The solids are the substances which have definite volume and definite shape. In terms of kinetic molecular model, solids have regular order of their constituent particles (atoms, molecules or ions). These particles are held together by fairly strong forces, therefore, they are present at fixed positions. The properties of the solids not only depend upon the nature of the constituents but also on their arrangements.

Types and Classification of solids

(1) Types of solids

Solids can be broadly classified into following two types,

(i) Crystalline solids/True solids,

(ii) Amorphous solids/Pseudo solids

Crystalline solids	Amorphous solids
They have long range order.	*They have short range order.*
They have definite melting point	Not have definite melting point
They have a definite heat of fusion	Not have definite heat of fusion
They are rigid and incompressible	Not be compressed to any appreciable extent
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
They are anisotropic because of these substances show different property in different direction	*They are isotropic because of these substances show same property in all directions*
There is a sudden change in volume when it melts.	There is no sudden change in volume on melting.
These possess symmetry	Not possess any symmetry.
These possess interfacial angles.	Not possess interfacial angles.

(2) Crystalline and amorphous silica (SiO_2)

Silica occurs in crystalline as well as amorphous states. Quartz is a typical example of crystalline silica. Quartz and the amorphous silica differ considerably in their properties.

Quartz	Amorphous silica
It is crystalline in nature	It is light (fluffy) white powder
All four corners of SiO_4^{4-} tetrahedron are shared by others to give a network solid	The SiO_4^{4-} tetrahedra are randomly joined, giving rise to polymeric chains, sheets or three-dimensional units
It has high and sharp melting point $(1710°C)$	It does not have sharp melting point

(3) Diamond and graphite

Diamond and graphite are tow allotropes of carbon. Diamond and graphite both are covalent crystals. But, they differ considerably in their properties.

Diamond	Graphite
It occurs naturally in free state	It occurs naturally, as well as manufactured artificially
It is the hardest natural substance known.	It is soft and greasy to touch
It has high relative density (about 3.5)	Its relative density is 2.3
It is transparent and has high refractive index (2.45)	It has black in colour and opaque
It is non-conductor of heat and electricity.	Graphite is a good conductor of heat and electricity
It burns in air at $900°C$ to give CO_2	It burns in air at $700°C$ to give CO_2
It occurs as octahedral crystals	It occurs as hexagonal crystals

(4) Classification of crystalline solids

Table : 5.1 Some characteristics of different types of crystalline solids

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, BaSO₄ and K₂SO₄ etc.	Hard but brittle	High ($\simeq 1000\,K$)	High ($\simeq 2000\,K$)	Conductor (in molten state and in aqueous solution)
Covalent	Atoms connected in covalent bonds	Electron sharing	SiO₂ (Quartz), SiC, C (diamond), C(graphite) etc.	Hard Hard Hard	Very high ($\simeq 4000\,K$)	Very high ($\simeq 5000\,K$)	Insulator except graphite
Molecular	Polar or non-polar molecules	(i) Molecular interactions (intermolecular forces) (ii) Hydrogen bonding	I₂, S, P, CO, CH₄, CCl₄ etc. Starch, sucrose, water, dry ice or drycold (solid CO₂) etc.	Soft Soft	Low ($\simeq 300\,K$ to 600K) Low ($\simeq 400\,K$)	Low ($\simeq$ 450 to 800 K) Low ($\simeq 373\,K$ to 500K)	Insulator Insulator
Metallic	Cations in a sea of electrons	Metallic	Sodium , Au, Cu, magnesium, metals and alloys	Ductile malleable	High ($\simeq 800\,K$ to 1000 K)	High ($\simeq 1500\,K$ to 2000K)	Conductor
Atomic	Atoms	London dispersion force	Noble gases	Soft	Very low	Very low	Poor thermal and electrical conductors

