

Solid State

Matter is classified into three states solid, liquid and gases. Intermolecular forces are responsible for the stability of these states. These forces hold the constituent particles closer.

Characteristic properties of solid state:

- Solids have definite shape, mass and volume.
- In case of solid, intermolecular distances are short and intermolecular forces are strong.
- Solids are rigid and incompressible.
- Solid's constituent particles have fixed position and they oscillate at their mean position.

Classification of solids:

Solids are classified on the basis of nature of arrangement of constituent particles in to two categories:

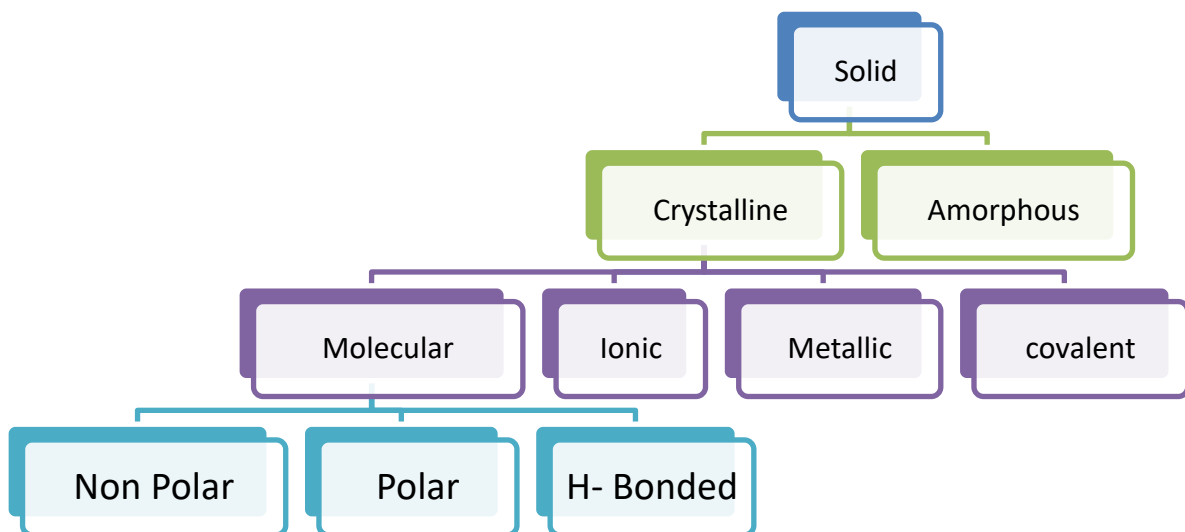


Figure: Classification of solid

I. Crystalline solids:

- Crystalline solids have definite geometrical shape. They are made of small particles like atoms, molecules or ions. The arrangement of these particles is ordered and repetitive in 3-D.
- They have regular pattern of arrangement which repeats itself in entire crystal. It is known as long range order.
- They have sharp melting point.
- They are anisotropic in nature which means properties like electrical resistance show different values in different direction in the crystal structure.
- Examples – quartz, $ZnCl_2$, NaCl, etc.
- Crystalline solids are classified on the basis of nature of intermolecular forces or bonds (Vander Waals, ionic, covalent and metallic) that hold the constituent particles in crystal structure.

Classification of crystalline solids

1. Molecular solids- These are categorised into three categories which are as follows-

A. Non polar molecular solids:

- Helium, Argon and molecules like H_2 , Cl_2 and I_2 form this type of solids.
- The constituent particles are held by weak London forces. These solids are soft solid and non-conductor of electricity.
- Non polar molecular solids have low melting point and are in gaseous or liquid state at room temperature.

B. Polar molecular solids:

- The molecules of HCl, SO_2 etc. are formed by polar covalent bonds.
- The constituent particles are held together by dipole-dipole interaction.
- They are soft and non-conductor of electricity.
- Examples- solid NH_3 and solid SO_2 .

C. Hydrogen bonded molecular solids:

- These solids contain polar covalent bonds between H and F, O or N atoms.

- They are non-conductors of electricity.
- They are volatile liquids or soft solids at room temperature.

2. Ionic Solids

- These types of solids are formed by three dimensional arrangements of anions and cations.
- The constituent particles are held together by columbic forces.
- They are brittle and hard.
- They have high B.P. and high M.P.
- They are electrical insulator as the ions are not free to move.
- They conduct electricity when dissolved in water because ions are free to move about.

3. Metallic solids

- These solid are made up of positive ions surrounded by sea of free electrons.
- These free electrons are responsible for high thermal and electrical conductivity of metals.
- Metals have lustre. They show colour due to presence of free electrons.
- Metals are ductile and malleable.

4. Covalent solids

- The constituent particles held together by covalent bonds. Covalent bonds are strong and direction.
- They are giant molecules, very hard and brittle.
- They have high melting point.
- They act as insulators.
- Example- silicon carbide, diamond.
- Graphite is exception. It is soft and conductor of electricity due to presence of free electrons.

II. Amorphous solids:

- The Greek word Amorphous means 'no form'. Amorphous solids lacking of crystals.
- The constituent particles are in short range order.
- They start melting over a range of temperature; thus, they are soft and easy to mould in different shapes.
- They are isotropic in nature which means properties such as mechanical strength and electrical conductivity is same in all the directions in the amorphous solid.
- Examples- rubber, plastic etc.

