The Solid State

We know solids are the substances which have definite volume and definite shape. A solid is nearly incompressible state of matter. This is because the particles or units (atoms, molecules or ions) making up the solid are in close contact and are in fixed positions or sites. Now, let us study some characteristic properties of solids.

Characteristic Properties of Solids.

Solids can be distinguished from liquids and gases due to their characteristic properties. Some of these are as follows:

- Solids have definite volume, irrespective of the size of the container.

- Solids are rigid and have definite shape.

- Solids are almost incompressible.

- Many solids are crystalline in nature. *These crystals have definite pattern of angles and planes.*

- The density of solids is generally greater than that of liquids and gases.

- Solids diffuse very slowly as compared to liquids and gases.

- Most solids melt on heating and become liquids. The temperature at which the solid melts and changes into liquid state under normal atmospheric pressure is called its normal melting point.

- *Solids are not always crystalline in nature.*

- Solids can be broadly classified into following two types :

(i) Crystalline solids/True solids   (ii) Amorphous solids/Pseudo solids

(1) **Difference between crystalline and amorphous solids**

Property	Crystalline solids	Amorphous solids
Shape	They have long range order.	They have short range order.
Melting point	They have definite melting point	They do not have definite melting point
Heat of fusion	They have a definite heat of fusion	They do not have definite heat of fusion
Compressibility	They are rigid and incompressible	These may not be compressed to any appreciable extent
Cutting with a sharp edged tool	They are given cleavage i.e. they break into two pieces with plane surfaces	They are given irregular cleavage i.e. they break into two pieces with irregular surface
Isotropy and Anisotropy	They are anisotropic	They are isotropic
Volume change	There is a sudden change in volume when it melts.	There is no sudden change in volume on melting.
Symmetry	These possess symmetry	These do not possess any symmetry.
Interfacial angles	These possess interfacial angles.	These do not possess interfacial angles.

Note : ✴ **Isomorphism and polymorphism :** *Two substances are said to be isomorphous if these possess similar crystalline form and similar chemical composition e.g., Na_2SeO_4 and Na_2SO_4. $NaNO_3$ and KNO_3 are not isomorphous because they have similar formula but different crystalline forms. The existence of a substance in more than one crystalline form is known as polymorphism e.g., sulphur shows two polymorphic forms viz. rhombic and monoclinic sulphur.*

✴*Glass is a supercooled liquid.*

(2) **Classification of solids :** Depending upon the nature of interparticle forces the solids are classified into four types :

Types of Solid	Constituents	Bonding	Examples	Physical Nature	M.P.	B.P.	Electrical Conductivity
Ionic	Positive and negative ions network systematically arranged	Coulombic	NaCl, KCl, CaO, MgO, LiF, ZnS, BaSO$_4$ and K$_2$SO$_4$ etc.	Hard but brittle	High ($\simeq$1000K)	High ($\simeq$2000K)	Conductor (in molten state and in aqueous solution)
Covalent	Atoms connected in covalent bonds	Electron sharing	SiO$_2$ (Quartz), SiC, C (diamond), C(graphite) etc.	Hard Hard Hard	Very high ($\simeq$4000K)	Very high ($\simeq$500K)	Insulator except graphite
Molecular	Polar or non-polar molecules	(i) Molecular interactions (intermolecu-lar forces) (ii) Hydrogen bonding	I$_2$,S$_8$, P$_4$, CO$_2$, CH$_4$, CCl$_4$ etc. Starch, sucrose, water, dry ice or drikold (solid CO$_2$) etc.	Soft Soft	Low ($\simeq$300K to 600K) Low ($\simeq$400K)	Low ($\simeq$ 450 to 800 K) Low ($\simeq$373K to 500K)	Insulator Insulator
Metallic	Cations in a sea of electrons	Metallic	Sodium , Au, Cu, magnesium, metals and alloys	Ductile malleable	High ($\simeq$800K to 1000 K)	High ($\simeq$1500K to 2000K)	Conductor
Atomic	Atoms	London dispersion force	Noble gases	Soft	Very low	Very low	Poor thermal and electrical conductors

(i) **Liquid Crystal** *: There are certain solids which when heated undergo two sharp phase transformations one after the other. Such solids first fuse sharply yielding turbid liquids and then further heating to a higher temperature these sharply change into clear liquids. The first temperature at which solids changes into turbid liquid is known as **transition point** and the second temperature at which turbid liquid changes into clear liquid is known as **melting point**. Such substances showing liquid crystal character are as follows :*

p-chloesteryl benzoate, p – Azoxyamisole, Diethylbenzidine etc.

$$p\text{-}\underset{(Solid)}{\text{Chloesteryl benzoate}} \xrightleftharpoons{145^oC} p - \underset{(liquidcrystal)}{\text{Chloesteryl benzoate}} \xrightleftharpoons{178^oC} p - \underset{(Liquid)}{\text{Chloesteryl benzoate}}$$

A liquid crystal reflects only one colour, when light falls on it. If the temperature is changed it reflects different colour light. So, such liquid crystals can be used to detect even small temperature changes. The liquid crystals are of two types : (i) *Nematic liquid crystals, (needle like),* (ii) *Smectic liquid crystals (soap like)*

(ii) **Dispersion forces or London forces in solids :** When the distribution of electrons around the nucleus is not symmetrical then there is formation of instantaneous electric pole. Field produced due to this distorts

the electron distribution in the neighbouring atom or molecule so that it acquires a dipole moment itself. The two dipole will attract and this makes the basis of London forces or dispersion forces these forces are attractive in nature and the interaction energy due to this is proportional to $\left(\dfrac{1}{r^6}\right)$. Thus, these forces are important as short distances $(\simeq 500\,pm)$. This force also depends on the polarisability of the molecules.

(3) **Amorphous Solids (Supercooled liquid) :** Solids unlike crystalline solids, do not have an ordered arrangement of their constituent atoms or ions but have a disordered or random arrangement, are called amorphous solids. Ordinary glass (metal silicate), rubber and most of the plastics are the best examples of amorphous solids. In fact, any material can be made amorphous or glassy either by rapidly cooling or freezing its vapours for example, SiO_2 crystallises or quartz in which SiO_4^{4-} tetrahedra are linked in a regular manner but on melting and then rapid cooling, it gives glass in which SiO_4^{4-} tetrahedron are randomly joined to each other.

Properties of Amorphous solids

(i) *Lack of long range order/Existence of short range order* : Amorphous solids do not have a long range order of their constituent atoms or ions. However, they do have a short range order like that in the liquids.

(ii) No sharp melting point/Melting over a range.

(iii) Conversion into crystalline form on heating.

Uses of Amorphous solids

(i) The most widely used amorphous solids are in the inorganic glasses which find application in construction, house ware, laboratory ware etc.

(ii) Rubber is amorphous solid, which is used in making tyres, shoe soles etc.

(iii) Amorphous silica has been found to be the best material for converting sunlight into electricity (in **photovoltaic cells**).

Crystallography.

"*The branch of science that deals with the study of structure, geometry and properties of crystals is called crystallography*".

(1) **Laws of crystallography :** Crystallography is based on three fundamental laws. Which are as follows

(i) *Law of constancy of interfacial angles* **:** This law states that angle between adjacent corresponding faces of the crystal of a particular

Constancy of interfacial angles

substance is always constant inspite of different shapes and sizes. The size and shape of crystal depend upon the conditions of crystallisation. This law is also known as **Steno's Law**.

(ii) *Law of rational indices* **:** This law states that the intercepts of any face of a crystal along the crystallographic axes are either equal to unit intercepts (i.e., intercepts made by unit cell) *a*, *b*, *c* or some simple whole number multiples of them e.g., *na*, *n' b*, *n''c*, where *n*, *n'* and *n''* are simple whole numbers. The whole numbers *n*, *n'* and *n''* are called **Weiss indices.** This law was given by **Hally.**

(iii) *Law of constancy of symmetry* **:** According to this law, all crystals of a substance have the same elements of symmetry.
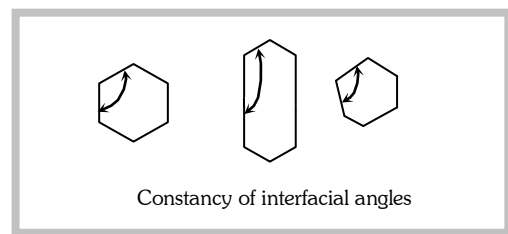
(2) Designation of planes in crystals (Miller indices) : Planes in crystals are described by a set of integers (h, k and l) known as Miller indices. Miller indices of a plane are the reciprocals of the fractional intercepts of that plane on the various crystallographic axes. For calculating Miller indices, a reference plane, known as parametral plane, is selected having intercepts a, b and c along x, y and z-axes, respectively. Then, the intercepts of the unknown plane are given with respect to a, b and c of the parametral plane.

Thus, the Miller indices are :

$$h = \frac{a}{\text{intercept of the plane along } x \text{ - axis}}$$

$$k = \frac{b}{\text{intercept of the plane along } y \text{ - axis}}$$

$$l = \frac{c}{\text{intercept of the plane along } z \text{ - axis}}$$

A parametral plane (intercepts, a, b, c along x, y and z axes)

Consider a plane in which Weiss notation is given by $\infty a : 2b : c$. The Miller indices of this plane may be calculated as below.

(i) Reciprocals of the coefficients of Weiss indices $= \dfrac{1}{\infty}, \dfrac{1}{2}, \dfrac{1}{1}$

(ii) Multiplying by 2 in order to get whole numbers $= 0, 1, 2$

Thus the Miller indices of the plane are 0, 1, and 2 and the plane is designated as the (012) plane, *i.e.* $h = 0$, $k = 1$, $l = 2$.

The distance between the parallel planes in crystals are designated as d_{hkl}. For different cubic lattices these interplanar spacing are given by the general formula,

$$d_{(hkl)} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Where a is the length of cube side while h, k and l are the Miller indices of the plane.

Note : ✹ When a plane is parallel to an axis, its intercept with that axis is taken as infinite and the Miller will be zero.

✹ Negative signs in the Miller indices is indicated by placing a bar on the intercept.

✹ All parallel planes have same Miller indices.

✹ The Miller indices are enclosed within parenthesis. *i.e.,* brackets. Commas can be used for clarity.

Example 1: Calculate the Miller indices of crystal planes which cut through the crystal axes at (i) ($2a$, $3b$, c), (ii) (∞, $2b$, c)

(a) 3, 2, 6 and 0, 1, 2   (b) 4, 2, 6 and 0, 2, 1   (c) 6, 2, 3 and 0, 0, 1   (d) 7, 2, 3 and 1, 1, 1

Solution: (a)

(i)	x	y	z		(ii)	x	y	z	
	$2a$	$3b$	c	Intercepts		∞	$2b$	c	Intercepts
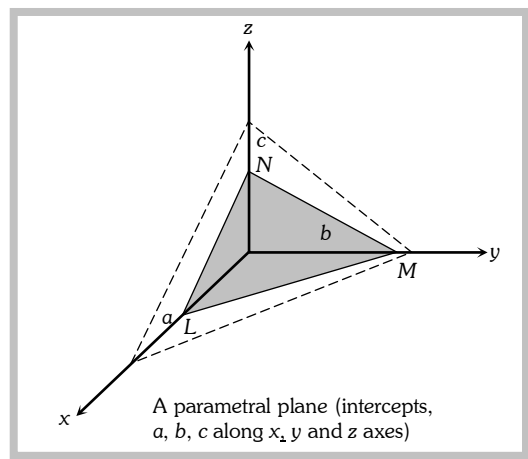
$\frac{2a}{a}$	$\frac{3b}{b}$	$\frac{c}{c}$	Lattice parameters
$\frac{1}{2}$	$\frac{1}{3}$	$\frac{1}{1}$	Reciprocals
3	2	6	Multiplying by LCM (6)

Hence, the Miller indices are (3, 2, 6)

$\frac{\infty}{a}$	$\frac{2b}{b}$	$\frac{c}{c}$	Lattice parameters
$\frac{1}{\infty}$	$\frac{1}{2}$	$\frac{1}{1}$	Reciprocals
0	1	2	Multiplying by LCM (2)

Hence, the Miller indices are (0, 1, 2).

Example 2. Caculate the distance between 111 planes in a crystal of *Ca*. Repeat the calculation for the 222 planes. ($a=0.556nm$)

(a) 016.1 *nm*   (b) 01.61 *nm*   (c) 0.610 *nm*   (d) None of the above

Solution: (b) We have, $d = \dfrac{a}{\sqrt{h^2+k^2+\ell^2}}$; $d_{111} = \dfrac{0.556}{\sqrt{1^2+1^2+1^2}} = 0.321nm$ and $d_{222} = \dfrac{0.556}{\sqrt{2^2+2^2+2^2}} = 0.161nm$

The separation of the 111 planes is twice as great as that of 222 planes.

Study of Crystals.

(1) **Crystal :** It is a homogeneous portion of a crystalline substance, composed of a regular pattern of structural units (ions, atoms or molecules) by plane surfaces making definite angles with each other giving a regular geometric form.

(2) **Space lattice and Unit cell :** A regular array of points (showing atoms/ions) in three dimensions is commonly called as a space lattice, or lattice.