Crystallography

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

(1) **Symmetry in Crystal :** 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.
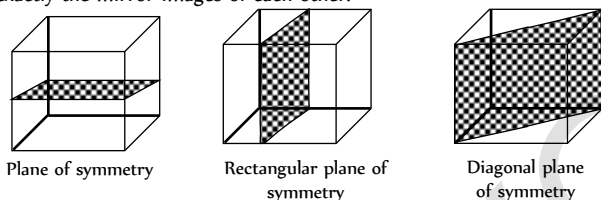

| Plane of symmetry | Rectangular plane of symmetry | Diagonal plane of symmetry |

Fig. 5.1

(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.
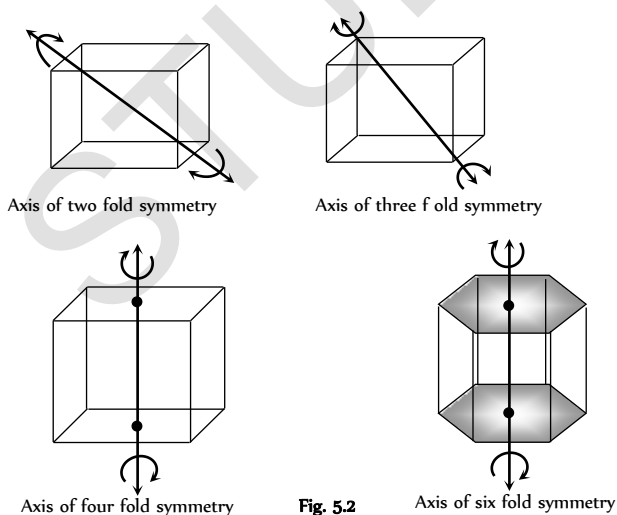

Axis of two fold symmetry   Axis of three f old symmetry

Axis of four fold symmetry   **Fig. 5.2**   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.
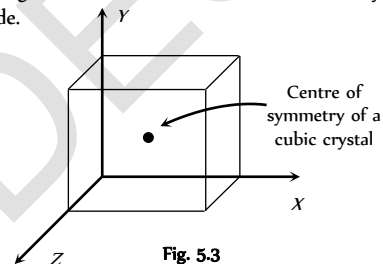

Centre of symmetry of a cubic crystal

Fig. 5.3

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

The total number of planes, axes and centre of symmetries possessed by a crystal is termed as **elements of symmetry**.

A cubic crystal possesses total 23 elements of symmetry.

Plane of symmetry	(3 + 6)	= 9
Axes of symmetry	(3 + 4 + 6)	= 13
Centre of symmetry	(1)	= 1
	Total symmetry	= 23

(2) **Laws of crystallography :** Crystallography is based on three fundamental laws.

(i) *Law of constancy of interfacial angles* : This law states that angle between adjacent corresponding faces is inter facial angles of the crystal of a particular substance is always constant inspite of different shapes and sizes and mode of growth of crystal. The size and shape of crystal depend upon the conditions of crystallisation. This law is also known as **Steno's Law**.
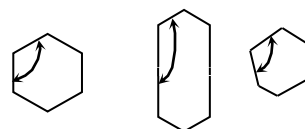

Fig. 5.4. Constancy of interfacial angles

(ii) *Law of rational indices* : This law states that the ratio of intercepts of different faces of a crystal with the three axes are constant and can be expressed by rational numbers 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 **Hauy**.

(iii) Law of constancy of symmetry : According to this law, all crystals of a substance have the same elements of symmetry is plane of symmetry, axis of symmetry and centre of symmetry.

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 :

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

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

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

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.

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.

Space lattice and Unit cell

Crystal 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.

