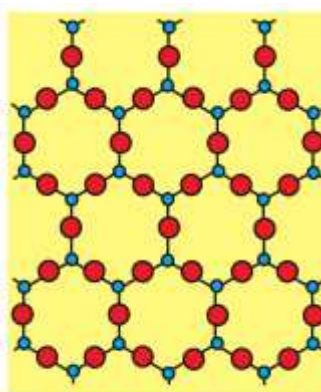- Solid:

  Solid is a state of matter in which the constituting particles are arranged very closely. The constituent particles can be atoms, molecules or ions.
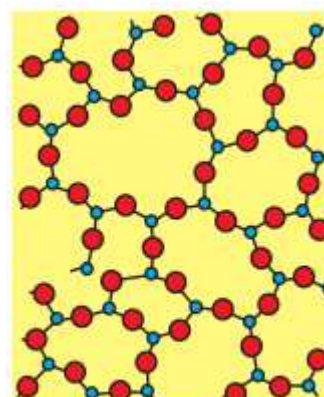
- Properties of solids:

  a) They have definite mass, volume and shape.

  b) They are incompressible and rigid.

  c) Intermolecular distances are short and hence the intermolecular forces are strong.

  d) Their constituent particles have fixed positions and can only oscillate about their mean positions.

- Classification of on the basis of the arrangement of constituent particles:

  a) Crystalline solids: The arrangement of constituent particles is a regular orderly arrangement. Example: iron, copper, diamond, graphite etc.

  b) Amorphous solids: The arrangement of constituent particles is an irregular arrangement. Example: Glass, plastics, rubber etc.
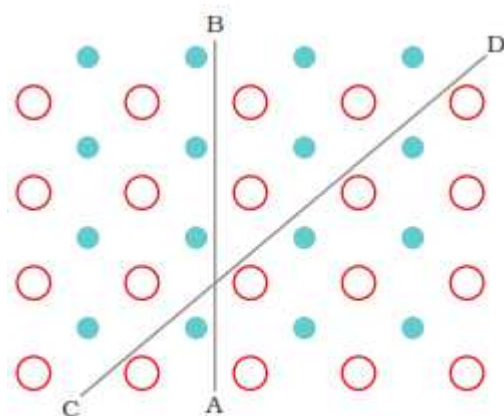

Crystalline Solids

Amorphous Solids

- Properties of crystalline solids:

  c) They have a definite characteristic geometrical shape.

  d) They have a long range order.

  e) They have a sharp melting point.

  f) They are anisotropic in nature i.e. their physical properties show different values when measured along different directions in the same crystal.

  g) They have a definite and characteristic heat of fusion.

  h) They are called true solids.

  i) When cut with a sharp edged tool, they split into two pieces and the newly generated surfaces are plain and smooth.

Anisotropic nature of crystalline solids

- **Polymorphic forms or polymorphs:**

  The different crystalline forms of a substance are known as polymorphic forms or polymorphs. For example: graphite and diamond.

- **Characteristics of amorphous solids:**

  a) They have an irregular shape.

  b) They have a short range order.

  c) They gradually soften over a range of temperature.

  d) They are isotropic in nature i.e. their physical properties are the same in all directions.

  e) When cut with a sharp edged tool, they cut into two pieces with irregular surfaces.

  f) They do not have definite heat of fusion.

  g) They are called pseudo solids or super cooled liquids. This is because they have a tendency to flow, though very slowly.

Types of crystalline solids:

A. **Molecular Solids**

  Constituent Particles: Molecules

ype of Solid	Const t ent Particles	Bon in / Attractive Forces	E ect cal conductivity	P ys al nature	M ting point	Example
Non-polar solids	Molecules	isp rsion or London forces	Insulator	Soft	Very low	r, Cl_4, H_2, I_2, CO_2
Polar solids	Molecules	ip e ip e interactions	Insulator	Soft	Low	H l, so solid NH_3
H drog n bonded	Molecules	H d og n bonding	Insulator	Hard	Low	H_2O (e

B. **Ionic Solids**

  Constituent Particles: Ions

Bonding/Attractive Forces: Coulombic or Electrostatic

Electrical Conductivity: Insulators in solid state but conducts in molten state and in aqueous solutions