(i) Each point in a space lattice represents an atom or a group of atoms.

(ii) Each point in a space lattice has identical surroundings throughout.

A three dimensional group of lattice points which when repeated in space generates the crystal called unit cell.

The unit cell is described by the lengths of its edges, *a*, *b*, *c* (which are related to the spacing between layers) and the angles between the edges, α, β, γ.
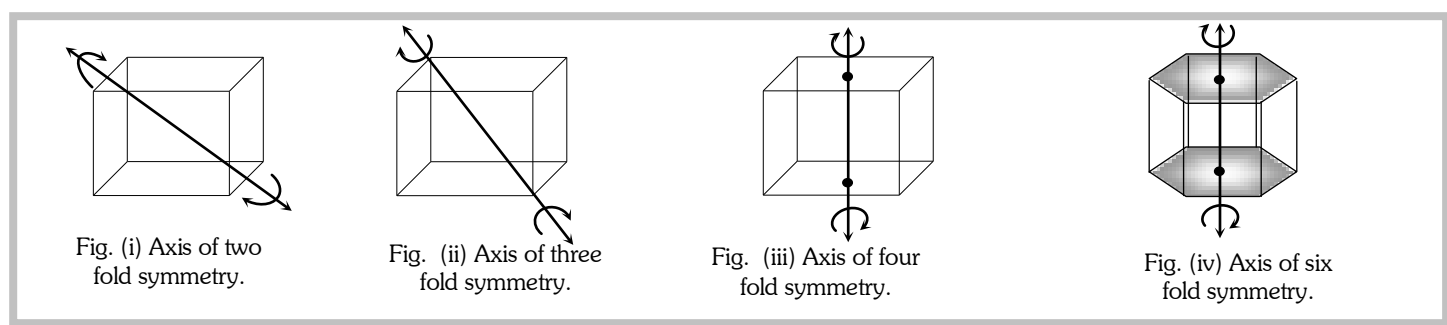

Unit cell
Space lattice & unit cell
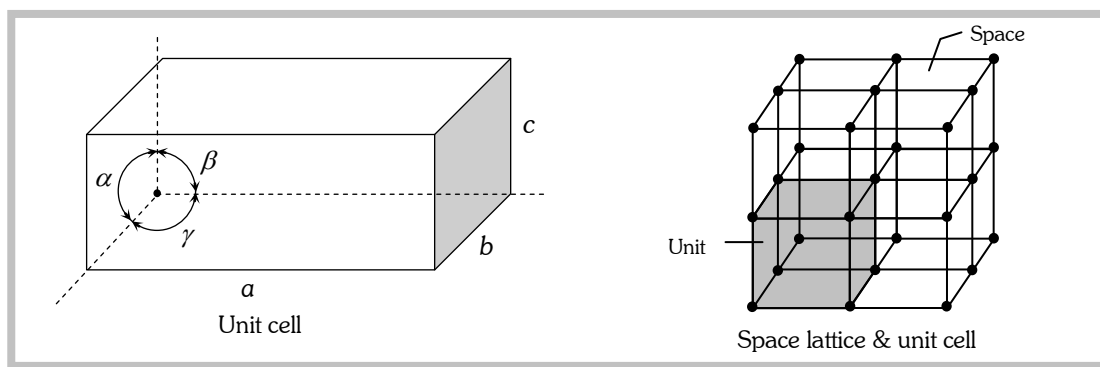
(3) **Symmetry in Crystal systems :** *Law of constancy of symmetry* : *According to this law, all crystals of a substance have the same elements of symmetry*. A crystal possess following three types of symmetry :

(i) *Plane of symmetry* **:** It is an imaginary plane which passes through the centre of a crystal can divides it into two equal portions which are exactly the mirror images of each other.

(a)	(b)	(c)
Plane of symmetry	Rectangular plane of symmetry	Diagonal plane of symmetry
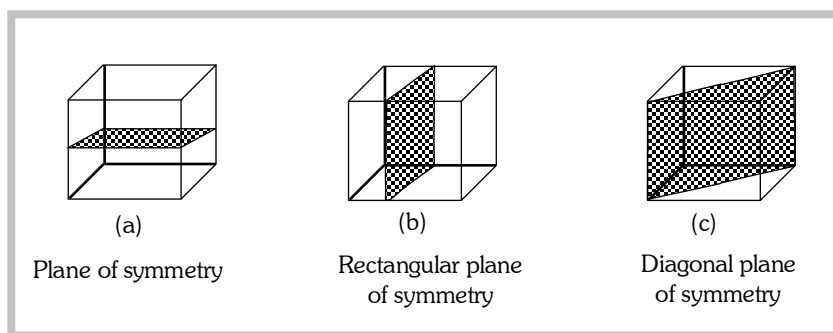
(ii) *Axis of symmetry* : An axis of symmetry or axis of rotation is an imaginary line, passing through the crystal such that when the crystal is rotated about this line, it presents the same appearance more than once in one complete revolution *i.e.*, in a rotation through 360°. Suppose, the same appearance of crystal is repeated, on rotating it through an angle of 360°/*n*, around an imaginary axis, is called an **n-fold axis** where, *n* is known as the order of axis. By order is meant the value of n in $2\pi/n$ so that rotation through $2\pi/n$, gives an equivalent configuration. For example, If a cube is rotated about an axis passing perpendicularly through the centre so that the similar appearance occurs four times in one revolution, the axis is called a four – fold or a tetrad axis, [Fig (iii)]. If similar appearance occurs twice in one complete revolution *i.e.,* after 180°, the axis is called two-fold axis of symmetry or diad axis [Fig (i)]. If the original appearance is repeated three times in one revolution *i.e.* rotation after 120°, the axis of symmetry is called three-fold axis of symmetry or triad axis [Fig (ii)]. Similarly, if the original appearance is repeated after an angle of 60° as in the case of a hexagonal crystal, the axis is called six-fold axis of symmetry or hexad axis [Fig (iv)].

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Fig. (i) Axis of two fold symmetry.	Fig. (ii) Axis of three fold symmetry.	Fig. (iii) Axis of four fold symmetry.	Fig. (iv) Axis of six fold symmetry.

(iii) *Centre of symmetry* : It is an imaginary point in the crystal that any line drawn through it intersects the surface of the crystal at equal distance on either side.

Note : ✸ Only simple cubic system have one centre of symmetry. Other system do not have centre of symmetry.

Centre of symmetry of a cubic crystal

(4) **Element of symmetry :** (i) The total number of planes, axes and centre of symmetries possessed by a crystal is termed as elements of symmetry.
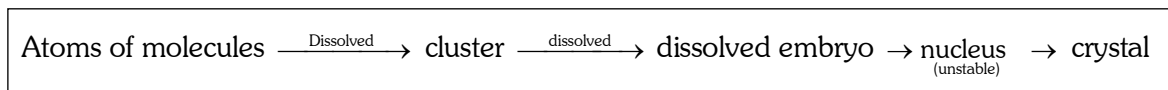
(ii) A cubic crystal possesses total 23 elements of symmetry.
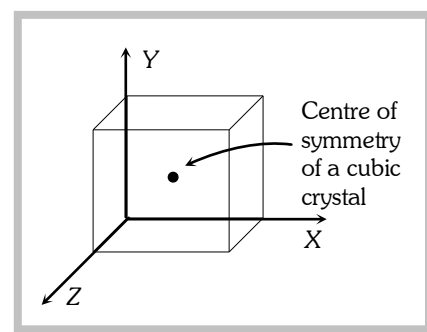
(a) Plane of symmetry   (3 + 6)   = 9

(b) Axes of symmetry   (3 + 4 + 6)   = 13

(c) Centre of symmetry   (1)   = 1

Total symmetry = 23

(5) **Formation of crystals :** The crystals of the substance are obtained by cooling the liquid (or the melt) of the solution of that substance. The size of the crystal depends upon the rate of cooling. If cooling is carried out slowly, crystals of large size are obtained because the particles (ions, atoms or molecules) get sufficient time to arrange themselves in proper positions.

Atoms of molecules $\xrightarrow{\text{Dissolved}}$ cluster $\xrightarrow{\text{dissolved}}$ dissolved embryo $\rightarrow \underset{\text{(unstable)}}{\text{nucleus}} \rightarrow$ crystal
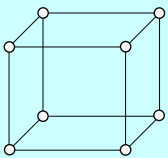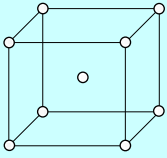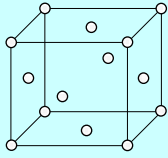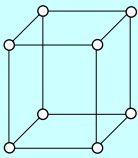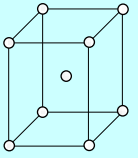
(If loosing units dissolves as embryo and if gaining unit grow as a crystals).

(6) **Crystal systems :** Bravais (1848) showed from geometrical considerations that there can be only 14 different ways in which similar points can be arranged. Thus, there can be only 14 different space lattices. These 14 types of lattices are known as **Bravais Lattices**. But on the other hand Bravais showed that there are only seven types of crystal systems. The seven crystal systems are :

(a) Cubic   (b) Tetragonal   (c) Orthorhombic   (d) Rhombohedral

(e) Hexagonal   (f) Monoclinic   (g) Triclinic

Bravais lattices corresponding to different crystal systems

Crystal system	Space lattice			Examples
Cubic $a = b = c$, Here a, b and c are parameters (diamensions of a unit cell along three axes) size of crystals depend on parameters. $\alpha = \beta = \gamma = 90^o$ $\alpha\beta$ and γ are sizes of three angles between the axes.	**Simple :** Lattice points at the eight corners of the unit cells.	**Body centered :** Points at the eight corners and at the body centred.	**Face centered :** Points at the eight corners and at the six face centres.	$Pb, Hg, Ag,$ Au, Cu, ZnS, diamond, KCl, $NaCl, Cu_2O, CaF_2$ and alums. etc.
Tetragonal $a = b \neq c$, $\alpha = \beta = \gamma = 90^o$	**Simple :** Points at the eight corners of the unit cell.	**Body centered :** Points at the eight corners and at the body centre		$SnO_2, TiO_2,$ $ZnO_2, NiSO_4$ $ZrSiO_4 . PbWO_4$, white Sn etc.
Orthorhombic	**Simple:** Points	**End centered :** Also	**Body centered** **Face centered:**	$KNO_3, K_2SO_4,$

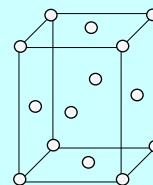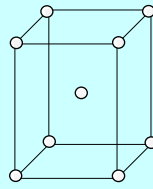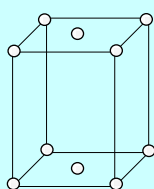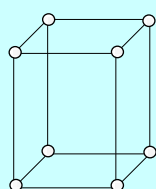|				
(Rhombic) $a \neq b \neq c$, $\alpha = \beta = \gamma = 90^o$	at the eight corners of the unit cell.	called side centered or base centered. Points at the eight corners and at two face centres opposite to each other.	: Points at the eight corners and at the body centre	Points at the eight coreners and at the six face centres.

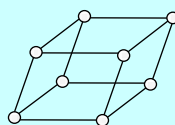$PbCO_3$, $BaSO_4$, **rhombic sulphur**, $MgSO_4 . 7H_2O$ **etc.**

Rhombohedral or Trigonal

$a = b = c$,
$\alpha = \beta = \gamma \neq 90^o$

Simple : Points at the eight corners of the unit cell

$NaNO_3$, $CaSO_4$, **calcite, quartz,** As, Sb, Bi **etc.**
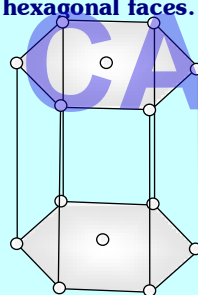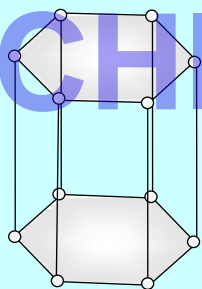
Hexagonal

$a = b \neq c$,
$\alpha = \beta = 90^o$
$\gamma = 120^o$

Simple : Points at the twelve corners of the unit cell out lined by thick line.

or Points at the twelve corners of the hexagonal prism and at the centres of the two hexagonal faces.

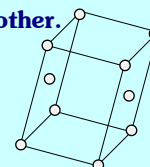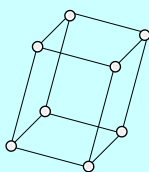ZnO, PbS, CdS, HgS, **graphite, ice,** Mg, Zn, Cd **etc.**

Monoclinic

$a \neq b \neq c$,
$\alpha = \gamma = 90^o, \beta \neq 90^o$

Simple : Points at the eight corners of the unit cell

End centered : Point at the eight corners and at two face centres opposite to the each other.

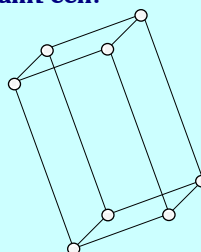$Na_2SO_4 . 10H_2O$, $Na_2B_4O_7 . 10H_2O$, $CaSO_4 . 2H_2O$, **monoclinic sulphur etc.**

Triclinic

$a \neq b \neq c$,
$\alpha \neq \beta \neq \gamma \neq 90^o$

Simple : Points at the eight corners of the unit cell.