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

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

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   **Fig. 5.5**   Space lattice & unit cell

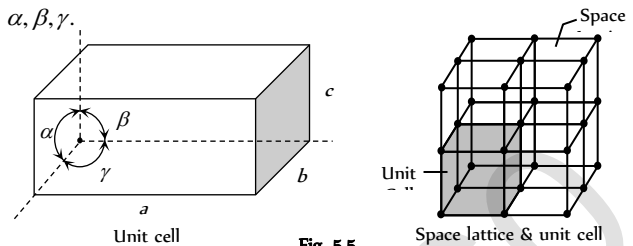### Types of units cells

A units cell is obtained by joining the lattice points. The choice of lattice points to draw a unit cell is made on the basis of the external geometry of the crystal, and symmetry of the lattice. There are four different types of unit cells. These are,

(1) **Primitive or simple cubic** (sc) : Atoms are arranged only at the corners of the unit cell.
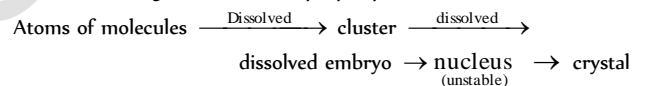
(2) **Body centred cubic** (bcc) : Atoms are arranged at the corners and at the centre of the unit cell.

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

(4) **Side centered :** Atoms are arranged at the centre of only one set of faces in addition to the atoms at the corner of the unit cell.

Formation of crystal and Crystal systems

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.
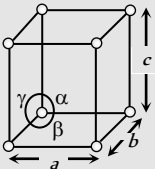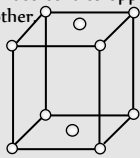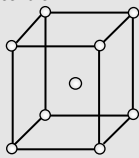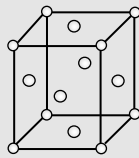
Atoms of molecules $\xrightarrow{\text{Dissolved}}$ cluster $\xrightarrow{\text{dissolved}}$

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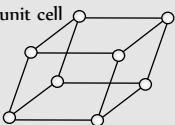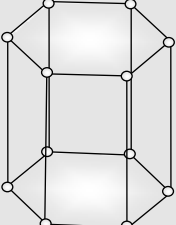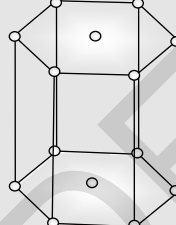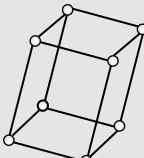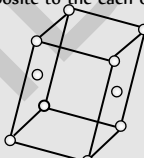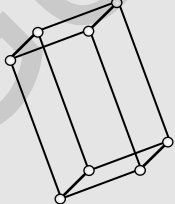
(If loosing units dissolves as embryo and if gaining unit grow as a crystals).

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.

Table : 5.2 Bravais lattices corresponding to different crystal systems

Crystal system	Space lattice			Examples
Cubic $a = b = c$, $\alpha = \beta = \gamma = 90^o$	**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, $KCl, CsCl,$ $NaCl, Cu_2O, CaF_2$ 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 (Rhombic) $a \neq b \neq c$, $\alpha = \beta = \gamma = 90^o$	**Simple:** Points at the eight corners of the unit cell. 	**End centered :** Also called side centered or base centered. Points at the eight corners and at two face centres opposite to each other. 	**Body centered :** Points at the eight corners and at the body centre 	**Face centered:** Points at the eight corners and at the six face centres. 	KNO_3, K_2SO_4, $PbCO_3$, $BaSO_4$, rhombic sulphur, $MgSO_4 . 7H_2O$ etc.
Rhombohedral or **Trigonal** $a = b = c$, $\alpha = \beta = \gamma \neq 90°$	**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.

Analysis of cubic system

(1) Number of atoms in per unit cell

The total number of atoms contained in the unit cell for a simple cubic called the unit cell content.

The simplest relation can determine for it is, $\dfrac{n_c}{8} + \dfrac{n_f}{2} + \dfrac{n_i}{1}$

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

(2) 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.

For simple cubic system C.N. = 6.

For body centred cubic system C.N. = 8

For face centred cubic system C.N. = 12.