Physical Nature: Hard but brittle

Melting Point: High

Examples: CaF_2, ZnS, MgO, $NaCl$

C.   Metallic Solids

Constituent Particles: Positive ions in a sea of delocalised electrons

Bonding/Attractive Forces: Metallic bonding

Electrical Conductivity: Conductors in solid state as well as in molten state

Physical Nature: Hard but malleable and ductile

Melting Point: Fairly high

Examples: Fe, Cu, Ag, Mg

D.   Covalent or Network Solids

Constituent Particles: Atoms

Bonding/Attractive Forces: Covalent bonding

Electrical Conductivity: Conductors in solid state as well as in molten state

Physical Nature: Hard but malleable and ductile

Melting Point: Fairly high

Examples: SiO_2, (quartz), SiC, C (diamond), C(graphite)

Network structure of diamond   Network structure of graphite
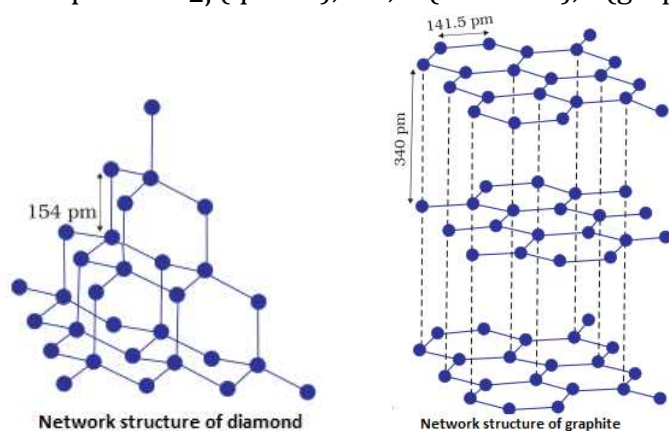
- Crystal lattice:

    A regular ordered arrangement of constituent particles in three dimensions is called crystal lattice.

Diagram showing a portion of 3Dcubic lattice and its unit cell
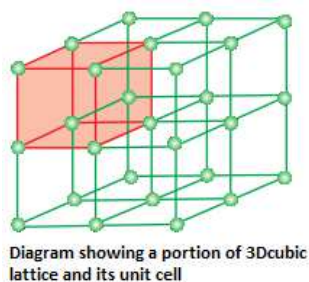
- Lattice points or lattice sites:

The fixed positions on which the constituent particles are present are called lattice points or lattice sites. A group of lattice points which when repeated over and over again in 3 dimensions give the complete crystal lattice.

- **Unit cell:**
  It is defined as the smallest repeating unit in space lattice which when repeated over and over again generates the complete crystal lattice. The crystal can consist of an infinite number of unit cells.
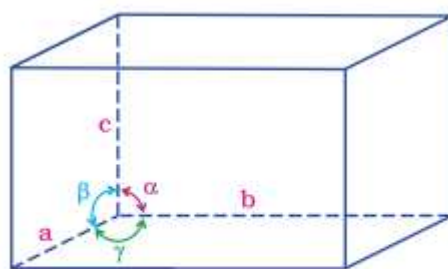
- **Parameters which characterize a unit cell:**
  a) Dimensions of the unit cell along the three edges, a, b and c:
     These edges may or may not be mutually perpendicular.
  b) Inclination of the edges to each other:
     This is denoted by the angle between the edges α, β, and respectively. α is the angle between the edges b and c, β is the angle between the edges a and c, and γ is the angle between a and b.

Parameters which characterise a unit cell

- **Seven crystal systems:**
  a) Cubic: $\alpha = \beta = \gamma = 90°$, a = b = c
  b) Tetragonal: $\alpha = \beta = \gamma = 90°$; a = b ≠ c
  c) Orthorhombic: $\alpha = \beta = \gamma = 90°$; a ≠ b ≠ c
  d) Monoclinic: $\alpha = \gamma = 90°$, $\beta ≠ 90°$; a ≠ b ≠ c
  e) Hexagonal: $\alpha = \beta = 90°$, $\gamma = 120°$; a = b ≠ c
  f) Rhombohedral or trigonal: $\alpha = \beta = \gamma ≠ 90°$; a = b = c
  g) Triclinic: $\alpha ≠ \beta ≠ \gamma ≠ 90°$; a ≠ b ≠ c

- **Types of unit cells:**
  a) Primitive or simple unit cells have constituent particles only at its corners.
  b) Centred unit cells are those unit cells in which one or more constituent particles are present at positions in addition to those present at the corners.