$CaSO_4 . 5H_2O$, $K_2Cr_2O_7$, H_3BO_3 **etc.**

Note : ✳ Out of seven crystal systems triclinic is the most unsymmetrical ($a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90$).

Packing constituents in Crystals.

(1) **Close packing in crystalline solids :** In the formation of crystals, the constituent particles (atoms, ions or molecules) get closely packed together. The closely packed arrangement is that in which maximum available space is occupied. This corresponds to a state of maximum density. The closer the packing, the greater is the stability of the packed system. It is of two types :

(i) **Close packing in two dimensions :** The two possible arrangement of close packing in two dimensions.

Square close packing

(a) **Square close packing :** In which the spheres in the adjacent row lie just one over the other and show a horizontal as well as vertical alignment and form square. Each sphere in this arrangement is in contact with four spheres.
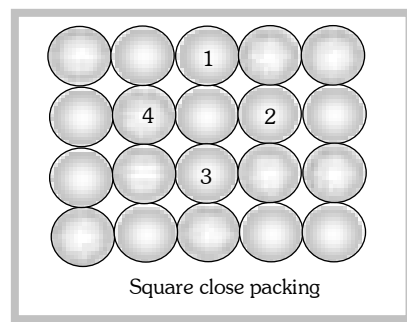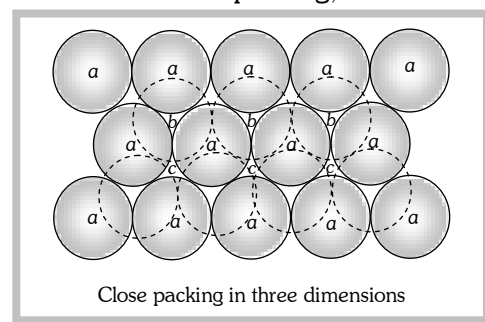
(b) **Hexagonal close packing :** In which the spheres in every second row are seated in the depression between the spheres of first row. The spheres in the third row are vertically aligned with spheres in first row. The similar pattern is noticed throughout the crystal structure. Each sphere in this arrangement is in contact with six other spheres.

Hexagonal close packing
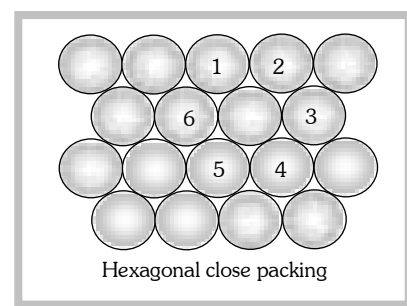
Note : ✱ Hexagonal close packing is more dense than square close packing.

✱ In hexagonal close packing about 60.4% of available space is occupied by spheres. Whereas, square close packing occupies only 52.4% of the space by spheres.

✱ In square close packing the vacant spaces (voids) are between four touching spheres, whose centres lie at the corners of a square are called **square voids**. While in hexagonal close packing the vacant spaces (voids) are between three touching spheres, whose centres lie at the corners of an equilateral triangle are called **triangular voids**.

(ii) **Close packing in three dimensions :** In order to develop three dimensional close packing, let us retain the hexagonal close packing in the first layer. For close packing each spheres in the second layer rests in the hollow at the centre of three touching spheres in the layer as shown in figure. The spheres in the first layer are shown by solid lines while those in second layer are shown by broken lines. **It may be noted that only half the triangular voids in the first layer are occupied by spheres in the second layer (*i.e., either b or c*).** The unoccupied hollows or voids in the first layer are indicated by (c) in figure.

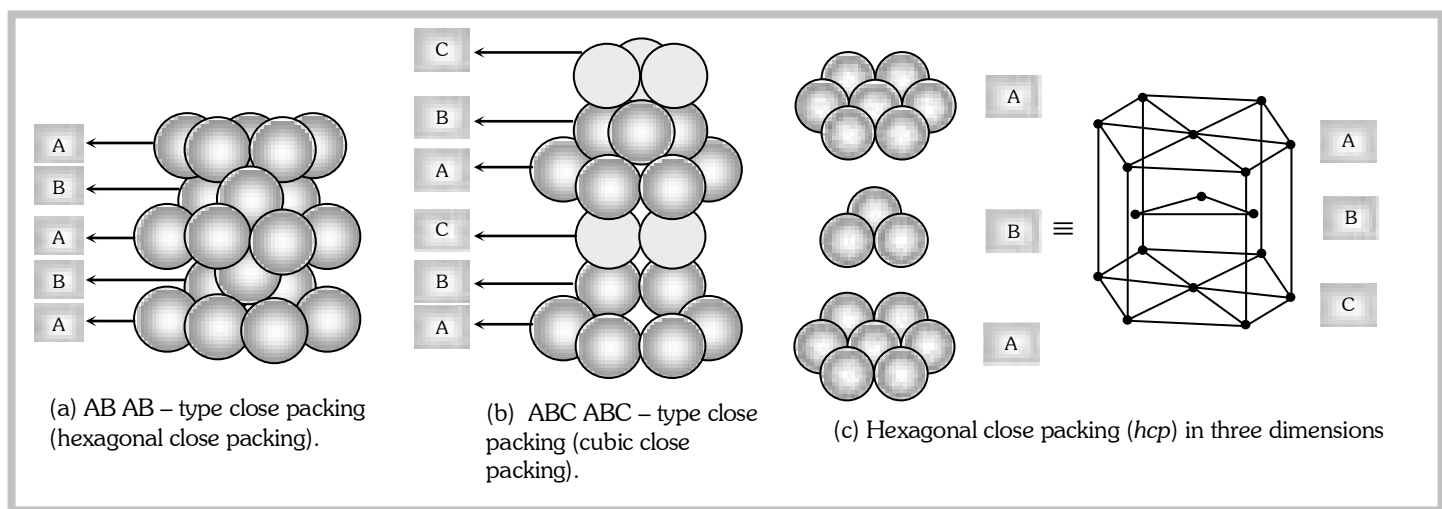Close packing in three dimensions

There are two alternative ways in which species in third layer can be arranged over the second layer,

(a) **Hexagonal close packing :** The third layer lies vertically above the first and the spheres in third layer rest in one set of hollows on the top of the second layer. This arrangement is called **ABAB ....** type and 74% of the available space is occupied by spheres.

(b) **Cubic close packing** : The third layer is different from the first and the spheres in the third layer lie on the other set of hollows marked 'C' in the first layer. This arrangement is called **ABCABC.....** type and in this also 74% of the available space is occupied by spheres. The cubic close packing has face centred cubic (*fcc*) unit cell.
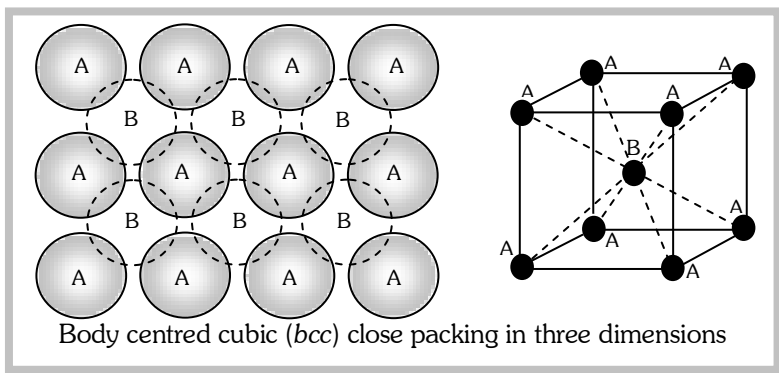

(a) AB AB – type close packing (hexagonal close packing).

(b) ABC ABC – type close packing (cubic close packing).

(c) Hexagonal close packing (*hcp*) in three dimensions

This arrangement is found in *Be, Mg, Zn, Cd, Sc, Y, Ti, Zr.*

Cubic close packing (*ccp*) in three dimensions

Cubic close packing (*ccp*) ≡ face – centred cubic (*fcc*)
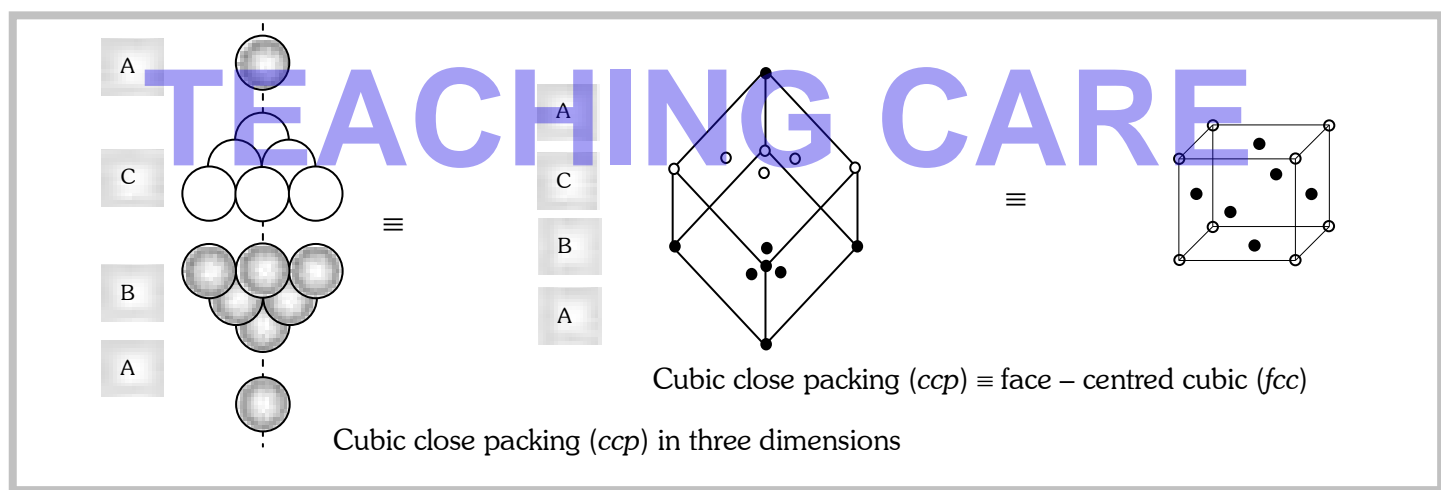
This arrangement is found in *Cu, Ag, Au, Ni, Pt, Pd, Co, Rh, Ca, Sr.*

(c) **Body centred cubic (bcc) :** This arrangement of spheres (or atoms) is not exactly close packed. This structure can be obtained if spheres in the first layer (A) of close packing are slightly opened up. As a result none of these spheres are in contact with each other. The second layer of spheres (B) can be placed on top of the first layer so that each sphere of the second layer is in contact with four spheres of the layer below it. Successive building of the third will be exactly like the first layer. If this pattern of building layers is repeated infinitely we get an arrangement as shown in figure. This arrangement is found in *Li, Na, K, Rb, Ba, Cs, V, Nb, Cr, Mo, Fe.*

Body centred cubic (*bcc*) close packing in three dimensions

(2) Comparison of *hcp*, *ccp* and *bcc*

| Property	Hexagonal close packed (hcp)	Cubic close packed (ccp)	Body centred cubic (bcc)
Arrangement of packing	Close packed	Close packed	Not close packed
Type of packing	AB AB AB A…..	ABC ABC A….	AB AB AB A……
Available space occupied	74%	74%	68%
Coordination number	12	12	8
Malleability and ductility	Less malleable, hard and brittle	Malleable and ductile	

(3) **Interstitial sites in close packed structures :** Even in the close packing of spheres, there is left some empty space between the spheres. This empty space in the crystal lattice is called site or void or hole. Voids are of following types

(i) **Trigonal void :** This site is formed when three spheres lie at the vertices of an equilateral triangle. Size of the trigonal site is given by the following relation.

$$r = 0.155R$$

where, r = Radius of the spherical trigonal site
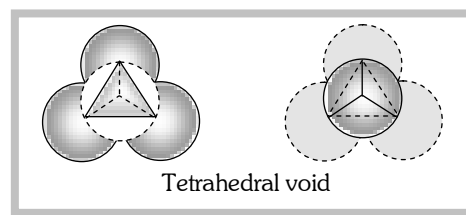
R = Radius of closely packed spheres

Trigonal
Triogonal void
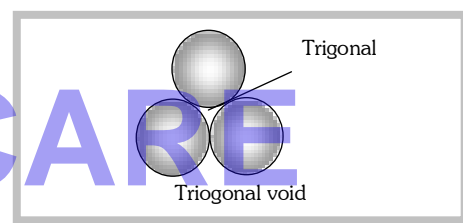
(ii) **Tetrahedral void :** A tetrahedral void is developed when triangular voids (made by three spheres in one layer touching each other) have contact with one sphere either in the upper layer or in the lower layer. This type of void is surrounded by four spheres and the centres of these spheres lie at the apices of a regular tetrahedron, hence the name tetrahedral site for this void.