Crystal Lattice and Unit Cells

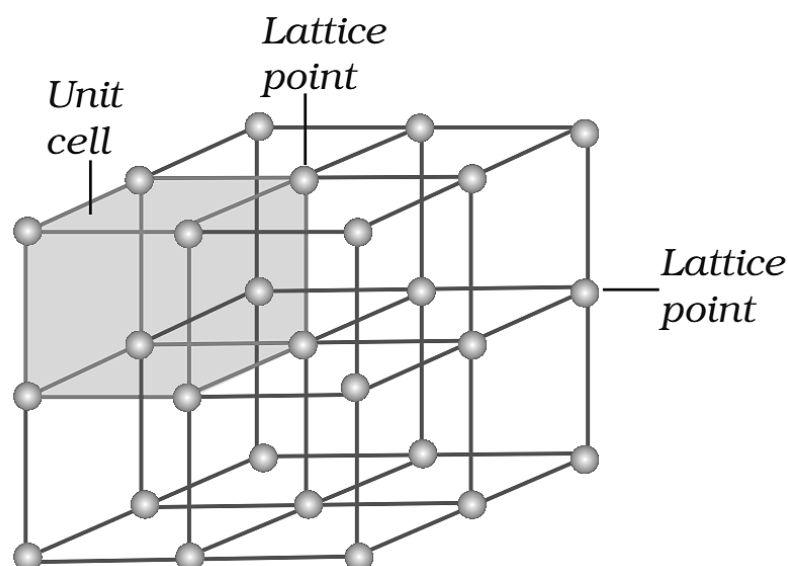


Figure: A three-dimensional cubic space of a crystal lattice and unit cell

Crystal lattice

- A regular three-dimensional arrangement of identical points in space is called crystal lattice.
- Each point in lattice is known as lattice point.
- This lattice point denotes constituent particle (atom/molecule/ion).
- Lattice points are joined by straight lines.

Unit cell

- If we deal with a crystal lattice then it is possible to select a group of lattices that's generating the whole lattice. So, the unit cell may be defined as 3-dimensional group of the lattice point that's generating the whole lattice by stacking or translation.
- The dimensions of unit cell along the three edges are a , b , and c . edges may or may not be perpendicular.
- Angles between the edges- α = Between b and c
 β = between a and c
 γ = between a and b
- The unit cell has six characteristic parameters- a , b , c , α , β and γ .

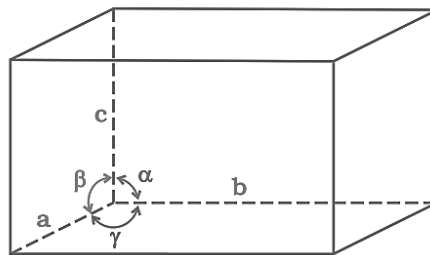


Figure: Parameters of a unit cell

- Unit cells are classified in to two categories-
A. Primitive Unit Cells/ simple cubic type unit cell

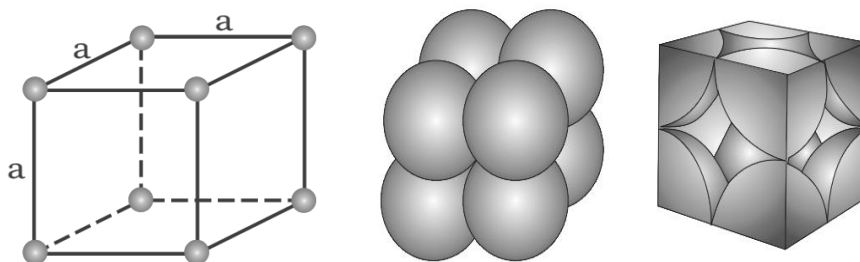


Figure: Primitive Unit cell

- The lattice points lie at each corner position of unit cell.
- Edge length = $a = 2r = d$

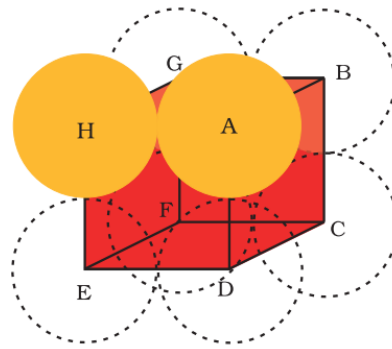


Figure: In simple cubic unit cell the sphere is in contact with each other along the edge

- Atoms in one unit cell = $8 \times \frac{1}{8} = 1$ atom

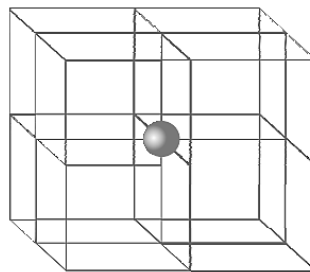


Figure: In simple-cubic unit cell, each corner atom is shared between 8-unit cells.

B. Centred unit cells

- When in a unit cell, constituent particles present not only at the corners but also at other positions. That unit cell is centred unit cell. There are three types of centred unit cells.

Body centred unit cells:

- The lattice point lies at each corner as well as at the centre of cube.
- Along the body diagonal atom touch each other.
- Edge length = $\sqrt{3} a = 4r = 2d$
- Atoms in a unit cell in
 - At 8 corners = $8 \times \frac{1}{8} = 1$ atom
 - At 1 body centre atom = $1 \times 1 = 1$ atom
- Total number of atoms per unit cell = 2 atoms.

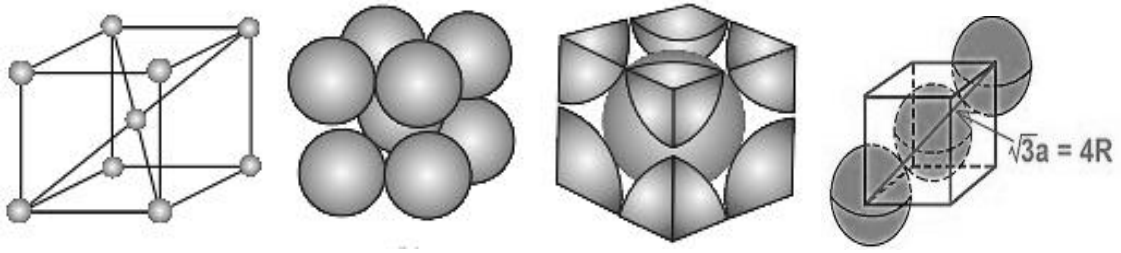


Figure: A body centred cubic unit cell

Face centred cubic unit cell

- Lattice point lies at each corner as well as the centre of each face.
- Along the face diagonal atom touch each other.

