# Solid State

1

SOLIDS

Solids are characterised by the state of matter in which particles are closely packed and held together by strong inter molecular attractive force.

Properties of solids

(a) In solid state the particles are not able to move randomly.

(b) They have definite shape and volume.

(c) Solids have high density.   .

(d) Solids have high and sharp melting point which is depend on the strength or value of binding energy.

(f) They are very low compressible.

(g) They show very slow diffusion.

Types of Solids

Solids

Crystalline Solids   Amorphous Solids
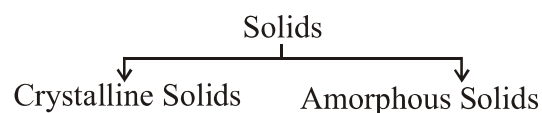
(I) Crystalline solids

(a) In this type of solids the atoms or molecule are arranged in a regular pattern in the three dimensional network.

(b) They have well defined geometrical pattern, sharp melting point, definite heat of fusion and anisotropic nature.

(c) Anisotropic means they exhibit different physical properties in all directions.

eg. The electrical and thermal conductivities are different in different directions.

(d) They are generally incompressible.   .

(e) The general examples of crystalline solids are as Quartz, diamond etc.

(II) Amorphous Solids

(a) In this type of solids, the arrangement of-building constituents is not regular.

(b) They are regarded as super cooled liquids with high viscosity in which the force of attraction holding the molecules together are so great, that the material becomes rigid but there is no regularity in structure.

(c) They do not have sharp melting points.

(d) They are isotropic as they exhibit same physical properties in all the directions.

(e) The general examples of this solids are as glass, Rubber, plastics etc.

<div align="center">**Difference between crystalline and amorphous solids**</div>

S.No	Property	Crystalline solids	Amorphus solids
1	Shape	They have definite and regular geo-metrical form.	They do not have definite and regular geometrical form.
2	Melting point	They have definite melting point.	They do not have definite melting point.
3	Heat of fusion	They have a definite heat of fusion.	They do not have definite heat of fusion
4	Compressibility	They are rigid and incompressible.	These may be compressed to any appreciable extent.
5	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.
6	Isotropy and Anisotropy	They are anisotropic.	They are isotropic.
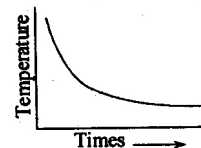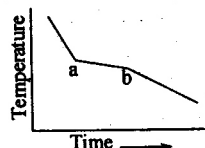
STUDY OF CYRSTALS

Crystal - A crystal is a homogenous portion of a solid substance made by regular pattern of structural units bonded by plane surface making definite angles with each other.

Space lattice: - The arrangement of constituents like atom, ions and molecules in different sites in three dimensional space is called space lattice.

Unit cell : - The smallest repeating unit in space lattice which when repeats over and over again, results in a crystal of the given substance called unit cell.

Face:- The plane surface of the crystal are called faces.

Edge:- An edge is formed by the intersection of two adjacent faces.

Interfacial angles:- The angle between the perpendiculars two intersecting faces called interfacial angles.
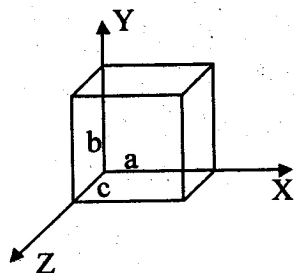
LAWS OF CRYSTALLOGRAPHY

The law of constancy of interfacial angle

(a) The interfacial angles for a given crystalline substance are always the same for all crystal structures of a space lattice. This is known as law of constancy of interfacial angles.

(b) The crystal of a substance can have different shapes depending upon the number and size of the faces but the angle at which the two adjacent faces intersect remains always constant.