In a close packed structure, there are two tetrahedral voids associated with each sphere because every void has four spheres around it and there are eight voids around each sphere. **So the number of tetrahedral voids is double the number of spheres in the crystal structure**. The maximum radius of the atoms which can fit in the tetrahedral voids relative to the radius of the sphere is calculated to be 0.225: 1, *i.e.*,

Tetrahedral void

$$\frac{r}{R} = 0.225,$$ where r is the radius of the tetrahedral void or atom occupying tetrahedral void and R is the radius of spheres forming tetrahedral void.

(a) **Octahedral void :** This type of void is surrounded by six closely packed spheres, *i.e.* it is formed by six spheres. Out of six spheres, four are placed in the same plane touching each other, one sphere is placed from above and the other from below the plane of these spheres. These six spheres surrounding the octahedral void are present at the vertices of regular octahedron. **Therefore, the number of octahedral voids is equal to the number of spheres**. The ratio of the radius (r) of the atom or ion which can exactly fit in the octahedral void formed by spheres of radius R has been calculated to be 0.414, *i.e.*
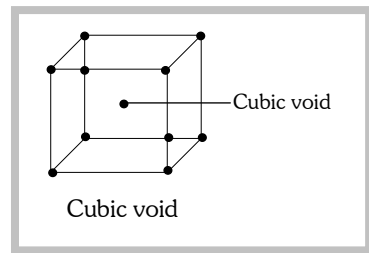

Octahedral void
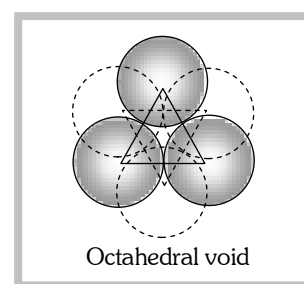
$$\boxed{\frac{r}{R} = 0.414}$$

(b) **Cubic void :** This type of void is formed between 8 closely packed spheres which occupy all the eight corner of cube *i.e.* this site is surrounded by eight spheres which touch each other. Here radius ratio is calculated to be 0.732, *i.e.*

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

Cubic void

Cubic void

Thus, the decreasing order of the size of the various voids is **Cubic > Octahedral > Tetrahedral > Trigonal**

Important Tips

➤ *At the limiting value of radius ratio r^+/r^-, the forces of attraction & repulsion are equal.*

➤ *The most malleable metals (Cu, Ag, Au) have cubic close packing.*

➤ *Cubic close packing has fcc (face centred cubic) unit cell*

➤ *Number of octahedral voids = Number of atoms present in the closed packed arrangement.*

➤ *Number of tetrahedral voids = 2 × Number of octahedral voids = 2 × Number of atoms.*

Mathematical analysis of Cubic system.

Simplest crystal system is to be studied in cubic system. Three types of cubic systems are following

- **Simple cubic (*sc*) :** Atoms are arranged only at the corners.

- **Body centred cubic (*bcc*) :** Atoms are arranged at the corners and at the centre of the cube.

- **Face centred cubic (*fcc*) :** Atoms are arranged at the corners and at the centre of each faces.

(1) **Atomic radius :** It is defined as the half of the distance between nearest neighbouring atoms in a crystal. It is expressed in terms of length of the edge (*a*) of the unit cell of the crystal.

(i) **Simple cubic structure (sc) :** Radius of atom '*r*' = $\frac{a}{2}$

(ii) **Face centred cubic structure (fcc) :** '*r*' = $\frac{a}{2\sqrt{2}}$

(iii) **Body centred cubic structure (bcc) :** '*r*' = $\frac{\sqrt{3}a}{4}$
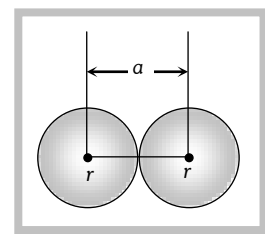
(2) **Number of atoms per unit cell/Unit cell contents :** The total number of atoms contained in the unit cell for a simple cubic called the unit cell content.

(i) **Simple cubic structure (sc)** : Each corner atom is shared by eight surrounding cubes. Therefore, it contributes for $\frac{1}{8}$ of an atom. $\therefore\ Z = 8 \times \frac{1}{8} = 1$ atom per unit cell in crystalline solid.

(ii) **Face centered cubic structure (fcc)** : The eight corners atoms contribute for $\frac{1}{8}$ of an atom and thus one atom per unit cell. Each of six face centred atoms is shared by two adjacent unit cells and therefore one face centred atom contribute half of its share. $\therefore Z = 6 \times \frac{1}{2} = 3$ atom per unit cell.

So, total $Z = 3 + 1 = 4$ atoms per unit cell.

(iii) *Body centered cubic structure* (*bcc*) : Eight corner atoms contribute one atom per unit cell.

Centre atom contribute one atom per unit cell. So, total $1 + 1 = 2$ atoms per unit cells. $Z = 8 \times \frac{1}{8} + 1 = 2$

Note : ❋ *Number of atoms in unit cell* : It can be determined by the simplest relation $= \frac{n_c}{8} + \frac{n_f}{2} + \frac{n_i}{1}$

Where $n_c =$ Number of atoms at the corners of the cube $= 8$

$n_f =$ Number of atoms at six faces of the cube $= 6$

$n_i =$ Number of atoms inside the cube $= 1$

Cubic unit cell	n_c	n_f	n_i	Total atom in per unit cell
Simple cubic (sc)	8	0	0	1
body centered cubic (bcc)	8	0	1	2
Face centered cubic (fcc)	8	6	0	4

(3) **Co-ordination number (C.N.)** : It is defined as the number of nearest neighbours or touching particles with other particle present in a crystal is called its co-ordination number. It depends upon structure of the crystal.

(i) *For simple cubic system* C.N. $= 6$.

(ii) *For body centred cubic system* C.N. $= 8$

(iii) *For face centred cubic system* C.N. $= 12$.

(4) **Density of the unit cell :** It is defined as the ratio of mass per unit cell to the total volume of unit cell.

Density of unit cell $(\rho) = \dfrac{\text{mass of unit cell}}{\text{volume of unit cell}} ; \rho = \dfrac{\text{Number of particles} \times \text{mass of each particle}}{\text{volume of the unit cell}}$ or $\dfrac{Z \times M}{a^3 \times N_0}$

Where $Z =$ Number of particles per unit cell, $M =$ Atomic mass or molecular mass, $N_0 =$ Avogadro number $(6.023 \times 10^{23} \, mol^{-1})$, $a =$ Edge length of the unit cell$= a \, pm = a \times 10^{-10} \, cm$, $a^3 =$ volume of the unit cell

i.e.

$$\rho = \frac{Z \times M}{a^3 \times N_0 \times 10^{-30}} g/cm^3$$

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

(5) **Packing fraction (P.F.) :** It is defined as ratio of the volume of the unit cell that is occupied by spheres of the unit cell to the total volume of the unit cell.

Let radius of the atom in the packing $= r$

Edge length of the cube $= a$

Volume of the cube $V = a^3$

Volume of the atom (spherical) $v = \frac{4}{3}\pi r^3$, then packing density $= \frac{vZ}{V} = \frac{\frac{4}{3}\pi r^3 Z}{a^3}$

(i) **Simple cubic unit cell :** Let the radius of atom in packing is r. Atoms are present at the corner of the cube, each of the eight atom present at the eight corners shared amongst eight unit cells.

Hence number of atoms per unit cell $= 8 \times \frac{1}{8} = 1$, again $r = \frac{a}{2}$

$\therefore$ P.F. $= \frac{\frac{4}{3}\pi r^3}{(2r)^3} = 0.52$; % P.F. = 52%, then % of void = 100 – 52 = 48%

(ii) **Body centred cubic unit cell** : Number of atoms per unit cell $= 8 \times \frac{1}{8} + 1 = 2$, $r = \frac{\sqrt{3}a}{4}$

P.F. $= \frac{2 \times \frac{4}{3}\pi r^3}{\left(\frac{4r}{\sqrt{3}}\right)^3} = 0.68$; % *P.F.* = 68%, then % of void = 100 – 68 = 32%

(iii) **Face centred cubic unit cell** : Number of atoms per unit cell $= 4$, $r = \frac{\sqrt{2}a}{4}$

P.F. $= \frac{4 \times \frac{4}{3}\pi r^3}{\left(\frac{4r}{\sqrt{2}}\right)^3} = 0.74$; % P.F. = 74%, then % of void = 100 – 74 = 26%

Structure	r related to a	Volume of the atom (v)	Packing density
Simple cubic	$r = \frac{a}{2}$	$\frac{4}{3}\pi\left(\frac{a}{2}\right)^3$	$\frac{\pi}{6} = 0.52$
Face-centred cubic	$r = \frac{a}{2\sqrt{2}}$	$\frac{4}{3}\pi\left(\frac{a}{2\sqrt{2}}\right)^3$	$\frac{\sqrt{2}\pi}{6} = 0.74$
Body-centred cubic	$r = \frac{\sqrt{3}a}{4}$	$\frac{4}{3}\pi\left(\frac{\sqrt{3}a}{4}\right)^3$	$\frac{\sqrt{3}\pi}{8} = 0.68$

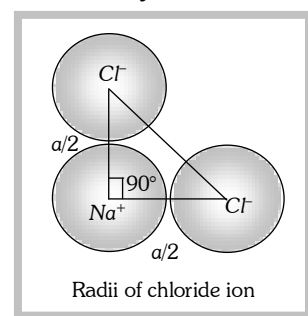(6) **Ionic radii :** X-ray diffraction or electron diffraction techniques provides the necessary information regarding unit cell. From the dimensions of the unit cell, it is possible to calculate ionic radii.

Let, cube of edge length 'a' having cations and anions say $NaCl$ structure.

Then, $\boxed{r_c + r_a = a/2}$
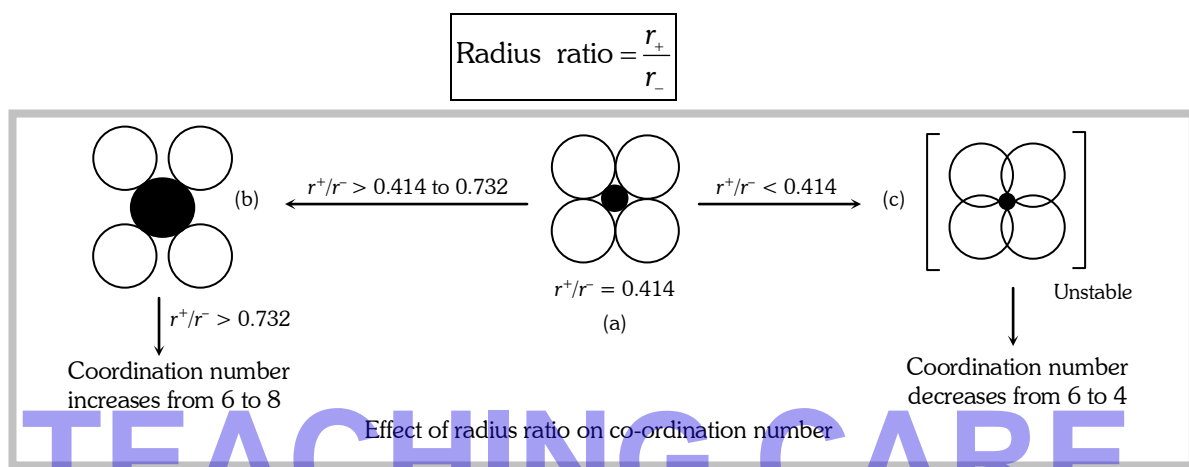
where r_c and r_a are radius of cation and anion.

Radii of chloride ion

Radius of $Cl^- = \sqrt{\dfrac{(a/2)^2 + (a/2)^2}{2}} = \dfrac{a}{4}$

For body centred lattice say $CsCl$. $r_c + r_a = \dfrac{\sqrt{3}a}{2}$

Radius ratio : Ionic compounds occur in crystalline forms. Ionic compounds are made of cations and anions. These ions are arranged in three dimensional array to form an aggregate of the type $(A^+B^-)_n$. Since, the Coulombic forces are non-directional, hence the structures of such crystals are mainly governed by the ratio of the radius of cation (r_+) to that of anion (r_-). The ratio r_+ to r_- (r_+/r_-) is called as radius ratio.

$$\boxed{\text{Radius ratio} = \dfrac{r_+}{r_-}}$$

r⁺/r⁻ > 0.414 to 0.732   (b)   r⁺/r⁻ < 0.414   (c)

r⁺/r⁻ = 0.414   (a)   Unstable

r⁺/r⁻ > 0.732

Coordination number increases from 6 to 8

Coordination number decreases from 6 to 4

Effect of radius ratio on co-ordination number

The influence of radius ratio on co-ordination number may be explained as follows : Consider an ideal case of octahedral voids in close packing of anions with radius ratio 0.414 and co-ordination number six. An increase in size of cation increases the radius ratio from 0.414, then the anions move apart so as to accommodate the larger cation. As the radius ratio increases more and more beyond 0.732, the anions move further and further apart till a stage is obtained when more anions can be accommodated and this cation occupies a bigger void *i.e.*, cubic void with co-ordination number eight.