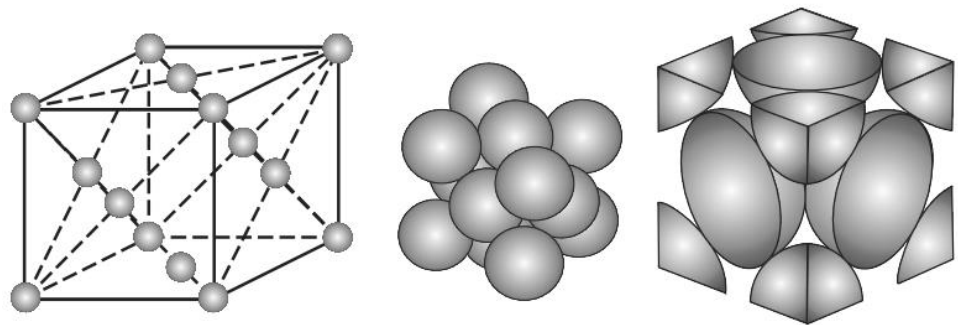


Figure: a face centred cubic unit cell

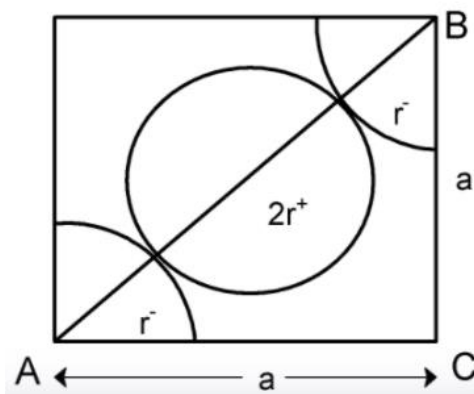


Figure: Edge length of face centred cubic unit cell

- Edge length = $\sqrt{2}a = 4r = 2d$
- Atoms in a face centred cubic unit cell
 - At 8 corner = $8 \times \frac{1}{8} = 1$ atom
 - At 6 face centred atom = $6 \times \frac{1}{2} = 3$ atom
- Total number of atoms per unit cell = 4 atom

End centred cubic unit cells

- Lattice point lies at each corner as well as the centre of alternate face.
- Atoms present in a unit cell
 - At 8 corners = $8 \times \frac{1}{8} = 1$
 - At the centre of alternate face = $2 \times \frac{1}{2} = 1$
- Total number of atoms per unit cell = 2 atom

❖ After study of various crystals, we came to know that there are seven crystal systems. According to a French mathematician Bravais there are 14 three dimensional lattices are possible. The characteristics of these seven-lattice system's unit cell as follows:

Crystal System	Edge lengths	Axial angles	Possible variations	Examples
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	Primitive BCC, FCC	NaCl, KCl, zinc blend
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Primitive BCC	SnO_2 , TiO_2
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Primitive BCC, FCC, ECC	BaSO_4 , KNO_3
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	Primitive	ZnO, Graphite
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	Primitive	Calcite, HgS

Monoclinic	$a \neq b \neq c$	$\alpha = \gamma \neq 90^\circ$ $\beta \neq 90^\circ$	Primitive ECC	Monoclinic sulphur
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	Primitive	$K_2Cr_2O_7$, H_3BO_3

Packing efficiency

- ❖ The percentage of volume occupied by the particles is called packing efficiency.

$$\text{Packing efficiency} = \frac{\text{Volume occupied by atoms}}{\text{Volume of unit cell}} \times 100$$

Packing efficiency for simple cubic lattice

- ❖ Edge length $a = 2r$
- ❖ The volume of simple cubic unit lattice = $a^3 = (2r)^3 = 8r^3$
- ❖ The volume of the occupied space = $\frac{4\pi r^3}{3}$
- ❖ Packing efficiency

$$= \frac{\frac{4}{3}\pi r^3}{8r^3} \times 100 = \frac{\pi}{6} \times 100$$

$$= 52.4\%$$

Packing efficiency for body centred cubic lattice

- ❖ Edge length = Edge length = $\sqrt{3} a = 4r = 2d$
- ❖ $r = \frac{\sqrt{3}a}{4}$
- ❖ Packing efficiency

$$= \frac{2 \times \left(\frac{4}{3}\right) \pi r^3 \times 100}{\left[\left(\frac{4}{\sqrt{3}}\right) r\right]^3} \%$$

$$= \frac{(8/3)\pi r^3 \times 100}{64 / (3\sqrt{3}) r^3} \% = 68\%$$

Packing efficiency for face centred cubic lattice

- ❖ Edge length = $\sqrt{2}a = 4r = 2d$
- ❖ $a = \frac{4r}{\sqrt{2}}$; $r = \frac{a}{2\sqrt{2}}$
- ❖ Packing efficiency

$$= \frac{4 \times (4/3) \pi r^3 \times 100}{(2\sqrt{2}r)^3} \%$$

$$= \frac{(16/3) \pi r^3 \times 100}{16\sqrt{2}r^3} \% = 74\%$$

Density of unit cell

- ❖ Density of unit cell = $\frac{\text{Mass of unit cell}}{\text{Volume of unit cell}}$
- ❖ Mass of unit cell = $\frac{Z \times M}{N_a}$
- ❖ Volume of unit cell = a^3
- ❖ Density of unit cell = $\frac{Z \times M}{N_a \times a^3}$

Closed packed structure

In solids constituent particles are closely packed with minimum vacant space. The constituent particles are like hard spheres and they build the 3-D structure.