(I)   **(II)**

(III)
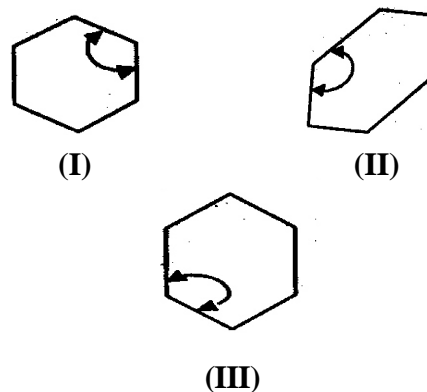
Law of Rationality of indices

(a) According to this law the ratio between the intercepts on the axis for the different faces of a crystal can always be expressed by rational numbers. Means the intercepts of any face of plane of a crystal on suitable crystallographic axes can be expressed by small multiples of three unit distances a, b, c or some sine integral multiple of these unit distance i.e. ma : nb : pc.

(b) a, b, c called weiss indices.

(c) This law was given by Hally.

Miller indices
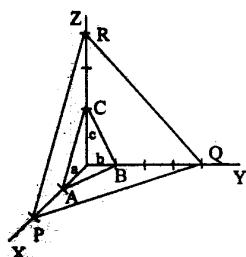
(a) It is a face of a crystal, which are inversely proportional to the intercepts of its face on the various axes.

(b) Miller indices is a reciprocal of weiss indices i.e. miller indices for a plane may be obtained from weiss indices.

(c) The distance between the parallel planes in a crystal are disignated as d_{hkl} for different cubic lattices these interplaner spacings are given by the following general formula as -

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + \ell^2}}$$

where, a = length of the cube side & h,k,l

= Miller indices of the plane

Law of constancy of Symmetry

(a) According to this law, all crystals of a substance have the same elements of symmetry.

(b) A crystal possess following three types of symmetry.

Plane of symmetry

It is an imaginary plane which passes through the centre of a crystal can divide it into two equal portions which are exactly the mirror images to each other.
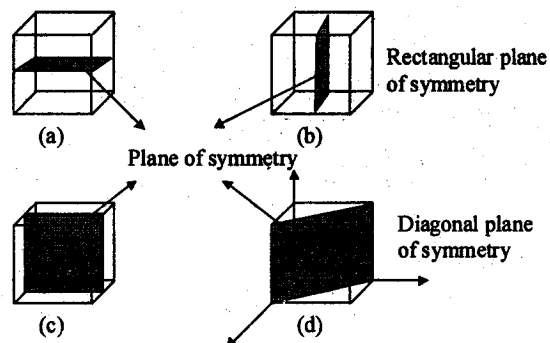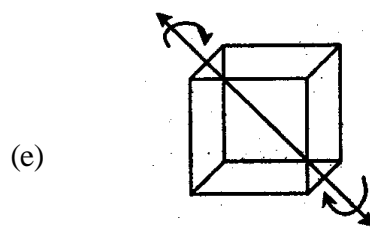

Axis of symmetry

(a) It is an imaginary line about which the crystal may be rotated so that it presents the same appearance more than once in a complete rotation through 360º.
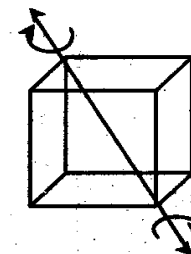
(b) The axes of symmetry are called diad, triad, tetrad and hexad respectively. It is the original appearance and is repeated twice (180º), thrice (120º), four times (90º) and six times (60º) in one rotation.

(c) These axes of symmetry are also called as two fold, three fold, four fold and six fold respectively.
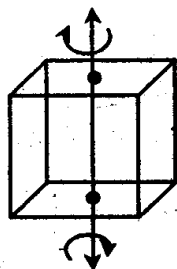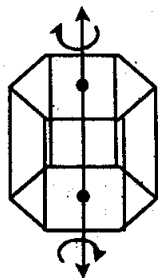
(d) Five fold symmetry is not found in crystals.

(e)

(i) Axis of two fold symmetry

(ii) Axis of three fold symmetry

(iii) Axis of four fold symmetry

(iv) Axis of six fold symmetry

Centre of symmetry

(a) It is a 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.

ELEMENTS OF SYMMETRY

(a) The total number of planes, axes and centre of symmetries possessed by a crystal is termed as elements of symmtery.