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

$$\rho = \frac{Z \times M}{a^3 \times N_0}$$

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

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

(4) **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) $v = \dfrac{4}{3}\pi r^3$

Packing density $= \dfrac{vZ}{V} = \dfrac{\dfrac{4}{3}\pi r^3 \, Z}{a^3}$

Structure	r related to a	Volume of the atom (v)	Packing density	% of void
Simple cubic	$r = \dfrac{a}{2}$	$\dfrac{4}{3}\pi\left(\dfrac{a}{2}\right)^3$	$\dfrac{\pi}{6} = 0.52$	100−52 = 48%
Face-centred cubic	$r = \dfrac{a}{2\sqrt{2}}$	$\dfrac{4}{3}\pi\left(\dfrac{a}{2\sqrt{2}}\right)^3$	$\dfrac{\sqrt{2}\pi}{6} = 0.74$	100 − 74 = 26%
Body-centred cubic	$r = \dfrac{\sqrt{3}a}{4}$	$\dfrac{4}{3}\pi\left(\dfrac{\sqrt{3}a}{4}\right)^3$	$\dfrac{\sqrt{3}\pi}{8} = 0.68$	100 − 68 = 32%

X-ray study of crystal structure

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.**

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

where, λ = Wave length of X-rays, n = order of reflection, θ = Angle of reflection, d = 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.

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

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

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

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

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.

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

(i) *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. In this arrangement each sphere is in contact with four spheres.
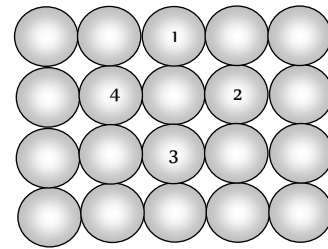

Fig. 5.6. Square close packing

(ii) *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. In this arrangement each sphere is in contact with six other spheres.
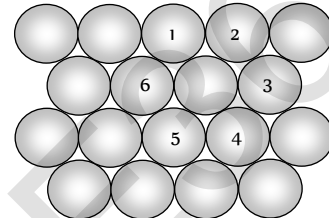

Fig. 5.7. Hexagonal close packing

(2) **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 of 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.
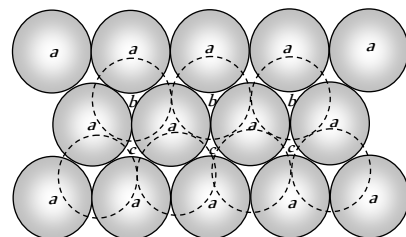

Fig. 5.8. Close packing in three dimensions

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

(i) *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. This arrangement is found in *Be, Mg, Zn, Cd, Sc, Y, Ti, Zr, Tc, Ru.*
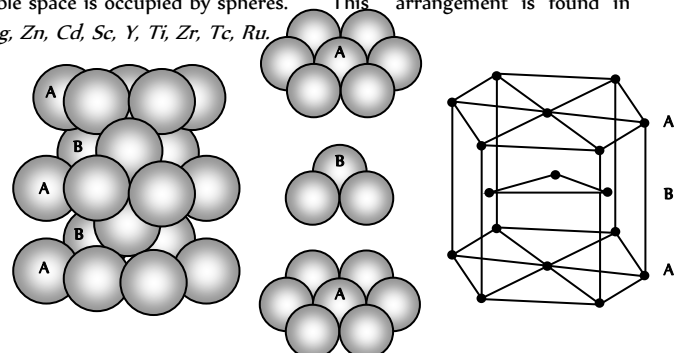

Fig. 5.9. Hexagonal close packing (*hcp*) in three dimensions

(ii) *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. This arrangement is found in *Cu, Ag, Au, Ni, Pt, Pd, Co, Rh, Ca, Sr.*
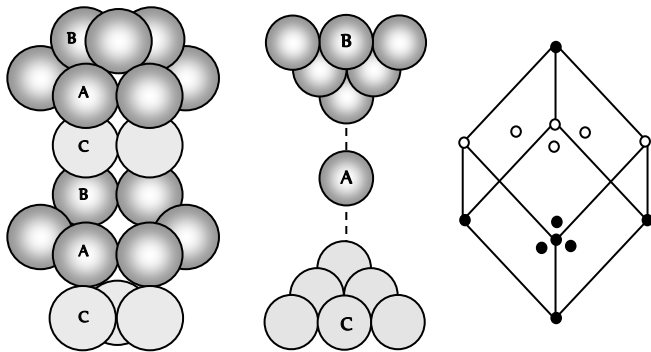