When the radius ratio decreases from 0.414, the six anions would not be able to touch the smaller cation and in doing so, they overlap each other. This causes the cation to occupy a smaller void *i.e.*, tetrahedral void leading to co-ordination number four

Limiting Radius ratios and Structure

Limiting radius ratio $(r^+)/(r^-)$	C.N.	Shape
< 0.155	2	Linear
0.155 – 0.225	3	Planar triangle
0.225 – 0.414	4	Tetrahedral
0.414 – 0.732	6	Octahedral
0.732 – 0.999 or 1	8	Body-centered cubic

Characteristics of Some Typical Crystal Structure

Crystal	Type of unit cell	Example	$\dfrac{r_+}{r_-}$	C.N.	Number of formula units of (AB, or AB₂) per unit cell
CsBr	Body-centred	CsBr, TiCl	0.93	8 – 8	1
NaCl	Face-centred	AgCl, MgO	0.52	6 – 6	4
ZnS	Face-centred	ZnS	0.40	4 – 4	4
CaF₂	Face-centred	CaF₂, SrF₂, CdF₂, ThO₂	0.73	8 – 4	4

Note : ✳ The ionic radius increases as we move from top to bottom in a group of periodic table for example :

$$Na^+ < K^+ < Rb^+ < Cs^+ \text{ and } F^- < Cl^- < Br^- < I^-$$

✳ Along a period, usually iso-electronic ions are obtained e.g. Na^+, Mg^{2+}, Al^{3+} (greater the nuclear charge, smaller the size, $Al^{3+} < Mg^{2+} < Na^+$)

Example : 3 A metallic element crystallizes into a lattice containing a sequence of layers of *ABABAB* .... Any packing of spheres leaves out voids in the lattice. The percentage by volume of empty space of this is

(a) 26% (b) 21% (c) 18% (d) 16 %

Solution :(a) The hexagonal base consists of six equilateral triangles, each with side *2r* and altitude *2r* sin 60°.

Hence, area of base $= 6\left[\dfrac{1}{2}(2r)(2r\sin 60^\circ)\right] = 6\sqrt{3}.r^2$

The height of the hexagonal is twice the distance between closest packed layers.
The latter can be determined to a face centred cubic lattice with unit cell length *a*. In such a lattice, the distance between closest packed layers is one third of the body diagonal, i.e. $\dfrac{\sqrt{3}a}{3}$, Hence

$$\text{Height }(h) = 2\left[\dfrac{\sqrt{3}a}{3}\right] = \dfrac{2a}{\sqrt{3}}$$

Now, in the face centred lattice, atoms touch one another along the face diagonal,
Thus, $4r = \sqrt{2}.a$

With this, the height of hexagonal becomes : $\text{Height }(h) = \dfrac{2}{\sqrt{3}}\left[\dfrac{4r}{\sqrt{2}}\right] = \left[4\dfrac{\sqrt{2}}{3}\right].r$

Volume of hexagonal unit is, $V = (\text{base area}) \times (\text{height}) = (6\sqrt{3}\,r^2)\left[\dfrac{4\sqrt{2}}{\sqrt{3}}.r\right] = 24\sqrt{2}.r^3$

In one hexagonal unit cell, there are 6 atoms as described below :

- 3 atoms in the central layer which exclusively belong to the unit cell.
- 1 atom from the centre of the base. There are two atoms of this type and each is shared between two hexagonal unit cells.
- 2 atoms from the corners. There are 12 such atoms and each is shared amongst six hexagonal unit cells.

Now, the volume occupied by atoms $= 6\left[\dfrac{4}{3}\pi r^3\right]$

Fraction of volume occupied by atoms $= \dfrac{\text{Volume occupied by atoms}}{\text{Volume of hexagonal unit cell}} = \dfrac{6\left(\dfrac{4}{3}\pi r^3\right)}{24\sqrt{2}.r^3} = \pi/3\sqrt{2} = 0.74.$

Fraction of empty space $= (1.00 - 0.74) = 0.26$

Percentage of empty space $= 26\%$

Example : 4 Silver metal crystallises in a cubic closest – packed arrangement with the edge of the unit cell having a length $a = 407\ pm.$. What is the radius of silver atom.

(a) $143.9\ pm$ (b) $15.6\ pm$ (c) $11.59\ pm$ (d) $13.61\ pm$
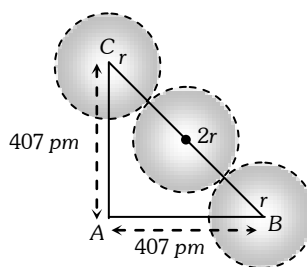
Solution :(a) $AC^2 + AB^2 = BC^2$

here $AC = AB = a,\ \ BC = 4r$

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

$2a^2 = 16r^2$

$\therefore \qquad r^2 = \dfrac{a^2}{8}$

$\therefore \qquad r = \dfrac{a}{2\sqrt{2}} = \dfrac{407}{2\sqrt{2}} = 143.9\ pm.$

Example : 5 From the fact that the length of the side of a unit cell of lithium is $351\ pm$. Calculate its atomic radius. Lithium forms body centred cubic crystals.

(a) $152.69\ pm$ (b) $62.71\ pm$ (c) $151.98\ pm$ (d) $54.61\ pm$

Solution : (c)   In (*bcc*) crystals, atoms touch each other along the cross diagonal.

Hence,   Atomic radius $(R) = \dfrac{a\sqrt{3}}{4} = 351 \times \dfrac{\sqrt{3}}{4} = 151.98\, pm$

Example : 6 Atomic radius of silver is $144.5\ pm$. The unit cell of silver is a face centred cube. Calculate the density of silver.

(a) $10.50\ g/cm^3$ (b) $16.50\ g/cm^3$ (c) $12.30\ g/cm^3$ (d) $15.50\ g/cm^3$

Solution :(a)   For (*fcc*) unit cell, atoms touch each other along the face diagonal.

Hence, Atomic radius $(R) = \dfrac{a\sqrt{2}}{4}$

$a = \dfrac{4R}{\sqrt{2}} = \dfrac{4}{\sqrt{2}} \times 144.5\, pm = 408.70\, pm = 408.70 \times 10^{-10}\, cm$

Density $(D) = \dfrac{ZM}{VN_0}, \quad V = a^3$

$D = \dfrac{ZM}{a^3 N_0}$; where Z for (*fcc*) unit cell $= 4$, Avagadro's number $(N_0) = 6.023 \times 10^{23}$, Volume of cube

$(V) = (408.70 \times 10^{-10})^3\, cm^3$ and M (*Mol. wt.*) of silver $= 108$,

$D = \dfrac{4 \times 108}{(408.70 \times 10^{-10})^3 \times 6.023 \times 10^{23}} = 10.50\, g/cm^3$

Example : 7 Lithium borohydride ($LiBH_4$), crystallises in an orthorhombic system with 4 molecules per unit cell. The unit cell dimensions are : $a = 6.81Å$, $b = 4.43Å$, $c = 717Å$. If the molar mass of $LiBH_4$ is 21.76 $g\,mol^{-1}$. The density of the crystal is –

(a) 0.668 $g\,cm^{-3}$ (b) $0.585\,g\,cm^2$ (c) $1.23\,g\,cm^{-3}$ (d) None

Solution : (a) We know that, $\rho = \dfrac{ZM}{N_0V} = \dfrac{4 \times (21.76\,gmol^{-1})}{(6.023 \times 10^{23}\,mol^{-1})(6.81 \times 4.43 \times 7.17 \times 10^{-24}\,cm^3)} = 0.668\,g\,cm^{-3}$

Example : 8 A metallic elements exists as a cubic lattice. Each edge of the unit cell is 2.88Å. The density of the metal is 7.20 $g\,cm^{-3}$. How many unit cells will be present in 100 gm of the metal.

(a) 5.82×10^{23} (b) 6.33×10^{23} (c) 7.49×10^{24} (d) 6.9×10^{24}

Solution : (a) The volume of unit cell $(V) = a^3 = (2.88Å)^3 = 23.9 \times 10^{-24}\,cm^3$

Volume of 100 g of the metal $= \dfrac{\text{Mass}}{\text{Density}} = \dfrac{100}{7.20} = 13.9\,cm^2$

Number of unit cells in this volume $= \dfrac{13.9\,cm^3}{23.9 \times 10^{-24}\,cm^3} = 5.82 \times 10^{23}$

Example : 9 Silver crystallizes in a face centred cubic system, 0.408 nm along each edge. The density of silver is 10.6 g/cm^3 and the atomic mass is 107.9 g/mol. Calculate Avogadro's number.

(a) 6.00×10^{23} $atom/mol$ (b) 9.31×10^{23} $atom/mol$

(c) 6.23×10^{23} $atom/mol$ (d) 9.61×10^{23} $atom/mol$

Solution: (a) The unit cell has a volume of $(0.408 \times 10^{-9}m)^3 = 6.79 \times 10^{-29}\,m^3$ per unit cell and contains four atoms. The volume of 1 $mole$ of silver is,

$107.9\,g/mol\left[\dfrac{(1 \times 10^{-2}m)^3}{10.6g}\right] = 1.02 \times 10^{-5}\,m^3/mol$;   where 107.9 g/mol is the molecular mass of the silver

The number of unit cells per $mol.$ is,

$1.02 \times 10^{-5}\,m^3/mol\left(\dfrac{1\text{unit cell}}{6.79 \times 10^{-29}\,m^3}\right) = 1.50 \times 10^{23}$ unit cells per $mol.$

and the number of atoms per $mol.$ is, $\left(\dfrac{4\text{atoms}}{\text{unit cell}}\right)\left(\dfrac{1.50 \times 10^{23}\text{unit cell}}{\text{mol}}\right) = 6.00 \times 10^{23}$ $atom/mol.$

Example: 10 Fraction of total volume occupied by atoms in a simple cube is

(a) $\dfrac{\pi}{2}$ (b) $\dfrac{\sqrt{3}\pi}{8}$ (c) $\dfrac{\sqrt{2}\pi}{6}$ (d) $\dfrac{\pi}{6}$

Solution: (d) In a simple cubic system, number of atoms $a = 2r$

$\therefore$ Packing fraction $= \dfrac{\text{Volume occupied by one atom}}{\text{Volume of unit cell}} = \dfrac{\frac{4}{3}\pi r^3}{a^3} = \dfrac{\frac{4}{3}\pi r^3}{(2r)^3} = \dfrac{\pi}{6}$

Example: 11 A solid AB has the $NaCl$ structure. If radius of cation A^+ is 120 pm, calculate the maximum possible value of the radius of the anion B^-

(a) 240 pm (b) 280 pm (c) 270 pm (d) 290 pm

Solution:(d)   We know that for the $NaCl$ structure

radius of cation/radius of anion $= 0.414$; $\dfrac{r_{A^+}}{r_{B^-}} = 0.414$; $r_{B^-} = \dfrac{r_{A^+}}{0.414} = \dfrac{120}{0.414} = 290\, pm$

Example: 12 $CsBr$ has a (bcc) arrangement and its unit cell edge length is 400 pm. Calculate the interionic distance in $CsCl$.   **[CBSE 1993]**

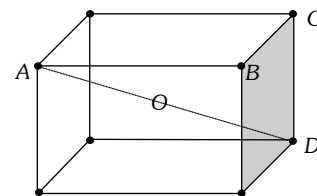(a) 346.4 pm (b) 643 pm (c) 66.31 pm (d) 431.5 pm

Solution:(a)   The (bcc) structure of $CsBr$ is given in figure

The body diagonal $AD = a\sqrt{3}$, where a is the length of edge of unit cell

On the basis of figure

$AD = 2(r_{Cs^+} + r_{Cl^-})$

$a\sqrt{3} = 2(r_{Cs^+} + r_{Cl^-})$ or $(r_{Cs^+} + r_{Cl^-}) = \dfrac{a\sqrt{3}}{2} = 400 \times \dfrac{\sqrt{3}}{2} = 200 \times 1.732 = 346.4\, pm$
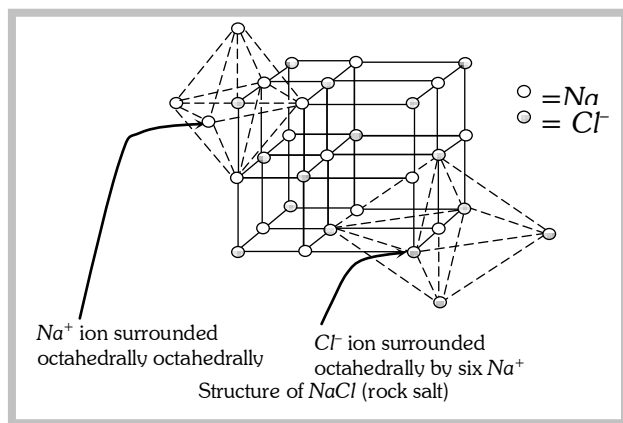
Crystal structures and Method of determination.

Ionic compounds consist of positive and negative ions arranged in a manner so as to acquire minimum potential energy (maximum stability). To achieve the maximum stability, ions in a crystal should be arranged in such a way that forces of attraction are maximum and forces of repulsion are minimum. Hence, for maximum stability the oppositely charged ions should be as close as possible to one another and similarly charged ions as far away as possible from one another. Among the two ions constituting the binary compounds, the larger ions (usually anions) form a close-packed arrangement (hcp or ccp) and the smaller ions (usually cations) occupy the interstitial voids. Thus in every ionic compound, positive ions are surrounded by negative ions and vice versa. Normally each ions is surrounded by the largest possible number of oppositely charged ions. This number of oppositely charged ions surrounding each ions is termed its coordination number.