(b) A cubic crystal possesses total 23 elements of symmetry

(i) Plane of symmetry	(3 + 6)	=	9
(ii) Axes of symmetry	(3 + 4 + 6)	=	13
(iii) Centre of symmetry	[1]	=	1
	Total symmetry	=	23

CRYSTAL SYSTEM

(a) On the basis of gemoetrical consideration theoritically there can be 32 different combinations of elements of symmetry of crystal.
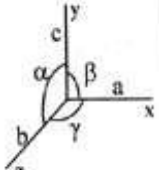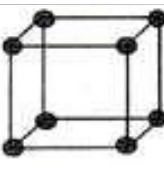
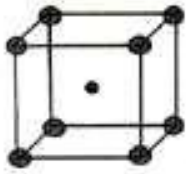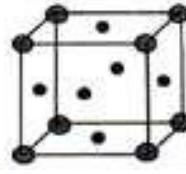(b) But on the other hand Bravais showed that there are only seven types of crystal system.
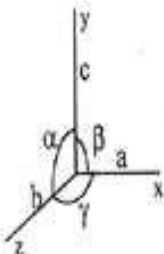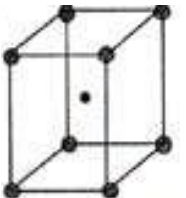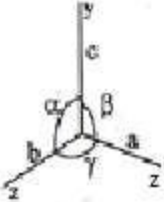
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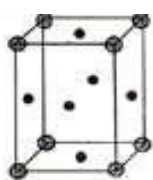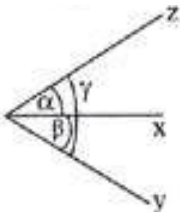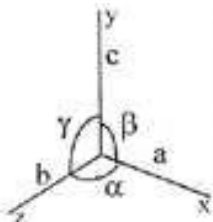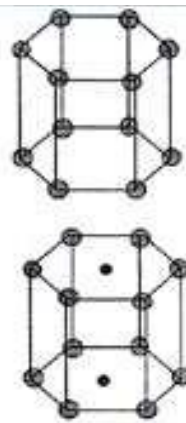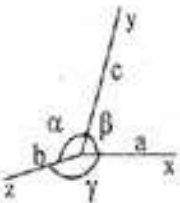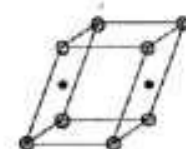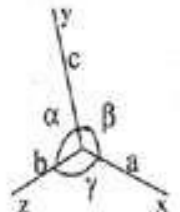
(a) Cubic (b) Tetragonal (c) Orthorhombic

(d) Rhombohedral (e) Hexagonal (f) Monoclinic

(g) Triclinic

(c) There are 14 Bravais lattices under seven crystal systems as follows :

The Bravals Lattices

S. No.	Crystal system	Axial distance	Axial angles	Space lattice		Unit cell
1.	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	a	Simple :- Lattice points at the eight corners of the unit cells.	

				b. Body centered :- Points at the eight corners and at the body centered.	
				c. Face centered :- Points at the eight corners and at the six face centeres.	
2.	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	d. Simple :- Points at the eight corners of the unit cell.	
				e. Body centered :- Points at the eight corners and at the body centre.	
3.	Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	f. Simple :- Points at the eight corners of the unit cell.	
				g. End centered :- Also called side centered or base centered. Points at the eight corners and tow face centeres opposite to each other.	
				h. Body centered :- Points at the eight corners and at the body centre.	

				i	Face centered :- Points at the eight corners and at the six face centres.
4.	Rhombohedral or Trigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	j.	Simple :- Points at the eight corners of the unit cell.
5.	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°$ $\gamma = 120°$	k. i. ii.	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.
6.	Monoclinic	$a \neq b \neq c$	$\alpha = \beta = 90° \neq \gamma$	l. m.	Simple :- Points at the eight corners of the unit cell. End centered :- Points at the eight corners and at two face centres oppisite to the each other.
7.	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \; 90°$	n.	Simple :- Points at the eight corners of the unit cell.