- **Types of centred unit cells:**
  a) **Face centred unit cell:**
     It consists of one constituent particle present at the centre of each face in addition to those present at the corners.
  b) **Body centred unit cell:**

It consists of a one constituent particle is present at its body centre in addition to those present at the corners.
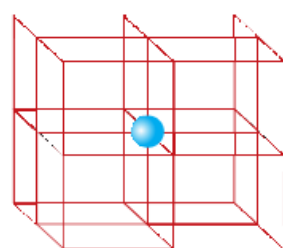
c) **End centred unit cell:**
It consists of one constituent particle present at the centre of any two opposite faces in addition to those present at the corners.

- **Number of particles at different lattice positions:**
  a) **Corner:**
  If an atom is present at any one corner, it is shared by eight unit cells. So, only one eighth of an atom actually belongs to the unit cell.

Number of particles at corner is shared by eight unit cells

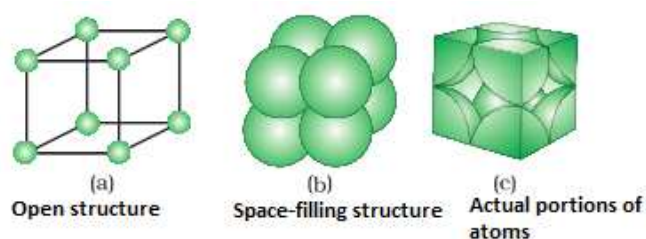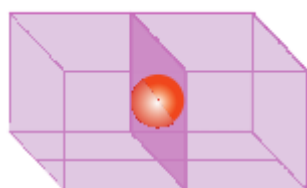(a) Open structure   (b) Space-filling structure   (c) Actual portions of atoms

Figure representing a primitive cubic unit cell

  b) **Face centre:**
  If an atom is present at the centre of the face, it is shared by two unit cells. So, only half of the atom actually belongs to the unit cell.

An atom is shared between two unit cells in face centred unit cell

(a) Open structure   (b) Space-filling structure   (b) Actual portion of of atom
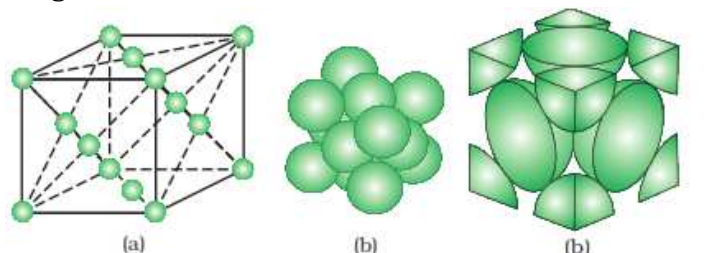
Figure representing a face centred cubic unit cell

  c) **Body centre:**
  If an atom is present at the body centre, it is not shared by any other unit cell. So, that one atom completely belongs to the same unit cell.

(a) Open structue   (b) Space-filling structure   (c) Actual portions of atom
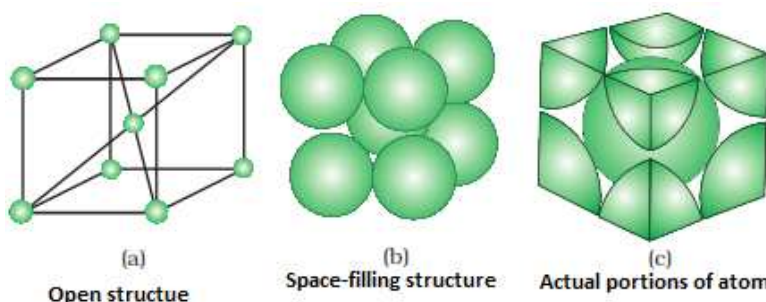
Figure representing a body centric cubic unit cell

  d) **End centre:**
  If an atom is present at the edge centre, it is shared by four unit cells. So, only one

fourth of an atom belongs to the unit cell.

- Number of atoms in different unit cells:
    a) Primitive unit cell have 1 atom
    b) Face centred unit cell have 3 atoms
    c) Body centred unit cell have 2 atoms
- Coordination number:
    Coordination number is the number of nearest neighbours of a particle.
- Close packed structures:
    a) Close packing in one dimension:
        Each sphere is in contact with two of its neighbours. Coordination number is two.