A. Closely packing in one dimension

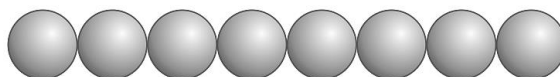


Figure: Close packed spheres in one dimension

- There is only one way to arrange the spheres in one dimension.

- In this arrangement each sphere is in contact with two other spheres.
- The number of nearest neighbour of a particle is known as its coordination number.
- In case of one dimensionally close packed arrangement, the coordination number is two.

B. Close packing in two dimensions

- The two-dimensional close packed structure is made by stacking the rows of closely packed spheres. It can be done in two ways.

I. AAAA type –

- The second row placed in contact with the first row in such a way that the second row is exactly above the first row.
- If the first row is of 'A' type then the second row is also of 'A' type due to same arrangement. Thus this arrangement is also called **AAAA** type.

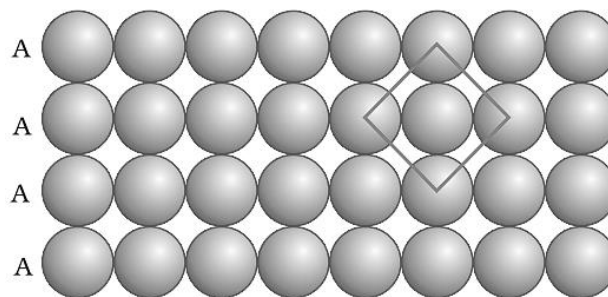


Figure: Square close packing

- In this arrangement each sphere is in contact with four neighbours. Coordination number is four. When the centres of these four spheres are connected by lines, a square is formed. So, this packing is also known as square close packing in 2D.

II. ABAB type –

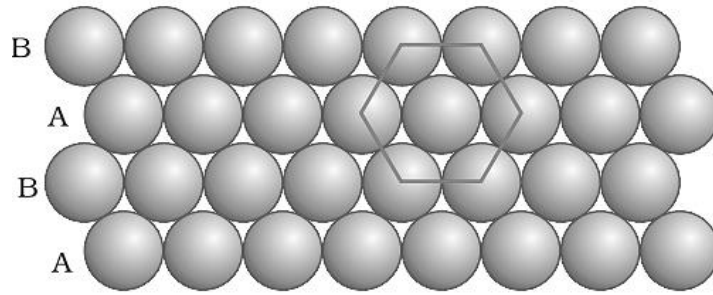


Figure: Hexagonal closes packing

- The second row placed above the first row in such a way that the spheres of second row fits exactly into the depressions of first row.
- First row arrangement is of 'A' type and second row arrangement is of 'B' type. Then this arrangement is known as **ABAB type** arrangement.
- Each sphere is in contact with six neighbours. When we connect the centres of these six spheres a regular hexagon is forms. This arrangement is also known as 2-D hexagonal close packing. The voids are in triangle shape.

C. Close packing in three dimensions - All the real structures are three dimensional. They are formed by stacking of two dimensional layers.

- I. **Three-dimensional close packing forms 2-D square close-packed layers:** It is made by stacking square close packed layers. Its unit cell is the primitive cubic unit cell.

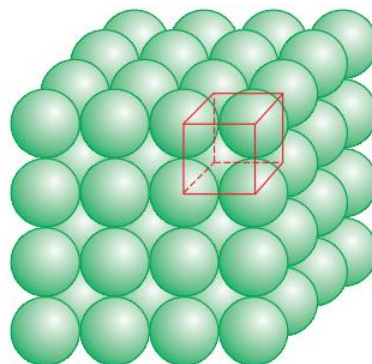


Figure: Simple cubic lattice formed by AAAA type arrangement

- II. **Three dimensional close packing from two dimensional hexagonal close packed layers:** it can be forms in two manner, these are as follows-

a. Placing second layer over the first layer-

If the two dimensional hexagonal close packed layer **A** is placed above the second layer in such a way that the spheres of second layer **B** fits exactly into the depressions of first layer. Due to this arrangement two types of void forms i.e. tetrahedral and octahedral.

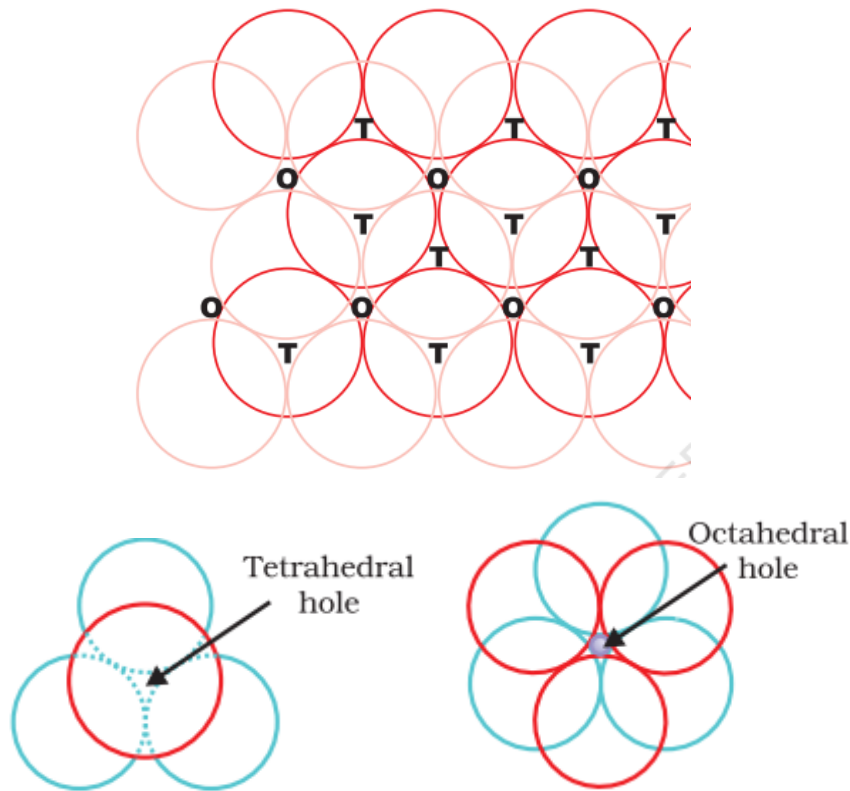


Figure: A stack of two layers of closely packed spheres and voids
O- Octahedral void T- Tetrahedral Void

b. Placing third layer over the second layer- There two possibilities generate when we place third layer above second layer.