Fig. 5.10. Cubic close packing (*ccp* or *fcc*) in three dimensions

(iii) **Body centred cubic :** 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.*
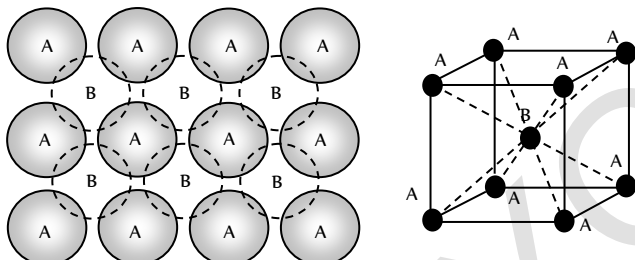

Fig. 5.11. Body centred cubic (*bcc*) close packing in three dimensions

Table : 5.3 Comparison of *hcp*, *ccp* and *bcc*

Property	*hcp*	*ccp*	*bcc*
Arrangement of packing	Close packed	Close packed	Not close packed
Type of packing	AB AB A...	ABC ABC A...	AB AB A...
Available space occupied	74%	74%	68%
Coordination number	12	12	8
Malleability and ductility	Less malleable, hard, brittle	Malleable and ductile	

Interstitial sites in close packing

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,

(1) **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,

$$r = 0.155R$$

r = Radius of the spherical trigonal void

R = Radius of closely packed spheres
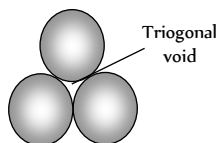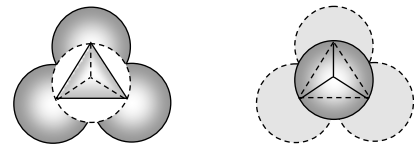

Triogonal void

Fig. 5.12

(2) **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.

The number of tetrahedral voids is double the number of spheres in the crystal structure.

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

where, r is the radius of the tetrahedral void or atom occupying tetrahedral void.

R is the radius of spheres forming tetrahedral void.

(3) **Octahedral void :** This type of void is surrounded by six closely packed spheres, *i.e.* it is formed by six spheres.

The number of octahedral voids is equal to the number of spheres.

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

Fig. 5.14. Octahedral void

(4) **Cubic void :** This type of void is formed between 8 closely packed spheres which occupy all the eight corner of cube.
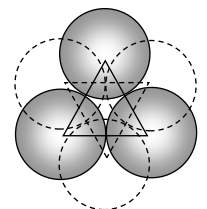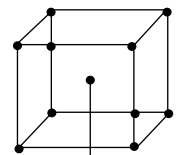
$$\frac{r}{R} = 0.732$$

Fig. 5.15. Cubic void

The decreasing order of the size of the various voids is,

Cubic > Octahedral > Tetrahedral > Trigonal

Ionic radii and Radius ratio

(1) **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, $r_c + r_a = a/2$

where r_c and r_a are radius of cation and anion.

Radius of Cl^-

$$= \sqrt{\frac{(a/2)^2 + (a/2)^2}{2}} = \frac{a}{4}$$

For bcc lattice say $CsCl$.

$$r_c + r_a = \frac{\sqrt{3}a}{2}$$

Fig. 5.16. Radii of chloride ion

(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 (AB). Since, the Coulombic forces are non-directional, hence the structures of such crystals
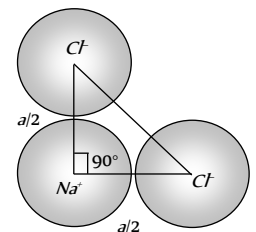
are mainly governed by the ratio of the radius of cation (r_+) to that of anion (r_-). The ratio r_+ to r_- (r_+ / r_-) is called as radius ratio.
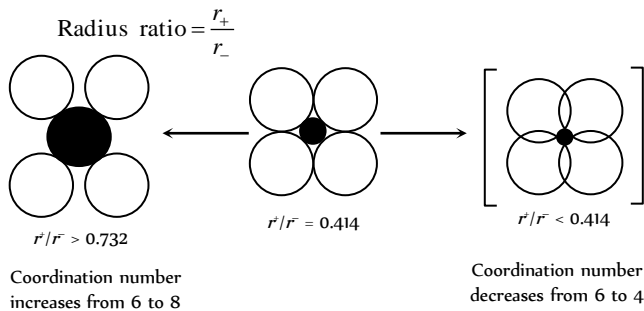
$$\text{Radius ratio} = \frac{r_+}{r_-}$$