One dimensional close packing of spheres

   b) Close packing in two dimensions: It is generated by stacking the rows of close packed spheres in two ways:
        i) Square close packing and ii) Hexagonal close packing.
    c) Close packing in three dimensions: They can be obtained by stacking the two dimensional layers one above the other. It can be obtained in two ways:
        i) Square close packed layers and ii) Hexagonal close packed layers.
- Square close packing:
    Here, the spheres of the second row are placed exactly above those of the first row. This way the spheres are aligned horizontally as well as vertically. The arrangement is AAA type. The coordination number is 4.
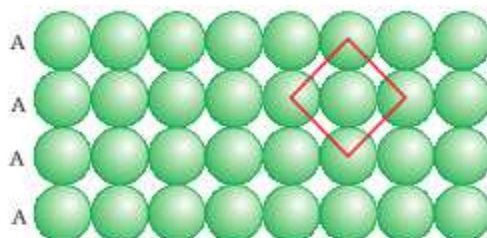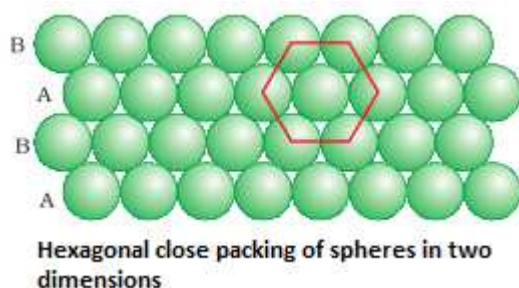

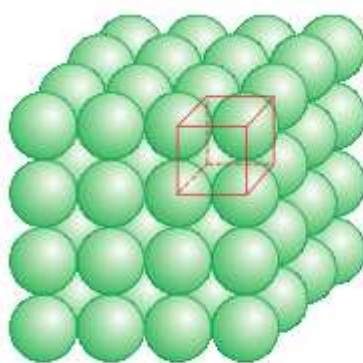Square close packing of spheres in two dimensions

- Hexagonal close packing:
    Here, the spheres of the second row are placed above the first one in a staggered manner in such a way that its spheres fit in the depression of the first row. The arrangement is ABAB type. The coordination number is 6.

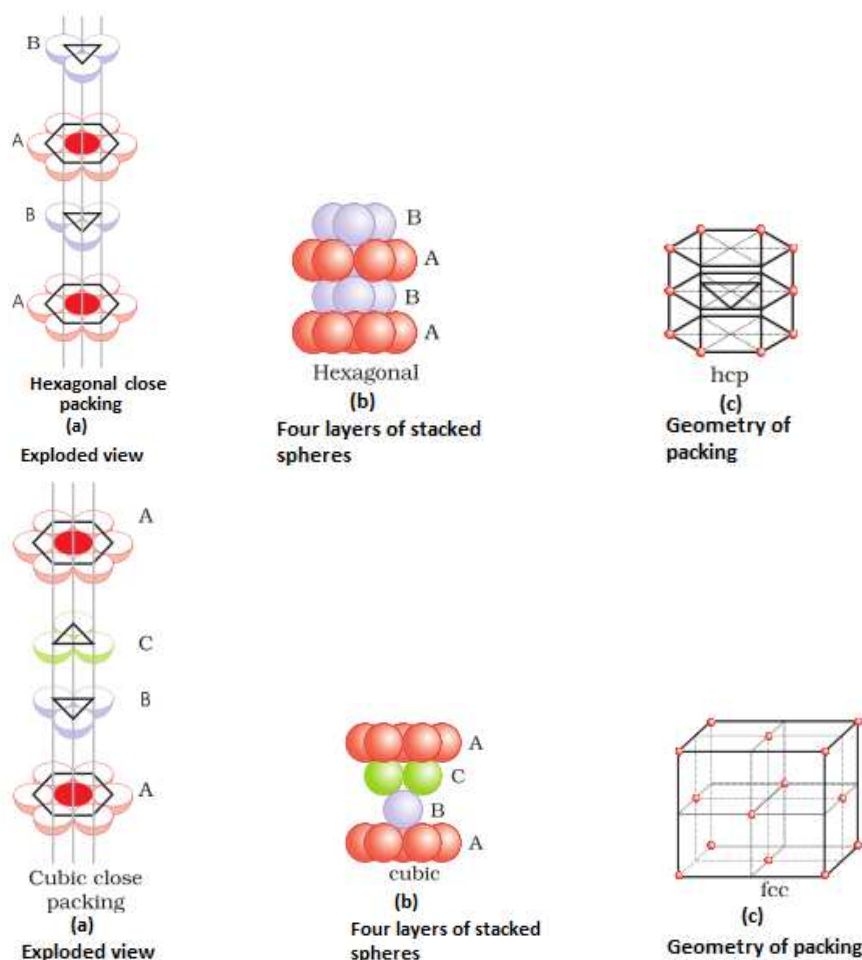Hexagonal close packing of spheres in two dimensions