S.No.	Crystal system	Space lattice	Examples
1.	Cubic	Simple	Pb, Hg, Ag, Au, Cu, Diamond, NaCl, KCl, ZnS, Cu_2, O, CaF_2, and Alums.
2.	Tetragonal	Simple	SnO_2, ZnO_2, TiO_2, $NiSO_4$, $ZrSio_4$, $PbWO_4$, White Sn.
3.	Orthorhombic	Simple	KNO_3, K_2SO_4, $PbCO_3$, $BaSO_4$, Rhombic sulphur, $MgSO_4$, $7H_2O$.
4.	Rhombohedral	Simple	$NaNO_3$, $CaSO_4$, Calcite, ICl, Quartz, As, Sb, Bi.
5.	Hexogonal	Simple	ZnO, PbI_2, CdS, HgS, Graphite, Ice, Beryl, Mg, Zn, Cd.
6.	Monoclinic	Simple	$Na_2\ SO_4$, $10\ H_2O$, $Na_2\ B_4O_7$, $10\ H_2O$, $CaSO_4$, $2H_2O$, Monoclinic sulphur
7.	Triclinic	Simple	$CaSO_4$, $5H_2O$, $K_2Cr_2O_7$, H_3BO_3.

MATHEMATICAL ANALYSIS OF CUBIC SYSTEM (TYPES AND ANALYSIS)

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

(a) Simple Cubic (SC) : Atoms are arranged at the corners of the cube.

(b) Body centered cubic (BCC) : Atoms are arranged at the corners and at the centre of the cube.

(c) Face Centred Cubic (FCC) : Atoms are arranged at the corners and at centred of the each faces.

Atomic radius

It is difined 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.

(a) Simple cubic structure (S.C.

Radius of atom 'r' = $\dfrac{a}{2}$
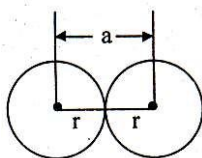
(b) Face centred cubic structure (FCC) 'r' = $\dfrac{a}{2\sqrt{2}}$

(c) Body centred cubic structure (BCC) 'r' $\dfrac{\sqrt{3}a}{4}$

$a = b = c$

$\alpha = \beta = \gamma = 90°$
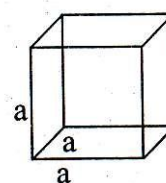
Number of atoms per unit cell I unit cell contents

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

(a) Simple cubic structure (sc)

∴ Each corner atom is shared by eight surrounding cubes. Therefore, it contributes for $\dfrac{1}{8}$ of an atom.

∴ z = 8 x $\dfrac{1}{8}$ = 1
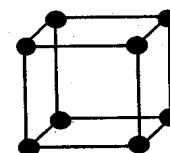
(b) Face centered cubic structure (fcc)

(i) The eight corners atoms contribute for $\frac{1}{8}$ of an atom and thus one atom per unit cell.

(ii) Each of six face centred atoms is shared by two adjacent unit cells and therefore one face centred atom contribute half of its share. Means.

$6 \times \frac{1}{2} = 3$ atom per unit cell.
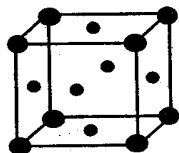
(iii) So, total $Z = 3 + 1 = 4$ atoms per unit cell.

(c) Body centred cubic structure (bcc)

(i) Eight corner atoms contribute one atom per unit cell.

(ii) Centre atom contribute one atom per unit cell.

(iii) So total $1 + 1 = 2$ atoms per unit cell.

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

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
1.	Simple cubic	8	0	0	1
2.	Body centered cubic	8	0	1	2
3.	Face centered cubic	8	6	0	4

Co-ordination number (C.N.)

(a) 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.

(b) It depends upon structure of the crystal.

(c) For simple cubic system CN = 6.

(d) For bcc CN = 8.

(e) For fcc CN = 12.

Density of lattice matter

(a) It is defined as the ratio of mass per'unit cell to the total volume of unit cell.