- I. **Covering tetrahedral voids:** in case of ABAB type tetrahedral void is covered by third layer. This structure is known as HCP (hexagonal close packed). This pattern is found in metals like Mg and Zn.

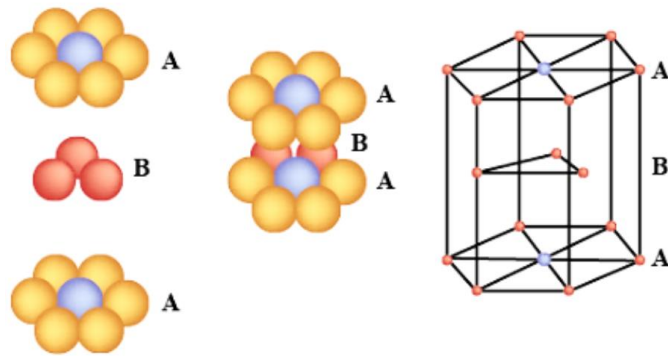


Figure: Hexagonal close packing – Stacking and geometry

- II. **Covering octahedral void-** The third layer cover the octahedral void. This pattern is known as ABCABC type. This structure is called cubic close packed (ccp) or face centred cubic (fcc) structure.

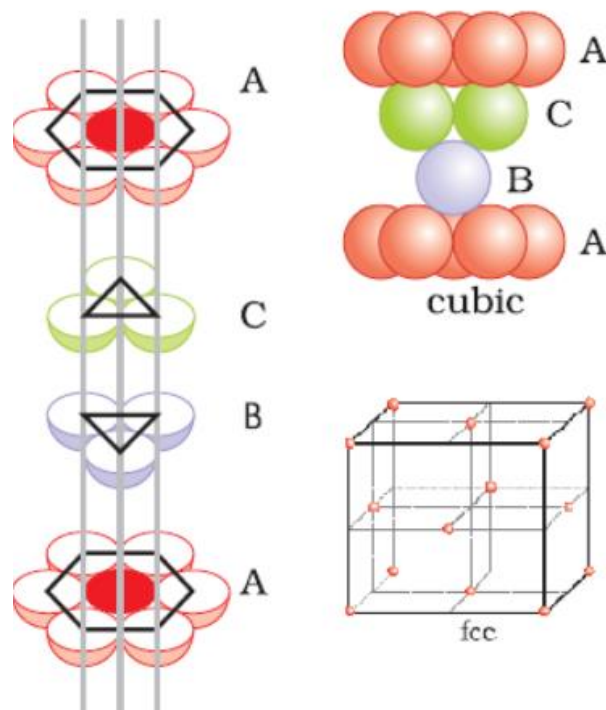


Figure: cubic close packing – stacking and geometry

Location of void

1. Cubic void-

- It lies at the centre of simple cubic (primitive type) unit cell.
- Number of cubic voids per unit cell = 1
- Coordination number = 8

2. Octahedral void-

- It lies at the centre of each edge as well as at the centre of cube in ccp/fcc type unit cell.
- Number of octahedral voids per unit cell = $12 \times \frac{1}{4} + 1 \times 1 = 3 + 1 = 4$
- Coordination number = 6

3. Tetrahedral void-

- Each body diagonal contain two tetrahedral voids.
- Number of tetrahedral voids per unit cells = $4 \times 2 = 8$
- Tetrahedral voids are present in fcc or ccp and hcp 3-d type unit cell.
- Coordination number = 4

Characteristic of crystalline solids

1. Ionic – NaCl/ rock salt/ table salt

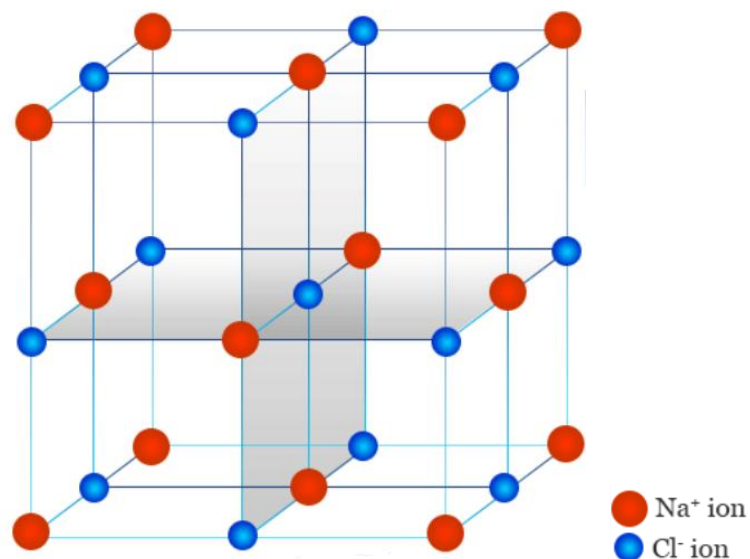
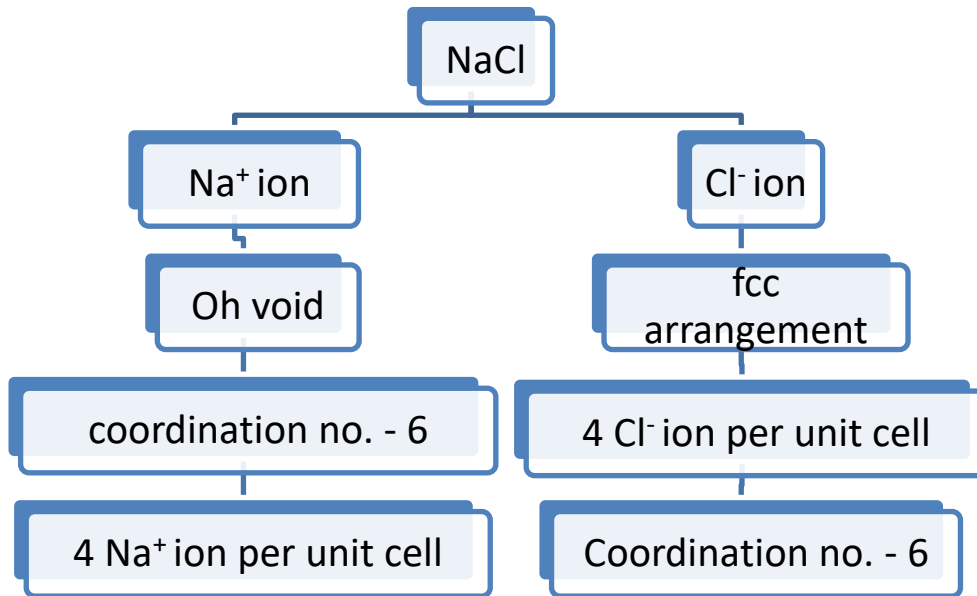