- Three dimensional close packing from two dimensional square close packed layers:
  Here, the spheres of the upper layer are placed exactly over the first layer such the spheres of the layers are perfectly aligned horizontally and vertically. It has a AAAA type pattern. The lattice is simple cubic lattice.
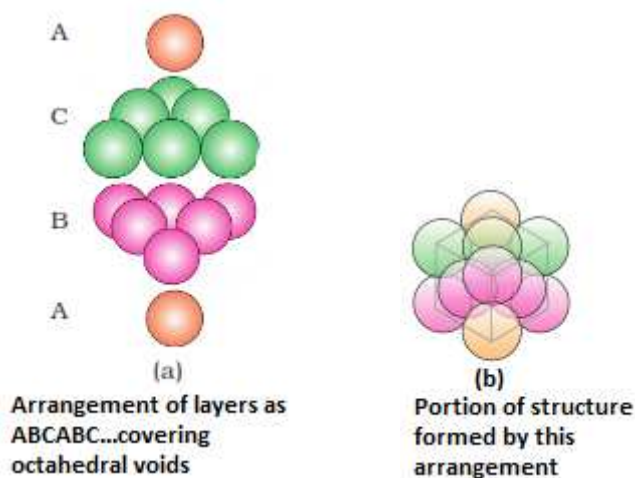

Three dimensional close packing from two dimensional square close packed layers

- Three dimensional close packing from two dimensional hexagonal close packed layers: There are two steps involved as:
  - i) Placing the second layer over the first layer
  - ii) Placing the third layer over the third layer
- Placing the second layer over the first layer:
  If a two dimensional layer is considered as A, the second layer which is placed above the first layer in such a way that the spheres of the second layer (considered as B) are placed in the depressions of the first layer. This gives rise to two types of voids: tetrahedral voids and octahedral voids.
- Placing the third layer over the third layer:
  There are two possibilities:
  - a) Covering the tetrahedral voids:
    Here, tetrahedral voids of the second layer may be covered by the spheres of the third layer. It gives rise to ABABAB type pattern. The three dimensional structure is called hexagonal close packed structure. The coordination number is 12. Examples: Mg, Zn.

Hexagonal close packing (a) Exploded view

Hexagonal (b) Four layers of stacked spheres

hcp (c) Geometry of packing

Cubic close packing (a) Exploded view

cubic (b) Four layers of stacked spheres

fcc (c) Geometry of packing

b) Covering the octahedral voids:
    Here, octahedral voids of the second layer may be covered by the spheres of the third layer. It gives rise to ABCABCABC type pattern. The three dimensional structure is called cubic close packed structure or face centred cubic structure. The coordination number is 12. Example: Cu, Ag.

(a) Arrangement of layers as ABCABC...covering octahedral voids

(b) Portion of structure formed by this arrangement

* Types of voids:
    a) Tetrahedral voids

It is formed at the centre when four spheres are joined in the form of a tetrahedron.

Tetrahedral hole

Tetrahedral hole

Tetrahedron

(a)
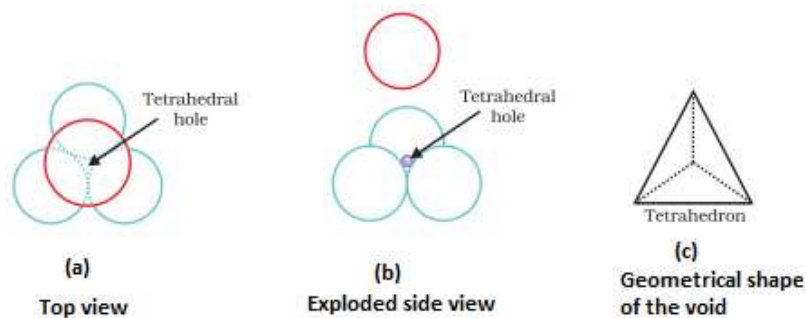Top view

(b)
Exploded side view

(c)
Geometrical shape of the void

Figure showing tetrahedral voids

b) Octahedral void

It is formed at the centre when six spheres are joined in the form of an octahedron.