Classification of ionic structures : In the following structures, a black circle would denote an anion and a white circle would denote a cation. In any solid of the type $A_x B_y$ the ratio of the coordination number of A to that of B would be $y : x$.

(1) **Rock salt structure :** The $NaCl$ structure is composed of Na^+ and Cl^- . The no. of Na^+ ions is equal to that of Cl^- . The radii of Na^+ and Cl^- are 95 pm and 181 pm respectively $\dfrac{rNa^+}{rCl^-} = \dfrac{95pm}{181pm} = 0.524$. The radius ratio of 0.524 for $NaCl$ suggests an octahedral voids. Chloride is forming a fcc unit cell in which Na^+ is in the octahedral voids. The coordination number of Na^+ is 6 and therefore that of Cl^- would also be 6. Moreover, there are 4 Na^+ ions and 4 Cl^- ions per unit cell. The formula is Na_4Cl_4 $i.e.$, $NaCl$. The other substances having this kind of a structure are halides of all alkali metals except cesium, halides and oxides of all alkaline earth metals except berylium oxide.

Na⁺ ion surrounded
octahedrally octahedrally

Cl⁻ ion surrounded
octahedrally by six Na⁺

Structure of $NaCl$ (rock salt)

(2) **Zinc blende structure :** Sulphide ions are face centred and zinc is present in alternate tetrahedral voids. Formula is Zn_4S_4, *i.e.*, *ZnS*. Coordination number of *Zn* is 4 and that of sulphide is also 4. Other substance that exists in this kind of a structure is *BeO*.

The zine sulphide crystals are composed of equal no. of Zn^{+2} and S^{2-} ions. The radii of two ions ($Zn^{+2} = 74\,pm$ and $S^{2-} = 184\,pm$) led to the radius ratio (r^+/r^-) as 0.40 which suggests a tetrahedral arrangement

$$\frac{rZn^{+2}}{rS^{2-}} = \frac{74\,pm}{184\,pm} = 0.40$$

$\bullet = Zn^{2+}$ ion

$\bigcirc = S^{2-}$ ion

Structure of *ZnS* (Zinc blende)
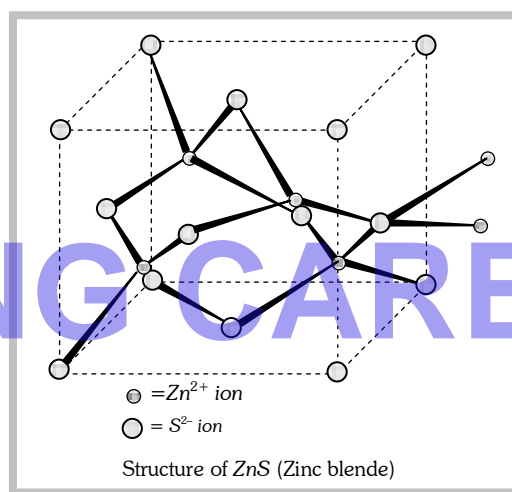
(3) **Fluorite structure :** Calcium ions are face centred and fluorite ions are present in all the tetrahedral voids. There are four calcium ions and eight fluoride ions per unit cell. Therefore the formula is Ca_4F_8, (*i.e.* CaF_2). The coordination number of fluoride ions is four (tetrahedral voids) and thus the coordination number of calcium ions is eight. Other substances which exist in this kind of structure are UO_2 and ThO_2.

$\bigcirc = Ca^{2+}$

$\circ = F^-$

Structure of CaF_2 (Fluorite)
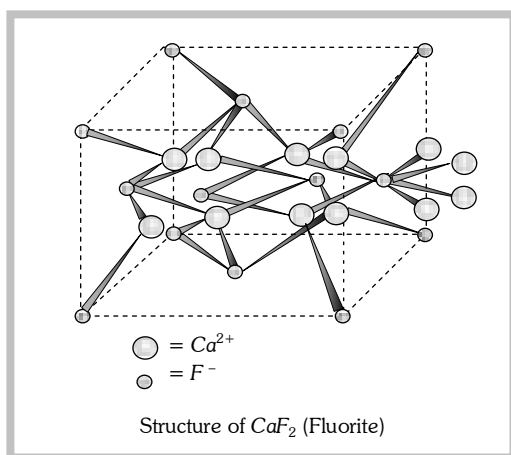
The Solid State

(4) **Anti-fluorite structure :** Oxide ions are face centred and lithium ions are present in all the tetrahedral voids. There are four oxide ions and eight lithium ions per unit cell. As it can be seen, this unit cell is just the reverse of fluorite structure, in the sense that, the position of cations and anions is interchanged. Other substances which exist in this kind of a structure are Na_2O, K_2O and Rb_2O.

(5) **Spinel and inverse spinel structure :** Spinel is a mineral ($MgAl_2O_4$). Generally they can be represented as $M^{2+}M_2^{3+}O_4$. Where M^{2+} is present in one-eighth of tetrahedral voids in a *fcc* lattice of oxide ions and M^{3+} present in half of the octahedral voids. M^{2+} is usually *Mg, Fe, Co, Ni, Zn* and *Mn*, M^{3+} is generally *Al, Fe, Mn, Cr* and *Rh*. e.g., $ZnAl_2O_4, Fe_3O_4, FeCr_2O_4$ etc.

(6) **Cesium halide structure :** Chloride ions are primitive cubic while the cesium ion occupies the centre of the unit cell. There is one chloride ion and one cesium ion per unit cell. Therefore the formula is *CsCl*. The coordination number of cesium is eight and that of chloride is ions is also eight. Other substances which exist in this kind of a structure are all halides of cesium.

The *CsCl* crystal is composed of equal no. of Cs^+ and Cl^- ions. The radii of two ions ($Cs^+ = 160pm$ and $Cl^- = 181pm$) led to radius ratio of rCs^+ to rCl^- as 0.884

$$\frac{rCs^+}{rCl^-} = \frac{160pm}{181pm} = 0.884$$

Suggests a body centred cubic structure cubic structure having a cubic hole.
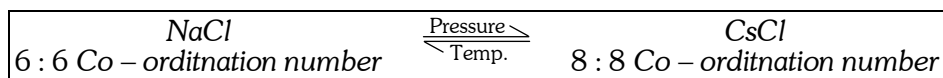

Structure of caesium chloride
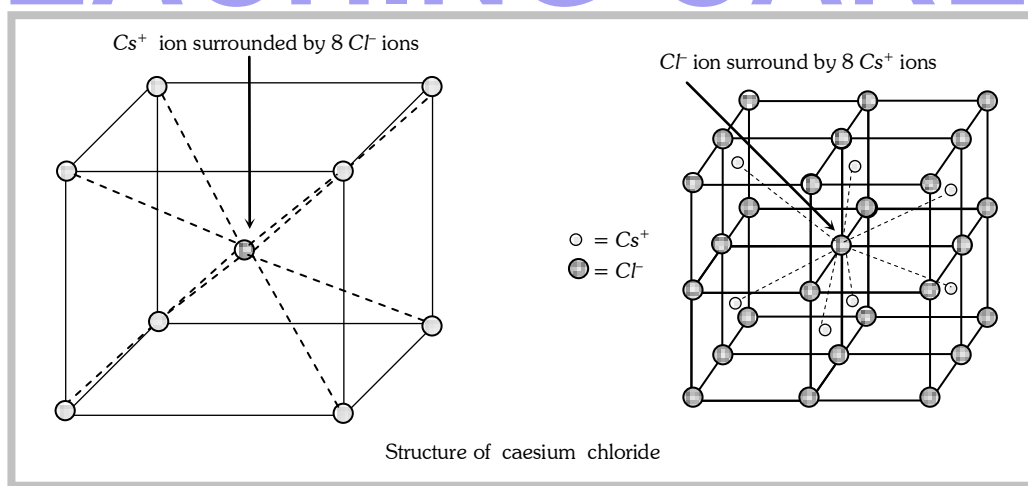
(7) **Corundum structure :** The general formula of compounds crystallizing in corundum structure is Al_2O_3. The closest packing is that of anions (oxide) in hexagonal primitive lattice and two-third of the octahedral voids are filled with trivalent cations. e.g., Fe_2O_3, Al_2O_3 and Cr_2O_3.

(8) **Pervoskite structure :** The general formula is ABO_3. One of the cation is bivalent and the other is tetravalent. e.g., $CaTiO_3, BaTiO_3$. The bivalent ions are present in primitive cubic lattice with oxide ions on the centres of all six square faces. The tetravalent cation is in the centre of the unit cell occupying octahedral void.

The Solid State

Note : ✹ *On applying high pressure, NaCl structure having 6:6 coordination number changes to CsCl structure having 8:8 coordination number similarly, CsCl having 8:8 coordination number on heating to 760 K changes to NaCl structure having 6:6 coordination number.*

$$\underset{6:6\ Co-orditnation\ number}{NaCl} \underset{\overset{\displaystyle Pressure\searrow}{\nwarrow Temp.}}{\rightleftharpoons} \underset{8:8\ Co-orditnation\ number}{CsCl}$$

Depending upon the relative number of positive and negative ions present in ionic compounds, it is convenient to divide them into groups like AB, AB_2, AB_3, etc. Ionic compounds of the type AB and AB_2 are discussed below.

S. No.	Crystal Structure	Brief description	Examples	Co-ordination number	Number of formula units per unit cell
1.	Type AB Rock salt (NaCl) type	It has fcc arrangement in which Cl^- ions occupy the corners and face centres of a cube while Na^+ ions are present at the body and edge of centres.	Halides of Li, Na, K, Rb, AgF, AgBr, NH$_4$Cl, NH$_4$Br, NH$_4$I etc.	$Na^+ = 6$ $Cl^- = 6$	4
2.	Zinc blende (ZnS) type	It has ccp arrangement in which S^{2-} ions form fcc and each Zn^{2+} ion is surrounded tetrahedrally by four S^{2-} ions and vice versa.	$CuCl, CuBr, CuI, AgI, BeS$	$Zn^{2+} = 4$ $S^{2-} = 4$	4
3.	Type AB$_2$ Fluorite (CaF$_2$) type	It has arrangement in which Ca^{2+} ions form fcc with each Ca^{2+} ions surrounded by $8F^-$ ions and each F^- ions by $4Ca^{2+}$ ions.	$BaF_2, BaCl_2, SrF_2$ $SrCl_2, CdF_2, PbF_2$	$Ca^{2+} = 8$ $F^- = 4$	4
4.	Antifluorite type	Here negative ions form the ccp arrangement so that each positive ion is surrounded by 4 negative ions and each negative ion by 8 positive ions	Na_2O	$Na^+ = 4$ $O^{2-} = 8$	4
5.	Caesium chloride (CsCl) type	It has the bcc arrangement with Cs^+ at the body centre and Cl^- ions at the corners of a cube or vice versa.	$CsCl, CsBr, CsI, CsCN,$ $TlCl, TlBr, TlI$ and $TlCN$	$Cs^+ = 8$ $Cl^- = 8$	1

(iii) **Crystal structure of some metals at room temperature and pressure :**
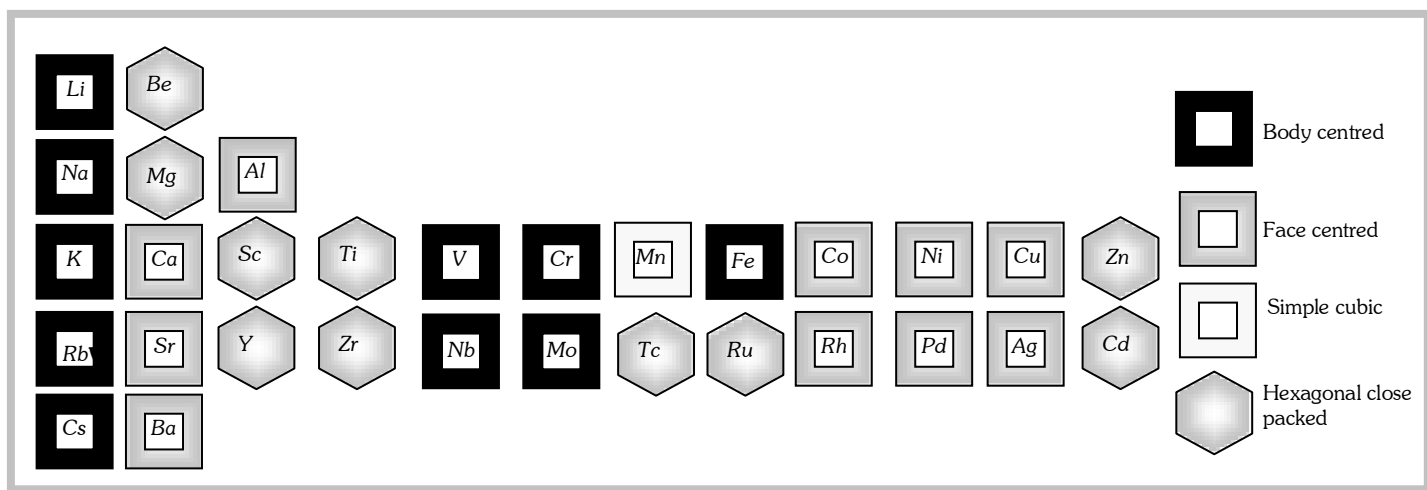
Experimental method of determining Crystal structure.

