depend ?

Solution:

An electron in atom creates two types of magnetic field due to two types of movements :



Demonstration of the magnetic moment associated with (a) an orbiting electron and (b) a spinning electron

(a) Orbital magnetic moment ⇒ Orbital motion of electron.
Moving electron creates current.

(b) Spin magnetic moment ⇒ Spinning of electron also generates current.

Generally (a) is weak and negligible but (b) is stronger (b) operates only when there are net unpaired electrons. If all electron are paired then (b) cancels out.

If substance has no unpaired electron only (a) will operate and it will get repelled by external magnetic field - such substances are called ***Dia-magnetic.***

If there are one or more unpaired electron then magnetic field (b) will attract external magnetic field. Such substances are called ***Paramagnetic.***

Illustration 34:

What is a ferromagnetic substance ? How is the very strong magnetic properties of ferromagnetic substances explained ?

Solution:

Metals which show permanent and strong magnetic moment, are called ferromagnetic substance. The stored magnetic properties of ferromagnetic substance are explained by domain theory. The solids consist of domains. Each domain contains large number of ions whose magnetic moment are aligned in one direction. In presence of magnetic field all the domains get oriented in single direction giving very strong magnetic field & these domains are permanently aligned.

Ex : Ferromagnetic substance Fe, Co, Ni

Illustration 35:

What is an antiferromagnetic substance ?

Solution:

A substance in which individual ions have magnetic moments but the solid shows zero magnetic moment is called antiferromagnetic substance. In these substances, the magnetic domains occur in pairs and in each pair, the magnetic moments are in opposite directions cancelling each other's effect. Thus, overall magnetic moment is equal to zero.

Ex : MnO show antiferromagnetic behaviour in spite of unpaired electrons.

Illustration 36:

What is ferrimagnetism ?

Solution:

If magnetic moments of domains in solid is not completely cancelled out, the substance shows small magnetic moment. The phenomenon is called ferrimagnetism.

Substance showing ferrimagnetism are Fe_3O_4 (Magnetite).

Illustration 37:

What type of substances would make better permanent magnets, ferromagnetic or ferrimagnetic. Justify your answer?

Solution:

Ferromagnetic substances will make better permanent magnets. All the domains are aligned in one single direction in a ferromagnetic substance, making it very strong magnet.

Miscellaneous Question (Advanced Level)

Illustration 1:

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) 59 pm

Ans. (A)

Solution:

$2r = \frac{\sqrt{3}a}{4}$ or $r = \frac{\sqrt{3}a}{8} = \frac{1.732 \times 356}{8} = 77.07$ pm

Illustration 2:

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

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

Ans. (C)

Solution:

In HCP, the number of octahedral void is equal to the number of atoms. Hence, the formula is $AC_{2/3}$ i.e. A_3C_2.

Illustration 3:

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

Solution:

$$\text{Theoretical density} = \frac{Z.M}{N_A.a^3} \Rightarrow \frac{4 \times 24 \times 10^{-3}}{6 \times 10^{23} \times (4 \times 10^{10})^3}$$

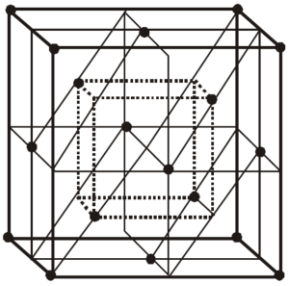
$$\text{Theoretical density d} = \frac{Z.M}{N_A.a^3} \Rightarrow 2.5 \times 10^3 \text{ kg/m}^3$$

$$\% \text{ occupancy} = \frac{\text{Observed density}}{\text{Ideal density}} \times 100 \Rightarrow \frac{2.4 \times 10^3}{2.5 \times 10^3} \times 100 = 96\%$$

Illustration 4:

The structure of diamond and silicon is same and can be described as atoms taking corners and faces of a cube and also taking positions of alternate tetrahedral voids. What is the value of $\frac{\text{density (diamond)}}{\text{density (silicon)}}$

At. mass (g/mol)	Covalent bond Length (Å)
Carbon : 12	C – C = 1.50
Silicon : 28	Si – Si = 2.25