Figure: NaCl Crystalline structure



- Total voids percentage = $\frac{4}{12} \times 100 = 33.33\%$
- 4 formula unit of NaCl per unit cell are present.
- Coordination ratio = 6:6
- Radius ratio = $\frac{r_+}{r_-} = 0.525$
- Example- KCl, RbCl, RbI, etc.

2. Metallic- ZnS

ZnS (Zinc sulphide) has two types:

Zinc Blende	Wurzite
Cubic structure	Hexagonal structure
High density	Low density
It has four Asymmetric units.	It has two asymmetric units.
It is thermodynamically more stable.	It is thermodynamically less stable.
It has ccp/fcc arrangement.	It has hcp arrangement.

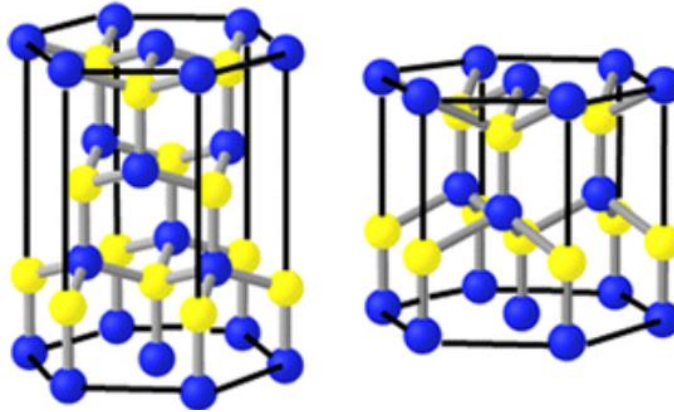
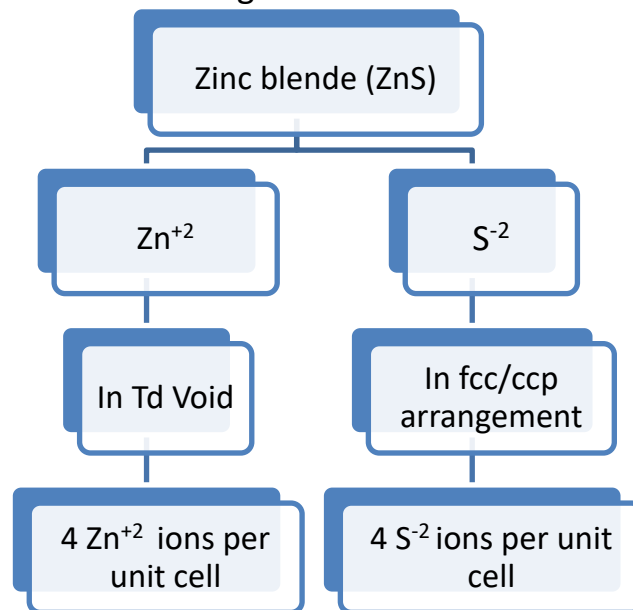


Figure: Wurzite and Zinc Blende



- Total T_d void present = $\frac{4}{8} \times 100 = 50\%$
- Total filled void = $\frac{4}{12} \times 100 = 33.33\%$
- 4 formula units of ZnS per unit cell present.
- Coordination ratio = 4:4
- Radius ratio = $\frac{r_+}{r_-} = 0.40$
- Example – CuCl, CuBr, AgI, etc.

3. Atomic – Diamond

- Diamond is one of the hardest substances on earth.
- It is an allotrope of carbon.
- Carbon is in sp^3 hybridization in diamond.