(b) Density of lattice matter $= \dfrac{\text{mass per unit cell}}{\text{volume of unit cell}}$

$= \dfrac{Z \times \text{At. wt.}}{N \times \text{volume of unit cell}}$

Where Z is the number of atoms per unit cell and N is the **Avogadro number.**

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.

(a) Simple cubic unit cell

Let the radius of atom in packing = 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 $r = \dfrac{a}{2}$
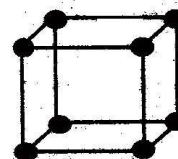
therefore, P.F. $= \dfrac{\frac{4}{3}\pi r^3}{(2r)^3} = 0.52$ % P.F. = 52%

% of void $= 100 - 52 = 48\%$

(b) Body centred cubic unit cell

Number of atoms per unit

cell $= 8 \times \frac{1}{8} + 1 = 2$
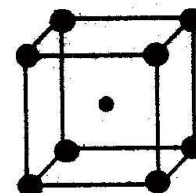
$r = \dfrac{\sqrt{3}a}{4}$ P.F. $= \dfrac{2 \times \frac{4}{3}\pi r^3}{\left(\frac{4r}{\sqrt{3}}\right)^3} = 0.68$

% P.F. = 68%

% of void $= 100 - 68 = 32\%$

(c) Face centered cubic unit cell

Number of atoms per unit cell = 4

$$r = \frac{\sqrt{2}a}{4}$$

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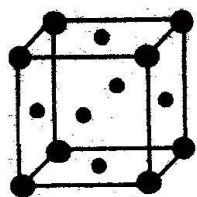
%P.F. = 74%   % of void = 100 – 74 = 26%

IONIC RADII

X-ray diffraction or electron diffraction technique 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 cation and anions say NaCl structure

Then

$r_c + r_a = a/2$

Where r_c and r_a are radius of cation and anion.

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

For body centered lattice say CsCl.

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

Limiting Radius Ratios and Structure

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

CLASSIFICATION OF CRYSTALS

According to attractive force which hold crystal together are generally of five types and thus crystal can be classified into five types:

Ionic Crystals

(a) The lattices in ionic crystal consists of alternative positive and negative ions in equivalent amount arranged in an order so that the potential energy of the ions in the lattice is minimum.

(b) Such crystal are normally found in ionic compound.

eg $NaCI \rightarrow Na^+ + CI$
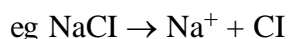
Covalent Crystals

(a) In covalent crystals, atoms attheir lattice point are held together by shared pairs of electrons between them.

(b) The covalent bonding extends through out the crystals in spatial direction and has no small molecules in the conventional sense.

eg. Diamond, Graphite.

Molecular Crystals

(a) In molecular crystals, the repeating unit is chemically identifiable atoms or molecules which do not carry a net charge.

(b) Molecular bonds are formed for those elements or compounds whose electronic configuration is such that there is little transfer of electrons between their atoms.

eg. Noble gases.

(c) The molecules having H-atom attached on N, O or F give hydrogen bonding crystals. The existence of H-bonding in the crystal lattice is beyond doubt.

eg. Ice Crystal etc.

Metallic Crystals

In metallic crystals, the lattice consists of assemblage of positive ions immersed in a sea of mobile electrons. The binding force is due to -

(a) Attraction between positive ions or ion cores of the metal and electron cloud.

{b) The mutual repulsion of free electrons.

(c) The mutual repulsion of ion cores.

PACKING OF CONSTITUENTS IN CRYSTALS

It is of two types

Close packing in two dimensions

The two possible arrangements of close packing in two dimensions.

Square close packing
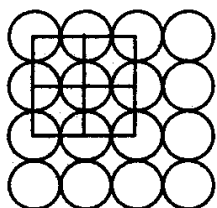
In which the spheres in the adjacent row lie just one over the other and show a horizontal as well as vertical alignment and form square. Each sphere in this arrangement is in contact with four other spheres.