Solution:

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

$$d_{dia} = \frac{8\times 12}{N_A \times a^3} \quad \text{... (1)}$$

$$\frac{a\sqrt{3}}{4} = 2r = 1.50;\ a = (1.50\ \text{Å}) \times \left(\frac{4}{\sqrt{3}}\right)$$

$$d_{si} = \frac{8\times 28\ g/mole}{N_A \times [(2.25)\times(4/\sqrt{3})]^3} \quad \text{... (2)}$$

$$\frac{d_{dia}}{d_{si}} = \frac{8\times 12}{N_A \times \left[(1.50)\left(4/\sqrt{3}\right)\right]^3} \times \frac{N_A \times \left[(2.25)\left(4/\sqrt{3}\right)\right]^3}{8\times 28}$$

$$= \left(\frac{12}{28}\right)\left(\frac{2.25}{1.5}\right)^3 = \frac{12}{28}\times\frac{27}{8} = 1.45$$

Illustration 5:

An element X (atomic wt. = 125) crystallises is simple cubic structure. If diameter of the largest atom which can be placed without disturbing unit cell is 366 pm. Find the density of pure element X in gm/cm^3.

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

[Fill your answer by multiplying it with 300.]

Solution:

For simple cubic unit cell

2r = a, r = radius of atom X

If Radius of the largest atom that can be placed = R

$\Rightarrow$ 2R = 366 pm

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

$a + 366 = a\sqrt{3}$

$366 = a\left(\sqrt{3}-1\right)$

$$a = \frac{366}{0.732} = 500\ \text{pm}$$

$= 5 \times 10^{-8}$ cm

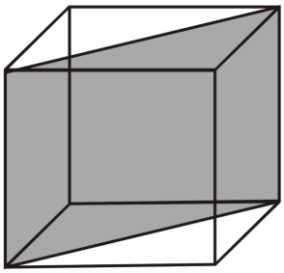
$$d = \frac{ZM}{a^3 N_A} \qquad \text{Given } N_A = 6 \times 10^{23}$$

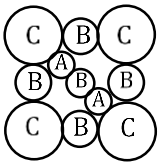
$$= \frac{1\times 125}{125\times 10^{-24}\times 6\times 10^{23}} = \frac{10}{6}$$

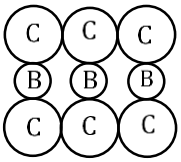
$$d = \frac{5}{3}\ g/cm^3$$

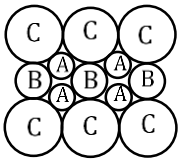
Illustration 6:

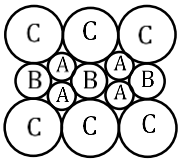
In a hypothetical solid 'C' atom are found to form cubical close packed lattice. 'A' atoms occupy all tetrahedral voids & 'B' atoms occupy all octahedral voids. 'A' and 'B' atoms are of appropriate size i.e. there is no distortion in ccp lattice of C atoms. Now if a plane as shown in the following figure is cut, then the cross section of this plane will look like.



(A) 

(B) 

(C) 

(D) 

Ans. (C)

Solution:

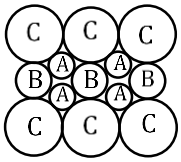
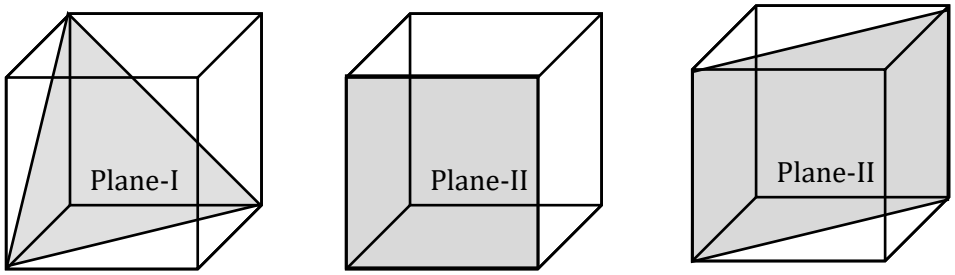


Illustration 7:

Following planes are shown in a FCC unit cell –



(A) Plane (I) contains tetrahedral voids

(B) Plane (II) contains tetrahedral voids

(C) Plane (II) contain octahedral voids

(D) Plane (III) contains both octahedral & tetrahedral voids

Ans. (C,D)

Solution:

In F.C.C unit cell,

All the octahedral voids are at edge centre & at the body centre.