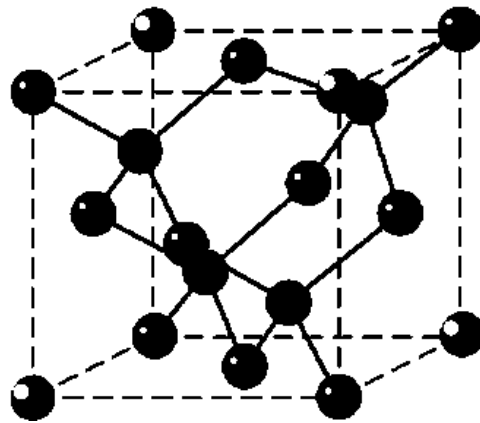
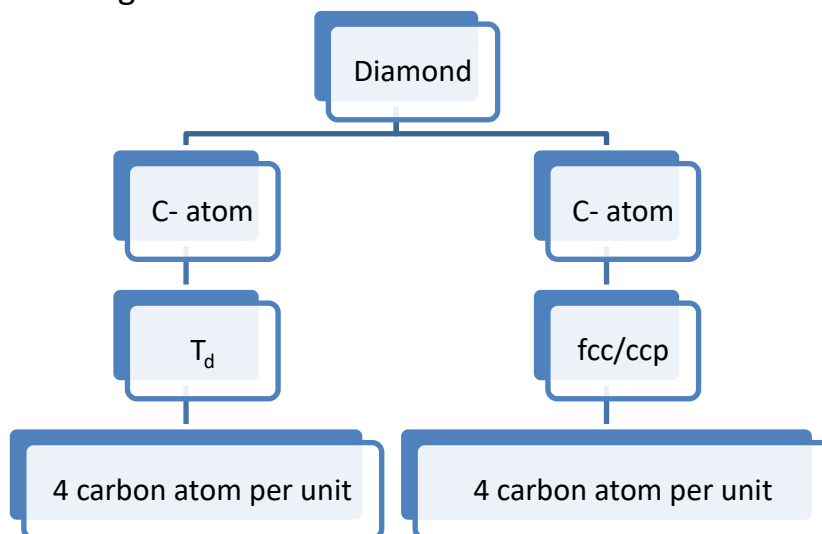


Figure: Structure of Diamond



- Tetrahedral void = 50%
- Total void = 33.3%
- 8 carbon atom per unit cell present.
- Coordination ratio= 4:4

Graphite:

- It is an allotrope of carbon.
- Carbon is in sp^2 hybridization in it.
- It shows conductivity due to presence of free electrons.
- It is soft and brittle.

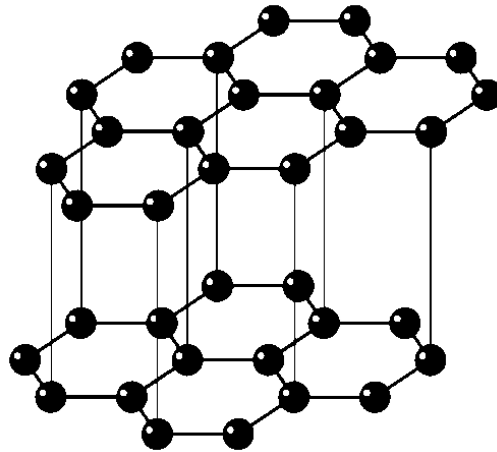


Figure: Structure of graphite

Imperfections in solids

- Crystals are made of large aggregation of small particles.
- Crystals form by crystallisation. Sometimes due to fast or slow rate of crystallization there some defects generate in the crystals.
- The defects are irregularities in the arrangement of constituent particles.
- There are two types of defects- Point and Line defects.

1. Point defects -

- The irregularities around a point or an atom in a crystal.
- Points defects are of three types:

I. **Stoichiometric Defects:**

- They do not disturb the stoichiometry of crystal.
- They are known as intrinsic or thermodynamic defects.
- They are of two types-

A. **Vacancy defects:**

- When some lattice sites are vacant, this type of defect generates.
- These defects decrease the density of substance.
- This defect can be generated when the substances are heated.
- This defect is found in non-ionic solids.

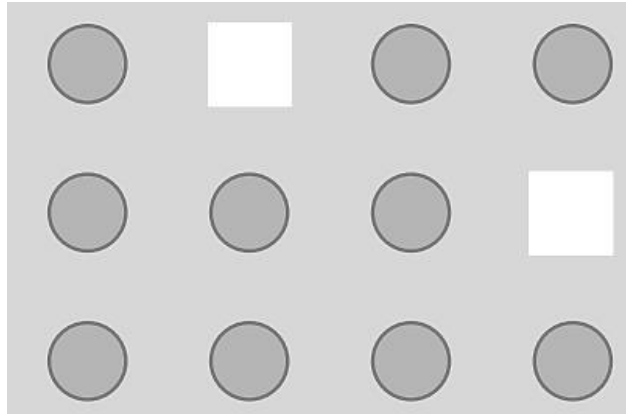


Figure: vacancy defects

B. Interstitial defects:

- When the constitutional particles occupy the interstitial site, the interstitial defect generates.
- These defects increase the density of substance.
- This defect is found in non-ionic solids.

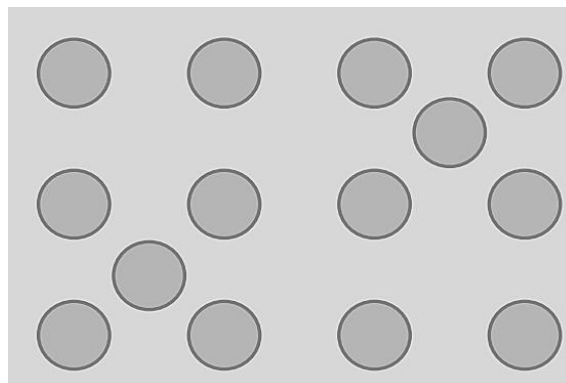


Figure: interstitial defects

C. Frenkel defects:

- This defect is found in ionic solids.
- The smaller ion is usually cation, dislocated from its normal site to an interstitial site.
- It creates a vacancy defect at original site. And interstitial defect at the new location.
- This defect is also known as dislocation defect.
- This defect does not change the density of substance.
- It shown by ionic solid in which cation and anion have large size difference.
- Examples- ZnS, AgI, AgCl, etc.