$r^+/r^- > 0.732$	$r^+/r^- = 0.414$	$r^+/r^- < 0.414$
Coordination number increases from 6 to 8		Coordination number decreases from 6 to 4

Fig. 5.17. Effect of radius ratio on co-ordination number

Table : 5.4 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

Effect of temperature and Pressure on C.N.

On applying high pressure $NaCl$ structure having $6:6$ co-ordination changes to $CsCl$ structure having $8:8$ co-ordination. Thus, increase in pressure increases the co-ordination number.

Similarly, $CsCl$ structure on heating to about $760\ K$, changes to $NaCl$ structure. In other words, increase of temperature decreases the co-ordination number.

$$\underset{(6\,:\,6)}{NaCl} \underset{\text{Temp}}{\overset{\text{Pressure}}{\rightleftharpoons}} \underset{(8\,:\,8)}{CsCl}$$

Structure of ionic crystals

Table : 5.5 Types of ionic crystal with description

Crystal structure type	Brief description	Examples	Co-ordination number	Number of formula units per unit cell
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,Cl, NH,Br, NH,I* etc.	$Na^+ = 6$ $Cl^- = 6$	4
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
Type AB, Fluorite (CaF) type	It has arrangement in which Ca^{2+} ions form *fcc* with each Ca^{2+} ions surrounded by $8\,F^-$ ions and each F^- ions by $4\,Ca$ ions.	$BaF_2, BaCl_2, SrF_2$ $SrCl_2, CdF_2, PbF_2$	$Ca^{2+} = 8$ $F^- = 4$	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
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

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.
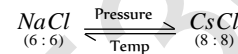
(1) **Electronic imperfections :** Generally, electrons are present in fully occupied lowest energy states. But at high temperatures, some of the electrons may occupy higher energy state depending upon the temperature. For example, in the crystals of pure *Si* or *Ge* some electrons are released thermally 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.

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

(b) **Schottky defect** : 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.

(c) **Frenkel defect** : 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 occur simultaneously.*

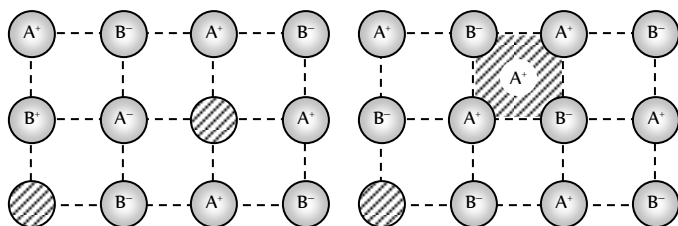Fig. 5.18. Schottky defect   Fig. 5.19. Frenkel defect

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 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 deficiency of 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.**
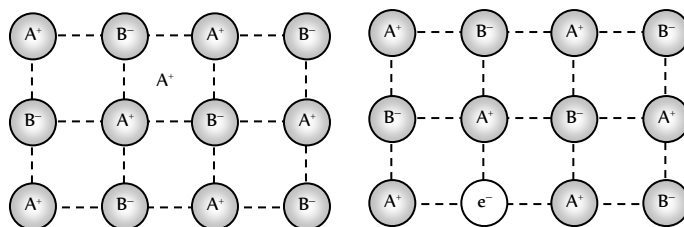
Fig. 5.20. Metal excess defect   Fig. 5.21. Metal excess defect
due to extra cation   due to anion vacancy

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.

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 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.