All the tetrahedral void is on the diagonal nearer to the corners.

So, by the above the conditions option C & D are most appro pirate.

Illustration 8:

Graphite having hcp arrangement of carbon atoms if distance between two consecutive layers is 1.6Å.

Calculate density of graphite in gm/cm^3 ($N_A = 6 \times 10^{23}$) $\left(\frac{\sqrt{2}}{\sqrt{3}} = 0.8\right)$

(Write your answer by multiplying with $\sqrt{2}$)

Solution:

Distance between two consecutive layers of hcp unit cell

$= \frac{2r\sqrt{2}}{\sqrt{3}} = 1.6Å$

$r = 1Å = 10^{-8}$ cm

volume of hexagonal prism = $24\sqrt{2}r^3$

$= 24\sqrt{2} \times 10^{-24}$ cm^3

$$\text{density} = \frac{Z \times \frac{M}{N_A}}{\text{Volume of unit cell}}$$

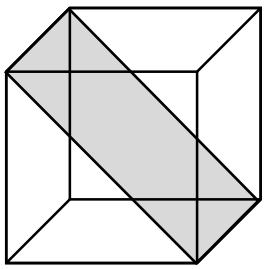
$$= \frac{6 \times 12}{6 \times 10^{23} \times 24\sqrt{2} \times 10^{-24}}$$

$$= \frac{5}{\sqrt{2}} \text{ gm/ cm}^{-3}$$

Correct answer is $\frac{5}{\sqrt{2}} \times \sqrt{2} = 5$.

Illustration 9:

Solid AB having NaCl structure, in which B atoms are at the corners. If all the atoms present in the plane shown are removed then formula of the compound left is-



(A) AB (B) A_3B_4 (C) A_4B_3 (D) A_3B_2

Ans. (A)

Solution:

Since AB has NaCl type structure with B at corners & face centre & A will occupy all octahedral void at edge centre & body centre according to question.

$A \rightarrow 10 \times \frac{1}{4} = \frac{5}{2}$ {Body centre O.V is removed & 2OV at edge will get removed}

$B \rightarrow \frac{1}{8} \times 4 + \frac{1}{2} \times 4$ {4 corners B atoms will get removed, 2 face centre B atom will get removed}

$= 2+\frac{1}{2}=\frac{5}{2}$

$\therefore\ A_{\frac{5}{2}}B_{\frac{5}{2}}$

(AB)

Illustration 10:

Calculate the density of NaCl type ionic solid AB (M_w = 60) in g/cm^3 if shortest distance between two nearest neighbour is 100 pm & solid having 20% Schottky defect. ($N_A = 6 \times 10^{23}$)

Solution:

$Z = 4 \times 0.8 = 3.2,\ \frac{a}{2} = 100$

a = 200 pm

$d = \frac{Z\times M}{N_A \times a^3}=\frac{3.2\times 60}{6\times 10^{23}\times\left(2\times 10^{-8}\right)^3}=\frac{3.2\times 60\times 10}{6\times 8}$

= 40 gm/cm^3

Illustration 11:

Mg crystallizes in hcp. Calculate total number of tetrahedral and octahedral voids in 12 milligrams of Mg ($N_A = 6 \times 10^{23}$). If your answer is $x \times 10^{20}$ then fill value of x

Solution:

Number of moles of Mg = $\frac{12\times 10^{-3}}{24} = 0.5 \times 10^{-3}$

$\because$ Number of Mg atoms = $0.5 \times 10^{-3} \times 6 \times 10^{23} = 3 \times 10^{20}$ atoms

Total number of voids = 3 × number of atoms = 9×10^{20} voids