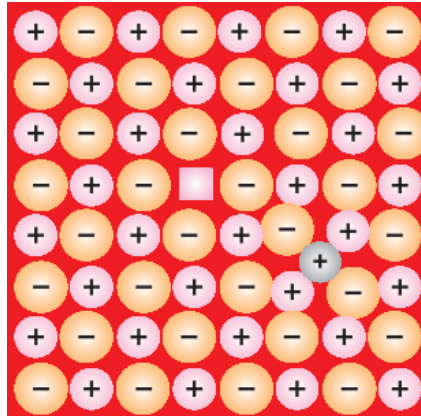


Figure: Frenkel defect

D. Schottky defect:

- It is a vacancy defect in ionic solids.
- The number of missing cations and anions are equal, to maintain the electrical neutrality.
- This defect decreases the density.
- This defect is found in ionic solids in which cations and anions are of similar size.
- Example- NaCl, KCl, CsCl, etc.

II. Impurity Defects:

- If we mix the strontium chloride into the molten sodium chloride, Sr^{+2} occupy some Na^+ sites.
- Each strontium ion replaces two sodium ions.
- The cationic vacancies are equal in number of strontium ions.
- Example- CdCl_2 , AgCl .

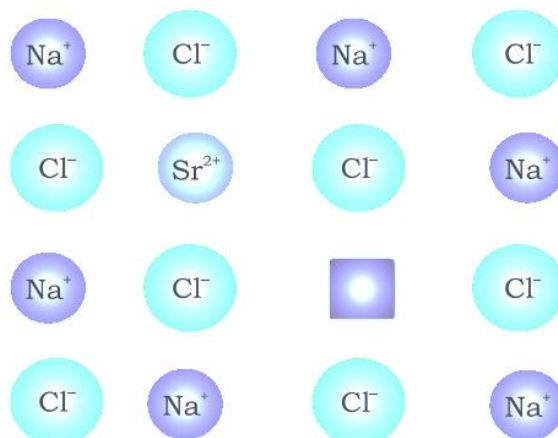


Figure: cation vacancy in NaCl by substitution of Na^+ by Sr^{+2}

III. Non- stoichiometric defects:

- In this type of defect, the constitutional particles are in non-stoichiometric ratio.
- These defects are of two types- metal excess defect and metal deficiency defect.

Metal excess defect

1. Metal excess defect due to anionic vacancies-

- It is found in alkali halides like KCl, NaCl, etc.
- When NaCl is heated in the presence of sodium vapour, sodium atoms are deposited on the surface of crystal. The chloride ions diffuse to the surface and combine with sodium ion to give NaCl.
- Sodium atom loses an electron to form sodium ion. The released electrons diffuse into crystal and occupy the anionic sites. The anionic sites occupied by unpaired electrons are known as F-centres. They impart yellow colour.

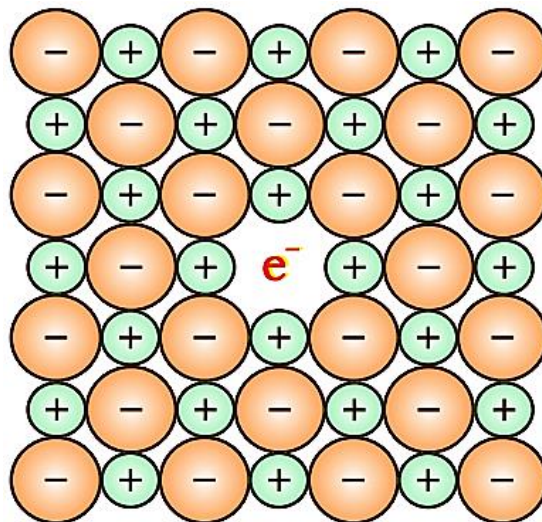
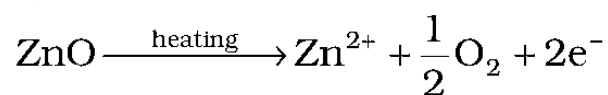


Figure: An F-centre in a crystal

2. Metal excess defects due to the presence of extra cations at interstitial sites:

- ZnO is white in colour at room temperature. When it is heated, it loses oxygen and turns yellow.



- This resulted excess of zinc in crystal, the formula of crystal becomes $Zn_{1+x}O$.

Metal deficiency defect

- There are some solids which are difficult to prepare in the stoichiometric composition.
- They contain lesser amount of metal as compare to the stoichiometric proportion.
- Example- FeO.

Magnetic properties

- Every substance has some magnetic properties due to the presence of electrons.
- Each electron in an atom is act like a tiny magnet. Its magnetic moment generated by two motions i.e. orbital motion around nucleus and spin around its own axis.
- This magnetic moment is very small in magnitude. Its unit is called **Bohr Magneton**. It is denoted by μ_B .

$$\mu_B = 9.27 \times 10^{-24} \text{ A m}^2$$

- On the basis of magnetic properties substances are classified into 5 classes:

1. Para magnetism:

- They are weakly attracted by magnetic field.
- Para-magnetism cause by presence of one or more unpaired electrons which are magnetised by magnetic field in the same direction.
- They lose their magnetism in the absence of magnetic field.
- Examples- Cu^{+2} , Fe^{+3} , Cr^{+3} .

2. Diamagnetism:

- They weakly repelled by magnetic field.
- Diamagnetism is shown by substances which have paired electrons only.
- Examples-water, sodium chloride, benzene.

3. Ferromagnetism:

- They are strongly attracted by magnetic field.
- The metal ions of ferromagnetic substances are grouped together into small regions called domains. When the substance is placed in magnetic field, these domains get oriented in the direction of magnetic field.
- Examples- CrO_2 , gadolinium, iron, nickel.

4. Anti-ferromagnetism:

- The domains oriented oppositely and cancel each other's magnetic moment.
- Example- MnO.

5. Ferrimagnetism:

- The magnetic moment of domains is aligned in parallel and anti-parallel directions in unequal numbers.
- They are weakly attracted by magnetic field.
- On heating these substances ferrimagnetism is lost and they become paramagnetic.
- Examples- Fe_3O_4 , MnFe_2O_4 .