(d) *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.
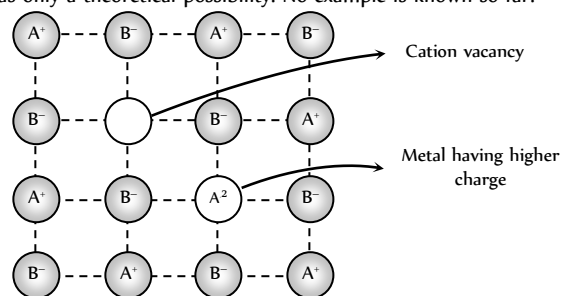
Fig. 5.22
Consequences of metal deficiency defects

Due to the movement of electron, an ion A changes to A⁻ ions. Thus, the movement of an electron from A ion is an apparent of positive hole and the substances are called *p*-type semiconductor

(iii) *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.

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. 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 5ᵗ 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 3ᵗ elements) we get *p*-type semiconductors.

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 (2-5K) are called **superconducting materials** and phenomenon is called *superconductivity.*

Examples, $Nb_3 Ge$ alloy (Before 1986)

$$La_{1.25} Ba_{0.15} CuO_4 \ (1986)$$

$$YBa_2 Cu_3 O_7 \ (1987)$$
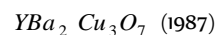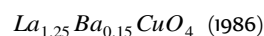
Following are the important applications of superconductivity,

(a) Electronics,   (b) Building supermagnets,

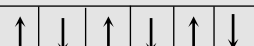(c) Aviation transportation,   (d) Power transmission

"*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 in other materials such as polymers and organic crystals. Examples are

(SN), polythiazyl, the subscript x indicates a large number of variable size.

$(TMTSF)$, PF, where *TMTSF* is tetra methyl tetra selena fulvalene.

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

Table : 5.6 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	–

(3) Dielectric properties : A dielectric substance is that which does not allow the electricity to pass through them but on applying the electric field, induced charges are produced on its faces. In an insulator, the electrons are strongly held by the individual atoms. When an electric field is applied polarization takes place because nuclei are attracted to one side and the electron cloud to the other side. As a result, dipoles are created. Such type of crystals shows the following properties,

(i) Piezoelectricity : In some of the crystals, the dipoles may align themselves is an ordered way so as to give some net dipole moment. When mechanical stress is applied in such crystals so as to deform them, electricity is produced due to the displacement of ions. The electricity thus produced is called piezoelectricity and the crystals are called piezoelectric

crystals. Examples, Quartz, Rochelle's salt (sod. pot. tartarate). Piezoelectric crystals act as mechanical-electric transducer. These crystals are used as pick-ups in record players where they produce electric signals by application of pressure.

(ii) Pyroelectricity : On heating, some polar crystals produce a small electric current. The electricity thus produced is called pyroelectircity.

(iii) Ferroelectricity : In some of the piezoelectric crystals, a permanent alignment of the dipoles is always there even in the absence of the electric field, however, on applying field the direction of polarization changes. This phenomenon is called ferroelectricity and the crystals as

ferroelectric crystal. Example, Potassium hydrogen phosphate (KH_2PO_4), Barium titanate $(BaTiO_3)$.

(iv) *Antiferroelectricity* **:** In some crystals, the dipoles in alternate polyhedra point up and down so that the crystals does not possess any net dipole moment. Such crystals are said to be antiferroelectric. Example, Lead zirconate $(PbZrO_3)$. Ferroelectrics are used in the preparation of small sized capacitors of high capacitance. Pyroelectric infrared detectors are based on such substances. These can be used in transistors, telephone, computer etc.

T Tips & Tricks

- ✍ The reverse of crystallization is the melting of the solid.

- ✍ The slower the rate of formation of crystal, the bigger is the crystal.

- ✍ The hardness of metals increases with the number of electrons available for metallic bonding. Thus *Mg* is harder than sodium.

- ✍ Isomorphism is applied to those substances which are not only similar in their crystalline form, but also possess an equal number of atoms united in the similar manner. The existence of a substance in more than one crystalline form is known as polymorphism.