Octahedral hole

Octahedral hole

Octahedron

(a)
Top view

(b)
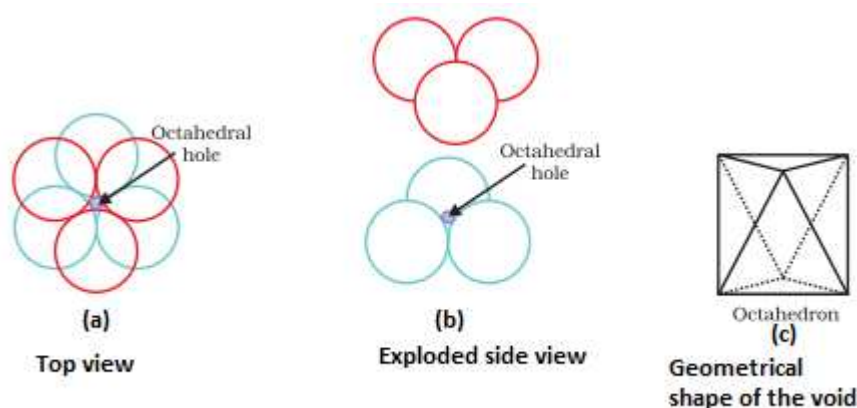Exploded side view

(c)
Geometrical shape of the void

Figure showing octahedral voids

- In hexagonal close packing or cubic close packing arrangement, the octahedral and tetrahedral voids are present. The number of octahedral voids present in a lattice is equal to the number of close packed particles. The number of tetrahedral voids is twice the number of octahedral voids.

  For example:

  If the number of close packed particles = n

  Number of particles present in octahedral voids = n

  Then, the number of particles present in tetrahedral voids = 2n

- Packing efficiency:

  It is the percentage of total space occupied by constituent particles (atoms, molecules or ions)

  $$\text{Packing Efficiency} = \frac{\text{Volume occupied by spheres}}{\text{Total volume of unit cell}} \times 100\%$$

- Packing efficiency for face centred unit cell = 74%

  <mark>Refer tb</mark>

- Packing efficiency for body centred cubic unit cell = 68%

  <mark>Refer tb</mark>

- Packing efficiency for simple cubic unit cell = 52.4%

- Radius ratio in an octahedral void:

  For an atom to occupy an octahedral void, its radius must be 0.414 times the radius of the sphere.

  $$\frac{r}{R} = 0.414$$

- Radius ratio for tetrahedral void:

  For an atom to occupy a tetrahedral void, its radius must be 0.225 times the radius of the sphere.

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

- Density of a unit cell is same as the density of the substance.
- Relationship between radius of constituent particle (r) and edge length(a):
  a) Simple cubic unit cell: a= 2r

  b) Face centred unit cell: $a = 2\sqrt{2}r$

  c) Body centred unit cell: a = $\dfrac{4r}{\sqrt{3}}$

- Volume of a unit cell = (edge length)^3 = a^3

  a) Simple cubic unit cell: Volume= (2r)^3

  b) Face centred unit cell: Volume $= \left(2\sqrt{2}r\right)^3$

  c) Body centred unit cell: Volume = $\left(\dfrac{4r}{\sqrt{3}}\right)^3$

- Number of atoms in a unit cell (z):
  a) Simple cubic unit cell: z = 1
  b) Face centred unit cell: z = 4
  c) Body centred unit cell: z = 2

- Density of unit cell =
- Crystal defects are basically irregularities in the arrangement of constituent particles.
- Types of defects:
  a) Point defects

     Point defects are the irregularities or deviations from ideal arrangement around a point or an atom in a crystalline substance.
  b) Line defects

     Line defects are the irregularities or deviations from ideal arrangement in entire rows of lattice points.

- Different types of point defects:
  a) Stoichiometric or intrinsic or thermodynamic defects

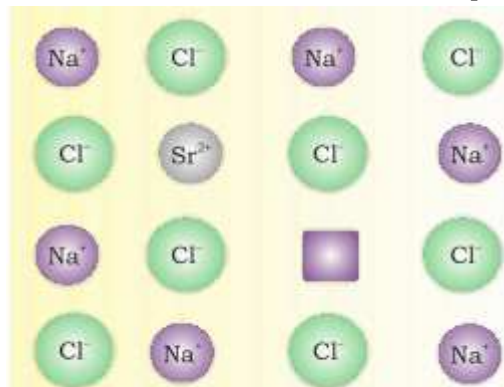   These are the point defects that do not disturb the stoichiometry of the solid.