X-ray diffraction and Bragg's Equation : Crystal structure has been obtained by studying on the diffraction of X-rays by solids. A crystal, having constituents particles arranged in planes at very small distances in three dimension array, acts as diffraction grating for X- rays which have wavelengths of the same order as the spacing in crystal.

When a beam of X-rays passes through a crystalline solid, each atom in the beam scatters some of the radiations. If waves are on same phase means if their peak and trough coincides they add together to give a wave of greater amplitude. This enhancement of intensity is called constructive interference. If waves are out of phase, they cancel. This cancellation is called destructive interference.

Thus X- ray diffraction results from the scattering of X-rays by a regular arrangement of atoms or ions.

Bragg's equation : Study of internal structure of crystal can be done with the help of X-rays. The distance of the constituent particles can be determined from diffraction value by *Bragg's equation*,**.**

$$n\lambda = 2d\sin\theta \text{ where, } \lambda = \text{Wave length of X-rays, } n = \text{order of diffraction,}$$

$$\theta = \text{Angle of reflection, } d = \text{Distance between two parallel surfaces}$$

The above equation is known as **Bragg's equation** or **Bragg's law**. The reflection corresponding to $n = 1$ (for a given family of planes) is called first order reflection; the reflection corresponding to $n = 2$ is the second order reflection and so on. Thus by measuring n (the order of reflection of the X-rays) and the incidence angle θ, we can know d/λ.

$$\frac{d}{\lambda} = \frac{n}{2\sin\theta}$$

From this, d can be calculated if λ is known and vice versa. In X-ray reflections, n is generally set as equal to 1. Thus Bragg's equation may alternatively be written as

$$\lambda = 2d\sin\theta = 2\,d_{hkl}\sin\theta$$

Where d_{hkl} denotes the perpendicular distance between adjacent planes with the indices *hkl*.

Example : 15 The first order reflection $(n = 1)$ from a crystal of the X-ray from a copper anode tube $(\lambda = 0.154 nm)$ occurs at an angle of 16.3°. What is the distance between the set of planes causing the diffraction.

    (a) $0.374 nm$ (b) $0.561 nm$ (c) $0.274 nm$ (d) $0.395 nm$

Solution :(c)   From Bragg's equation, $n\lambda = 2d \sin\theta$; $d = \dfrac{n \times \lambda}{2\sin\theta} = \dfrac{1 \times 0.154}{2(\sin 16.3)} = \dfrac{0.154 \, nm}{2 \times 0.281} = 0.274 nm$

Example : 16 The diffraction of barium with X-radiation of wavelength 2.29Å gives a first – order reflection at 30°. What is the distance between the diffracted planes.

    (a) $3.29 \, Å$ (b) $4.39 \, Å$ (c) $2.29 \, Å$ (d) $6.29 \, Å$

Solution :(c)   Using Bragg's equation $2d\sin\theta = n\lambda$

    $d = \dfrac{n\lambda}{2\sin\theta}$, where d is the distance between two diffracted planes, θ the angle to have maximum intensity of diffracted X-ray beam, n the order of reflection and λ is the wavelength

    $\therefore \; d = \dfrac{1 \times 2.29 Å}{2 \times \sin 30^o} = 2.29 Å$ $\left(\sin 30^o = \dfrac{1}{2}\right)$

Example : 17 When an electron in an excited Mo atom falls from L to the K shell, an X-ray is emitted. These X-rays are diffracted at angle of 7.75^o by planes with a separation of 2.64Å. What is the difference in energy between K-shell and L-shell in Mo assuming a first-order diffraction. $(\sin 7.75^o = 0.1349)$

    (a) $36.88 \times 10^{-15} J$ (b) $27.88 \times 10^{-16} J$ (c) $63.88 \times 10^{-17} J$ (d) $64.88 \times 10^{-16} J$

Solution : (b) $2d\sin\theta = n\lambda$

    $\lambda = 2d\sin\theta = 2 \times 2.64 \times 10^{-10} \times \sin 7.75^o = 0.7123 \times 10^{-10} \, m$

    $E = \dfrac{hc}{\lambda} = \dfrac{6.62 \times 10^{-34} \times 3 \times 10^8}{0.7123 \times 10^{-10}} = 27.88 \times 10^{-16} J$

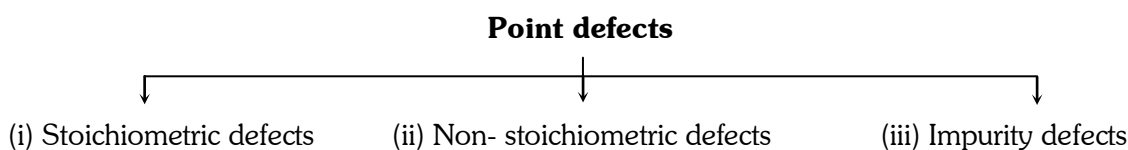## Defects or Imperfections in Solids.

Any deviation from the perfectly ordered arrangement constitutes a defect or imperfection. These defects sometimes called thermodynamic defects because the number of these defects depend on the temperature. Crystals may also possess additional defect due to the presence of impurities. Imperfection not only modify the properties of solids but also give rise to new properties. Any departure from perfectly ordered arrangement of atoms in crystals called imperfections or defects.

(1) **Electronic imperfections :** Generally, electrons are present in fully occupied lowest energy states. But at high temperatures, some of the electrons may occupy higher energy state depending upon the temperature. For example, in the crystals of pure Si or Ge some electrons are released thermally from the covalent bonds at temperature above 0 K. these electrons are free to move in the crystal and are responsible for electrical conductivity. This type of conduction is known as **intrinsic conduction**. The electron deficient bond formed by the release of an electron is called a hole. In the presence of electric field the positive holes move in a direction opposite to that of the electrons and conduct electricity. The electrons and holes in solids gives rise to electronic imperfections.

(2) **Atomic imperfections/point defects :** When deviations exist from the regular or periodic arrangement around an atom or a group of atoms in a crystalline substance, the defects are called point defects. Point defect in a crystal may be classified into following three types;

<div align="center">

Point defects

(i) Stoichiometric defects   (ii) Non- stoichiometric defects   (iii) Impurity defects

</div>

(i) **Stoichiometric defects** : The compounds in which the number of positive and negative ions are exactly in the ratios indicated by their chemical formulae are called stoichiometric compounds. The defects do not disturb the stoichiometry (the ratio of numbers of positive and negative ions) are called stoichiometric defects. These are of following types :

(a) **Schottky defects :** This type of defect when equal number of cations and anions are missing from their lattice sites so that the electrical neutrality is maintained. This type of defect occurs in highly ionic compounds which have high co-ordination number and cations and anions of similar sizes. *e.g.*, *NaCl, KCl, CsCl* and *KBr* etc.

(b) **Interstitial defects :** This type of defect is caused due to the presence of ions in the normally vacant interstitial sites in the crystals.

(c) **Frenkel defects :** This type of defect arises when an ion is missing from its lattice site and occupies an interstitial position. The crystal as a whole remains electrically neutral because the number of anions and cations remain same. Since cations are usually smaller than anions, they occupy interstitial sites. This type of defect occurs in the compounds which have low co-ordination number and cations and anions of different sizes. *e.g., ZnS, AgCl* and *AgI* etc. Frenkel defect are not found in pure alkali metal halides because the cations due to larger size cannot get into the interstitial sites. ***In AgBr both Schottky and Frenkel defects occurs simultaneously.***

Ideal Crystal   Schottky defect   Frenkel defect
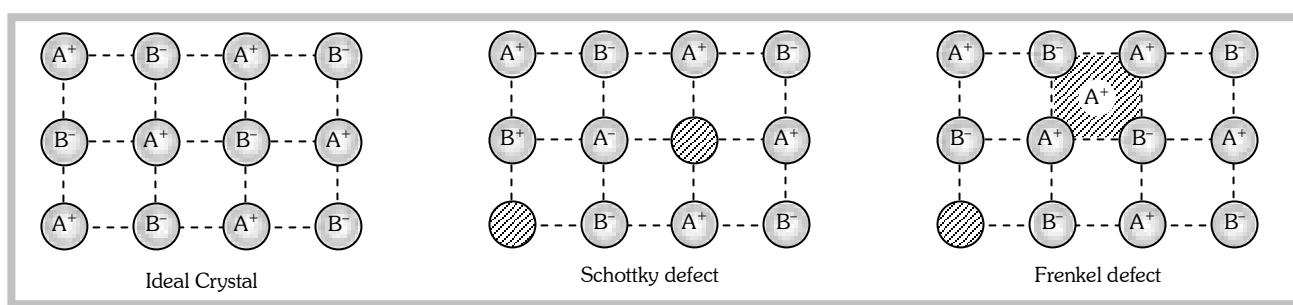
Consequences of Schottky and Frenkel defects : Presence of large number of Schottky defect lowers the density of the crystal. When Frenkel defect alone is present, there is no decrease in density. The closeness of the charge brought about by Frenkel defect tends to increase the dielectric constant of the crystal. Compounds having such defect conduct electricity to a small extent. When electric field is applied, an ion moves from its lattice site to occupy a hole, it creates a new hole. In this way, a hole moves from one end to the other. Thus, it conducts electricity across the crystal. Due to the presence of holes, stability (or the lattice energy) of the crystal decreases.

(ii) **Non-Stoichiometric defects** : The defects which disturb the stoichiometry of the compounds are called non-stoichiometry defects. These defects are either due to the presence of excess metal ions or excess non-metal ions.

(a) **Metal excess defects due to anion vacancies :** A compound may have excess metal anion if a negative ion is absent from its lattice site, leaving a 'hole', which is occupied by electron to maintain electrical neutrality. This type of defects are found in crystals which are likely to possess **Schottky defects**. Anion vacancies in alkali metal halides are reduced by heating the alkali metal halides crystals in an atmosphere of alkali metal vapours. The 'holes' occupy by electrons are called **F-centres** (or colour centres).

(b) **Metal excess defects due to interstitial cations :** Another way in which metal excess defects may occur is, if an extra positive ion is present in an interstitial site. Electrical neutrality is maintained by the presence of an electron in the interstitial site. This type of defects are exhibit by the crystals which are likely to exhibit **Frenkel defects** e.g., when ZnO is heated, it loses oxygen reversibly. The excess is accommodated in interstitial sites, with electrons trapped in the neighborhood. **The yellow colour and the electrical conductivity of the non-stoichiometric ZnO is due to these trapped electrons**.


Metal excess defect due to extra cation   Metal excess defect due to anion vacancy
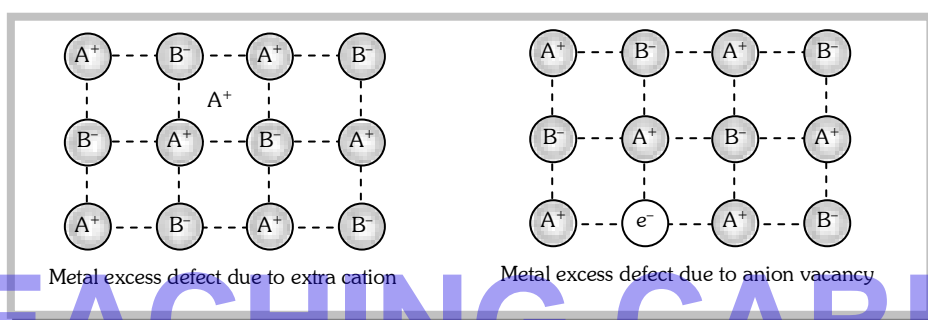
Consequences of Metal excess defects :

- The crystals with metal excess defects are generally coloured due to the presence of free electrons in them.

- The crystals with metal excess defects conduct electricity due to the presence of free electrons and are *semiconductors*. As the electric transport is mainly by "excess" electrons, these are called *n*-type (*n* for negative) semiconductor.

- The crystals with metal excess defects are generally paramagnetic due to the presence of unpaired electrons at lattice sites.