Hexagonal close packing
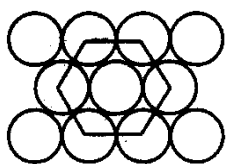
In which the spheres in every second row are seated in the depression between the spheres of first row. The spheres in the third row are vertically aligned with spheres in first row. The similar pattern is noticed throughout the crystal structure.

Comparison between Hexagonal Close Packing and Square Close Packing

1. Hexagonal close packing is more dense than square close packing.

2. 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.

3. 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.

Close packing in three dimensions

There are also two different ways to arrange spheres in three dimensional close packing.

Hexagonal close packing

To arrange the spheres vertically above those in the first layer so that each sphere of the third layer lies strictly above a sphere of the first layer. This arrangement if continued indefinitely in the same sequence is represented as AB AB AB ....

(a)   (b)
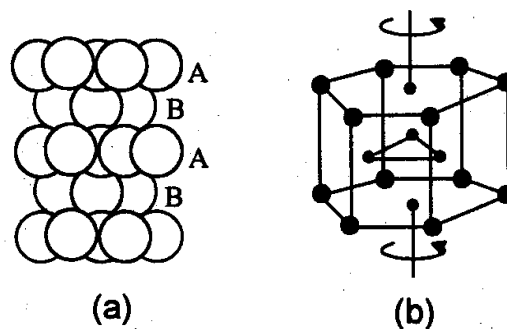
The arrangement is found to represent hexagonal close packing (hcp) symmetry which means that whole structure possesses one six fold of symmetry,

Cubic close packing

To arrange the spheres on the other set of hollows marked B. In this way the spheres in fourth layer will correspond with those in the first layer. This arrangement, If continued . indefinitely in the same sequence,isrepresentedas ABC, ABC ABC , This arrangement possesses cubic close packing (CCP).

(a)   (b)
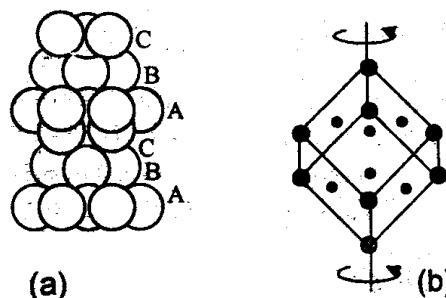
Body centred cubjc arrangement

This structure will be obtained-if the spheres in first layer (marked A) of cubic closed packing are slightly opened up and thus none of these is in contact with each other.

One can put the second layer of the spheres (marked B) on the top of the first layer in such a way that each sphere of the second layer is in contact with four spheres of the layer below it.

(A)   (B)
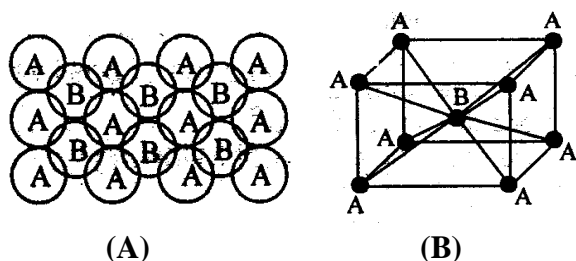
IMPERFECTIONS IN SOLID

Any deviation from the perfectly ordered arrangement constitutes a defect or imperfection. These defects sometimes called thermodynamic defects because the number of these defects depends 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.

Electronic imperfection

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 forrned 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.

Atomic imperfection

The compounds in which the number of irregularity present in the arrangement of atoms or ions are called- atomic imperfections. It is of two types -

Stoichiometric Defects

Those compounds in which the number of positive and negative ions are exactly in the ratio indicated by their chemical formula are called stoichiometric compounds. eg NaCI (1 : 1)

These solids show following types of defects:

(a) Schottky defect

This type of defect is created when same number of positive ion and negative ion are missing from their respective positions leaVing behind a pair of holes. Schottky defect is more common in ionic compounds with high co-ordination number and where the size of positive and negative ions are almost equal. The presence of large number of schottky defects in crystal results in significant decrease in its density.