b) Non – stoichiometric defects

These are the point defects that disturb the stoichiometry of the solid.

c) Impurity defects

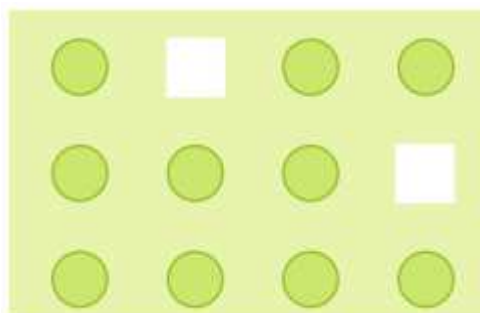These are the defects in ionic solids due to the presence of impurities present in them.

Impurity defects

- Different types of stoichiometric defects for non- ionic solids
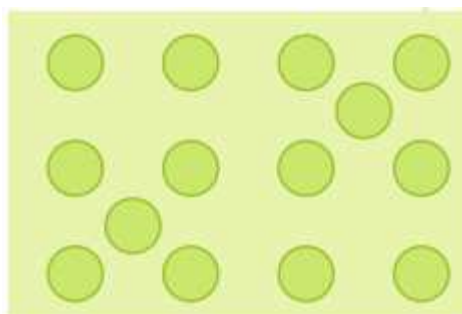
a) Vacancy defect

A crystal is said to have vacancy defect when some of the lattice sites are vacant. This defect results in decrease in density of the substance.

Vacancy defect

b) Interstitial defect

A crystal is said to have interstitial defect when some constituent particles (atoms or molecules) occupy an interstitial site. This defect results in increase in density of the substance.
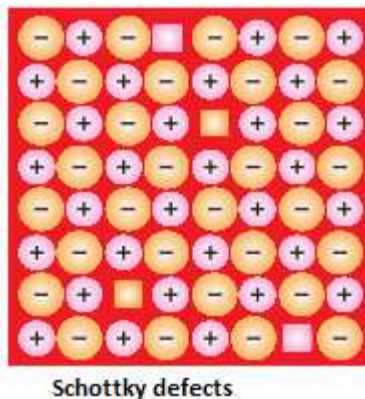

Interstitial defect

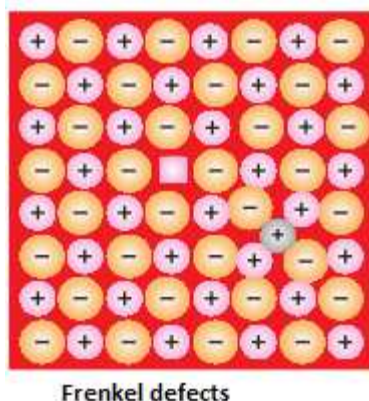- Different types of stoichiometric defects for ionic solids

a) Schottky defect

In this defect equal number of cations and anions are missing. It is basically a vacancy defect in ionic solids. It decreases the density of a solid. Schottky defect is shown by ionic substances in which the cation and anion are of almost similar sizes. It includes NaCl, KCl, CsCl and AgBr.


Schottky defects

b) Frenkel or dislocation defect

In this defect, the smaller ion (usually cation) is dislocated 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. 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. It includes ZnS, AgCl, AgBr and AgI.

Frenkel defects

- Different types of non-stoichiometric defects:
  a) Metal excess

     This type of defect is due to excess of metal cations.
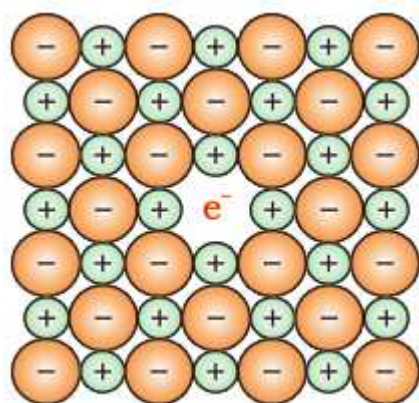
Metal excess defect

b) Metal deficiency

This defect arises because of absence of metal ions from its lattice sites. The electrical neutrality is maintained by an adjacent ion having a higher positive charge.