Note : ✸ **Colour Centres :** *Crystals of pure alkali metal halides such as NaCl, KCl, etc. are white. However, alkali metal halides becomes coloured on heating in excess of alkali metal vapour. For example, sodium chloride becomes yellow on heating in presence of sodium vapour. These colours are produced due to the preferential absorption of some component of visible spectrum due to some imperfections called colour centres introduced into the crystal.*

When an alkali metal halide is heated in an atmosphere containing an excess of alkali metal vapour, the excess alkali metal atoms deposit on the crystal surface. Halide ions then diffuse to the surface where they combine with the metal atoms which have becomes ionised by loosing valence electrons. These electrons diffuse back into the crystal and occupy the vacant

Cation vacancy
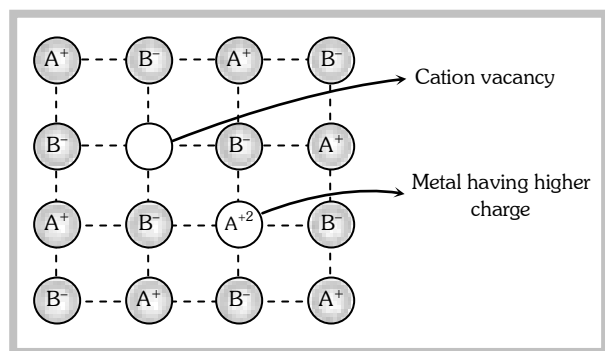
Metal having higher charge

sites created by the halide ions. Each electron is shared by all the alkali metal ions present around it and is thus a delocalized electrons. When the crystal is irradiated with white light, the trapped electron absorbs some component of white light for excitation from ground state to the excited state. This gives rise to colour. Such points are called **F-centres**. (German word Farbe which means colour) such excess ions are accompanied by positive ion vacancies. These vacancies serve to trap holes in the same way as the anion vacancies trapped electrons. The colour centres thus produced are called **V-centres**.

(c) **Metal deficiency defect** : These arise in two ways

● **By cation vacancy** : in this a cation is missing from its lattice site. To maintain electrical neutrality, one of the nearest metal ion acquires two positive charge. This type of defect occurs in compounds where metal can exhibit variable valency. *e.g.,* Transition metal compounds like *NiO*, *FeO*, *FeS* etc.

● **By having extra anion occupying interstitial site** : In this, an extra anion is present in the interstitial position. The extra negative charge is balanced by one extra positive charge on the adjacent metal ion. Since anions are usually larger it could not occupy an interstitial site. Thus, this structure has only a theoretical possibility. No example is known so far.

Consequences of metal deficiency defects : Due to the movement of electron, an ion A^+ changes to A^{+2} ions. Thus, the movement of an electron from A^+ ion is an apparent of positive hole and the substances are called *p*-type semiconductor

● **Impurity defect :** These defects arise when foreign atoms are present at the lattice site (in place of host atoms) or at the vacant interstitial sites. In the former case, we get substitutional solid solutions while in the latter case, we get interstitial solid solution. The formation of the former depends upon the electronic structure of the impurity while that of the later on the size of the impurity.

Important Tips

➤ *Berthallides is a name given to non-stoichiometric compounds.*

➤ *Solids containing F- centres are paramagnetic.*

➤ *When NaCl is dopped with MgCl$_2$ the nature of defect produced is schottky defect.*

➤ *AgBr has both Schottky & Frenkel defect.*

Properties of Solids .

Some of the properties of solids which are useful in electronic and magnetic devices such as, transistor, computers, and telephones etc., are summarised below :

(1) **Electrical properties :** Solids are classified into following classes depending on the extent of conducting nature.

(i) **Conductors :** The solids which allow the electric current to pass through them are called conductors. These are further of two types; Metallic conductors and electrolytic conductors. In the metallic conductors the current is carries by the mobile electrons without any chemical change occurring in the matter. In the electrolytic conductor like *NaCl*, *KCl*, etc., the current is carried only in molten state or in aqueous solution. This is because of

the movement of free ions. The electrical conductivity of these solids is high in the range $10^4 - 10^6 \, ohm^{-1}cm^{-1}$. Their conductance decrease with increase in temperature.

(ii) **Insulators :** The solids which do not allow the current to pass through them are called insulators. *e.g.,* rubber, wood and plastic etc. the electrical conductivity of these solids is very low *i.e.,* $10^{-12} - 10^{-22} \, ohm^{-1}cm^{-1}$.

(iii) **Semiconductors :** The solids whose electrical conductivity lies between those of conductors and insulators are called semiconductors. The conductivity of these solid is due to the presence of impurities. *e.g.* Silicon and Germanium. Their conductance increase with increase in temperature. The electrical conductivity of these solids is increased by adding impurity. This is called **Doping**. When silicon is doped with *P* (or *As*, group 15 elements), we get *n*-type semiconductor. This is because *P* has five valence electrons. It forms 4 covalent bonds with silicon and the fifth electron remains free and is loosely bound. This give rise to *n*-type semiconductor because current is carried by electrons when silicon is doped with *Ga* (or in *In/Al*, group 13 elements) we get *p*-type semiconductors.

🟢 Conductivity of the solids may be due to the movement of electrons, holes or ions.

🟢 Due to presence of vacancies and other defects, solids show slight conductivity which increases with temperature.

🟢 Metals show electronic conductivity.

🟢 The conductivity of semiconductors and insulators is mainly governed by impurities and defects.

🟢 Metal oxides and sulphides have metallic to insulator behavior at different temperatures.

Conductivity		
Insulator like	**Insulator – to –metal**	Metal like
FeO, Fe_2O_3	Ti_2O_3	**TiO**
MnO, MnO_2	V_2O_3	**VO**
Cr_2O_3	VO_2	**CrO$_2$**
CoO		**ReO$_3$**
NiO		
CuO		
V$_2$O$_5$		

(2) **Superconductivity :** When any material loses its resistance for electric current, then it is called superconductor, **Kammerlingh Onnes (1913)** observed this phenomenon at 4K in mercury. The materials offering no resistance to the flow of current at very low temperature (2-5 K) are called **superconducting materials** and phenomenon is called *superconductivity.* e.g., $Nb_3 \, Ge$ alloy (Before 1986), $La_{1.25}Ba_{0.15}CuO_4$ (1986), $YBa_2 \, Cu_3O_7$ (1987) – super conductive at a temperature up to 92 K.

Applications

(a) Electronics,

(b) Building supermagnets,

(c) Aviation transportation,

(d) Power transmission

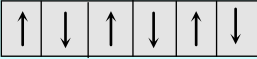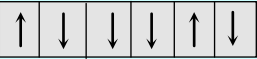*"The temperature at which a material enters the superconducting state is called the superconducting transition temperature, (T_c)".* *Superconductivity was also observed in lead (Pb) at 7.2 K and in tin (Sn) at 3.7K. The* phenomenon of superconductivity has also been observed in other materials such as polymers and organic crystals. Examples are

- $(SN)_x$, polythiazyl, the subscript x indicates a large number of variable size.
- $(TMTSF)_2PF_6$, where *TMTSF* is tetra methyl tetra selena fulvalene.

(3) **Magnetic properties :** Based on the behavior of substances when placed in the magnetic field, there are classified into five classes.

Magnetic properties of solids

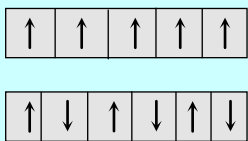| Properties	Description	Alignment of Magnetic Dipoles	Examples	Applications
Diamagnetic	Feebly repelled by the magnetic fields. Non-metallic elements (excepts O_2, S) inert gases and species with paired electrons are diamagnetic	All paired electrons ↑↓ ↑↓ ↑↓	TiO_2, V_2O_5, NaCl, C_6H_6 (benzene)	Insulator
Paramagnetic	Attracted by the magnetic field due to the presence of permanent magnetic dipoles (unpaired electrons). In magnetic field, these tend to orient themselves parallel to the direction of the field and thus, produce magnetism in the substances.	↑↓ ↑ ↑ At least one unpaired electron	$O_2, Cu^{2+}, Fe^{3+}, TiO,$ $Ti_2O_3, VO, VO_2,$ CuO	Electronic appliances
Ferromagnetic	Permanent magnetism even in the absence of magnetic field, Above a temperature called Curie temperature, there is no ferromagnetism.	Dipoles are aligned in the same direction ↑ ↑ ↑ ↑ ↑	Fe, Ni, Co, CrO_2	CrO_2 is used in audio and video tapes
Antiferromagnetic	This arises when the dipole alignment is zero due to equal and opposite alignment.	↑ ↓ ↑ ↓ ↑ ↓	MnO, MnO_2, Mn_2O, FeO, Fe_2O_3; NiO, Cr_2O_3, CoO, Co_3O_4,	–
Ferrimagnetic	This arises when there is net dipole moment	↑ ↓ ↓ ↓ ↑ ↓	Fe_3O_4, ferrites	–

(4) **Dielectric properties :** When a non-conducting material is placed in an electrical field, the electrons and the nuclei in the atom or molecule of that material are pulled in the opposite directions, and negative and positive charges are separated and dipoles are generated, In an electric field :

(i) These dipoles may align themselves in the same direction, so that there is net dipole moment in the crystal.

(ii) These dipoles may align themselves in such a manner that the net dipole moment in the crystal is zero.

Based on these facts, dielectric properties of crystals are summarised in table :

Dielectric properties of solids

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The Solid State

Property	Description	Alignment of electric dipoles	Examples	Applications
Piezoelectricity	When polar crystal is subjected to a mechanical stress, electricity is produced a case of piezoelectricity. Reversely if electric field is applied mechanical stress developed. Piezoelectric crystal acts as a mechanical electrical transducer. • Piezoelectric crystals with permanent dipoles are said to have ferroelectricity • Piezoelectric crystals with zero dipole are said to have antiferroelectricity	– ↑ ↑ ↑ ↑ ↑ ↑ ↓ ↑ ↓ ↑ ↓	Quartz, Rochelle salt $BaTiO_3$, KH_2PO_4, $PbZrO_3$	Record players, capacitors, transistors, computer etc.
Pyroelectricity	Small electric current is produced due to heating of some of polar crystals – a case of pyroelectricity	–		Infrared detectors

Important Tips

➢ **Doping :** *Addition of small amount of foreign impurity in the host crystal is termed as doping. It increases the electrical conductivity.*

➢ *Ferromagnetic property decreases from iron to nickel (Fe > Co > Ni) because of decrease in the number of unpaired electrons.*

➢ *Electrical conductivity of semiconductors and electrolytic conductors increases with increase in temperature, where as electrical conductivity of super conductors and metallic conductors decreases with increase in temperature.*

Silicates.

These are the compounds with basic unit of $(SiO_4)^{4-}$ anion in which each *Si* atom is linked directly to four oxygen atoms tetrahedrally. These tetrahedra link themselves by corners and never by edges. Which are of following types :

(1) **Ortho silicates :** In these discrete SiO_4^{4-} tetrahedra are present and there is no sharing of oxygen atoms between adjacent tetrahedra *e.g.*, Willamette $(Zn_2Si_2O_4)$, Phenacite (Be_2SiO_4), Zircons $(ZrSiO_4)$ and Forestrite (Mg_2SiO_4).

(2) **Pyrosilictes :** In these silicates the two tetrahedral units share one oxygen atom (corner) between them containing basic unit of $(Si_2O_7)^{6-}$ anion *e.g.*, Thortveitite $(Sc_2Si_2O_7)$ and Hemimorphite $Zn_3Si_2O_7Zn(OH)_2H_2O$

(3) **Cyclic or ring silicates :** In these silicates the two tetrahedral unit share two oxygen atoms (two corners) per tetrahedron to form a closed ring containing basic unit of $(SiO_3)_n^{2n-}$ *e.g.*, Beryl $(Be_3Al_2Si_6O_{18})$ and Wollastonite $(Ca_3Si_3O_9)$.

(4) **Chain silicates :** The sharing of two oxygen atoms (two corners) per tetrahedron leads to the formation of a long chain *e.g.*, pyroxenes and Asbestos $CaMg_3O(Si_4O_{11})$ and Spodumene $LiAl(Si_2O_6)$.

(5) **Sheet silicates :** In these silicates sharing of three oxygen atoms (three corners) by each tetrahedron unit results in an infinite two dimensional sheet of primary unit $(Si_2O_5)_n^{2n-}$. The sheets are held together by electrostatic force of the cations that lie between them *e.g.*, $[Mg_3(OH)_2(Si_4O_{10})]$ and Kaolin, $Al_2(OH)_4(Si_2O_5)$.

(6) **Three dimensional or frame work silicates :** In these silicates all the four oxygen atoms (four corners) of $(SiO_4)^{4-}$ tetrahedra are shared with other tetrahedra, resulting in a three dimensinal network with the general formula $(SiO_2)_n$ *e.g.*, Zeolites, Quartz.

Important Tips

➤ **Beckmann thermometer :** *Cannot be used to measure temperature. It is used only for the measurement of small differences in temperatures. It can and correctly upto 0.01°*

➤ **Anisotropic behaviour of graphite :** *The thermal and electrical conductivities of graphite along the two perpendicular axis in the plane containing the hexagonal rings is 100 times more than at right angle to this plane.*

➤ **Effect of pressure on melting point of ice :** *At high pressure, several modifications of ice are formed. Ordinary ice is ice –I. The stable high pressure modifications of ice are designated as ice –II, ice – III, ice- V, ice – VI and ice – VII. When ice –I is compressed, its melting point decreases, reaching $-22^o C$ at a pressure of about 2240 atm. A further increase in pressure transforms ice – I into ice – IIIs whose melting point increases with pressure. Ice- VII, the extreme high-pressure modification, melts to form water at about 100°C and 20,000 atm pressure. The existence of ice-IV has not been confirmed.*

➤ **Isotropic** *: The substances which show same properties in all directions.*

➤ **Anisotropic** *: Magnitude of some of the physical properties such as refractive index, coefficient of thermal expansion, electrical and thermal conductivities etc. is different in different directions, with in the crystal*