Eg. NaCl, KCI, CsCl, KBr etc.

Schottky Defect
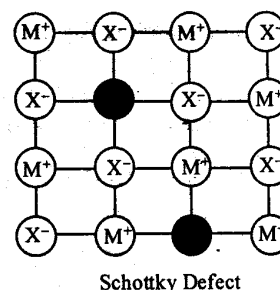
(b) Interstitial Defect

This type of defect is caused due to the presence of ions in the normally vacant interstitial sites in the crystal.

(c) Frenkel Defect

This type of defect is created when an ion leaves its correct lattice site and occupies an interstitial site. Frenkel defects are common in ionic compounds which have low co-ordination number and in which there is large difference in size between positive ahd negative ions. Eg. ZnS, AgCI, AgBr, Ag etc.
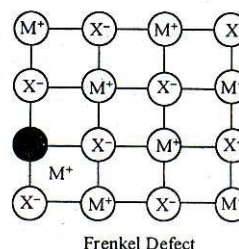
Frenkel Defect

Non Stoichiometric Defect Frenkel Defect

There are many compound in which the ratio of positive and negative ions present in the compound differs from that required by ideal formula of the compound. Such compounds are called Nonstoichiometric compounds.

eg. VO_x (Where x can vary between 0.6 to 1.3.)

In these compounds balance of positive and negative charges is maintained by having extra electrons or extra positive charge.

So, these defects are of following types:

(a) Metal excess defects due to anion vacancies

A compound may have excess metal ion if a negative ion is absent from its lattice site, leaving a hole which is occupied by electron to maintain electrical neutrality.

Metal excess defects
due to anion vacancies
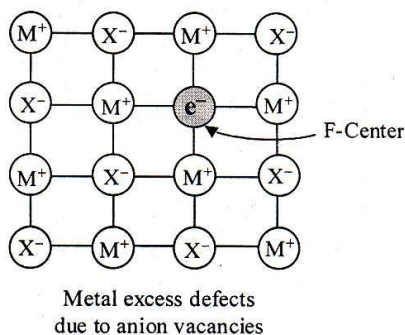
The holes occupied by electrons are called F-centres and are responsible for the colour of the compound. Eg.

• The excess sodium in NaCI makes the crystal appears yellow.

• Excess potassium in KCI makes it voilet.

• Excess lithium in LiCI makes it Pink.

Greater the number of F-centres greater is the intensity of colour. This type of defects are found in crystal which are likely to possess schottky Defects.

(b) Metal excess defects due to interstitial cations

It may occur if an extra positive ion is present in an interstitial site. Electrically neutrality is maintained by the presence of an electron in the interstitial site.

Metal excess defects
due to interstitial cations
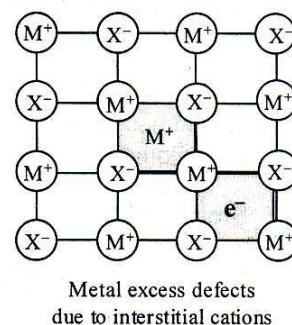
This type of defects are exhibited by the crystals which are likely to exhibit "Frenkel defects". Eg. Yellow colour of ZnS.

(c) Metal deficiency due to cation vacancies

The non-stoichiometric compound may have metal deficiency due to the absence of a metal ion from its lattice site. The charge is balanced by an adjacent ion having higher positive charge.

Metal deficiency
due to cation vacancies
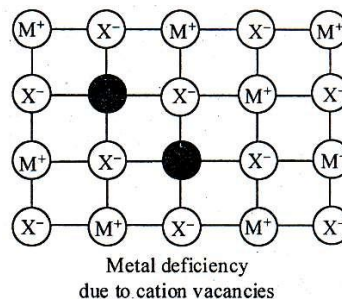
This type of defects are generally shown by compounds of transition metals.

EXPERIMENTAL METHOD OF DETRMINING CRYSTAL STRUCTURE

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.