* Reasons for the cause of metal excess defect:
  a) Anionic vacancies:

  A compound may have an extra metal ion if the negative ion is absent from its lattice site. This empty lattice site is called a hole. To maintain electrical neutrality this site is occupied by an electron. The hole occupied by an electron is called f-centre or Farbenzenter centre. The F- centre is responsible for the colour of the compound.

  b) Presence of extra cations:

  A compound is said to have extra cations if a cation is present in the interstitial site. An electron is present in the interstitial site to maintain the electrical neutrality.

* Classification of solids based on their electrical conductivities:
  a) Conductors

  The solids with conductivities ranging between 10^4 to 10^7 ohm^{-1}m^{-1} are called conductors.

  b) Insulators

  These are the solids with very low conductivities ranging between 10^{-20} to 10^{-10} ohm^{-1}m^{-1}.
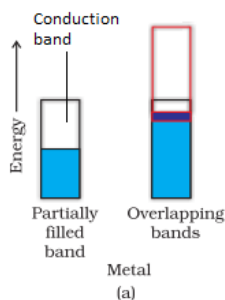
  c) Semi- conductors

  These are the solids with conductivities in the intermediate range from 10^{-6} to 10^4 ohm^{-1}m^{-1}.

* Band theory

  A metal is characterized by a band structure. The highest filled band is called valence band and the lowest unoccupied band is called conduction band. The gap between the two bands is called forbidden band.

* Band theory in different types of solids based on their electrical conductivity
  a) In case of conductors, the valence band and conduction band overlap.

Metal
(a)

b) In case of insulators, the forbidden gap is very large and the electrons are unable to excite to the conduction band.

Insulator
(b)
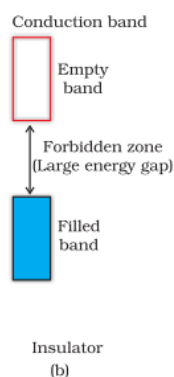
c) In case of semiconductors, forbidden gap is small. Therefore, some electrons may jump to conduction band and show some conductivity. Electrical conductivity of semiconductors increases with rise in temperature, since more electrons can jump to the conduction band.
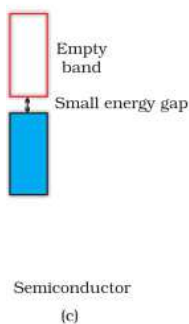
Semiconductor
(c)

- Types of semiconductors:
  a) Intrinsic semiconductors
     These are those semiconductors in which the forbidden gap is small. Only some electrons may jump to conduction band and show some conductivity. They have very low electrical conductivity. Example: Silicon, germanium.
  b) Extrinsic semiconductors
     When an appropriate impurity is added to an intrinsic semiconductor, it is called extrinsic semiconductors. Their electrical conductivity is high.
- Doping:
  The process of adding an appropriate amount of suitable impurity to increase the conductivity of semiconductors is known as doping.

- Types of extrinsic semiconductors:
  a) The n-type semiconductors

     They are formed when silicon is doped with electron rich impurity like group 15 elements. The increase in conductivity is due to the negatively charged electrons.
  b) The p –type semiconductors

     They are formed when silicon is doped with electron deficient impurity like group 13 elements. The increase in conductivity is due to the positively charged holes.
- Diode:

  It is a combination of n-type and p-type semiconductors and is used as a rectifier.
- Transistors:

  They are made by sandwiching a layer of one type of semiconductor between two layers of the other type of semiconductor. The npn and pnp type of transistors are used to detect or amplify radio or audio signals.
- The 12- 16 compounds:

  These compounds are formed by the combination of group 12 and group 16 compounds. They possess an average valency of 4. Examples - ZnS, CdS, CdSe and HgTe.
- The 13- 15 compounds:
- These compounds are formed by the combination of group 13 and group 15 compounds. They possess an average valency of 4. Examples - InSb, AlP and GaAs.
- 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.
- Classification of substances based on their magnetic properties:
  a) Paramagnetic substances

     These are those substances which are weakly attracted by the magnetic field. It is due to presence of one or more unpaired electrons.
  b) Diamagnetic substances

     Diamagnetic substances are weakly repelled by a magnetic field. Diamagnetism is shown by those substances in which all the electrons are paired and there are no unpaired electrons.
  c) Ferromagnetic substances

     These are those substances which are attracted very strongly by a magnetic field.
  d) Antiferromagnetic substances

     They have equal number of parallel and antiparallel magnetic dipoles resulting in a zero net dipole moment.
  e) Ferrimagnetic substances

     They have unequal number of parallel and antiparallel magnetic dipoles resulting in a net dipole moment.