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

Diffraction pattern

Crystal

Lead-box with slit

Photographic plate

10,000 – 40,000 volts

Spots from diffraction X -rays

Spots from incident beam

Photographic plate (Front view)
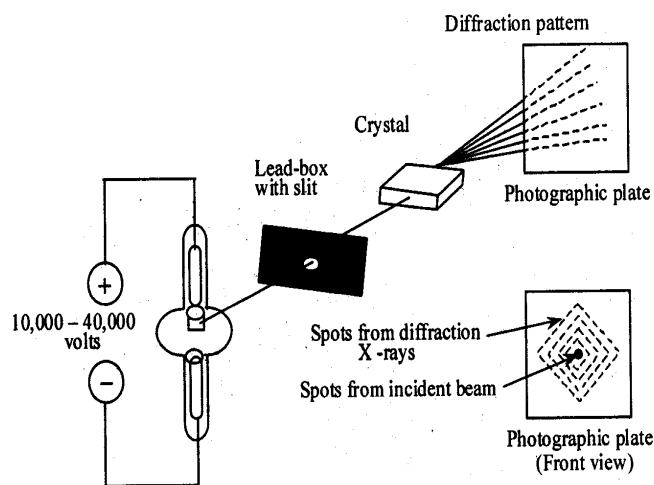
When a beam of X-rays passes through a crystalline solid, each atom in the beam scatters some of the radiations. If waves are on same phase means if their peak and through coincides they add together to give a wave of greater amplitude. This enhancement of intensity of called constructive interference.

If waves are out of phase, they cancel. This cancellation is called destructive interference.

(Addition)

(a) Constructive interference of waves

(Cancellation)

(b) Destructive interference of waves
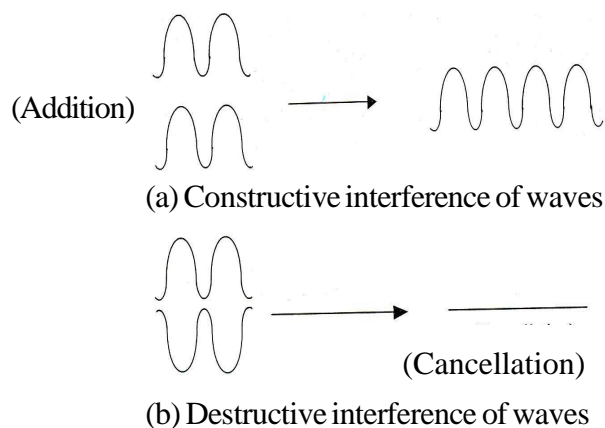
Bragg's Law

X-rays are electromagnetic waves of short wavelength and may be diffracted by suitable diffracting centres.

In solid crystals, atoms are arranged in fairly regular pattern with interatomic gaps of the order of 0.1 nm. Common salt is an example of a crystalline solid. Almost all the metals at ordinary temperature are crystalline. These metals may act as a natural three-dimensional gratings for the diffraction of X-rays.

The structure of a solid can be showed as a series of parallel planes of atoms separated by a distance d. Suppose, an X-ray beam is incident of a solid, making an angle q with the planes of the atoms. These X-ray are diffracted by different atoms and the interference is constructive and we are obtained strong reflected X-ray. The analysis show that there will be a strong reflected X-ray beam only if
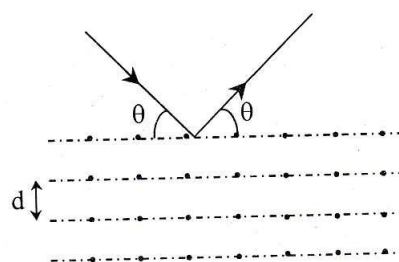
2d sin q = nl

Where 'n' is an integer. For monochromatic X-rays is fixed and there are some specific angle q_1, q_2, q_3 ...... etc. corresponding to n = 1, 2, 3 .... etc, in the above equation. Thus, if the X-rays are incident at one of these, they are reflected ; otherwise they are absorbed. When they are reflected, the laws of reflection are obeyed i.e. (a) the angle of incidence is equal to the angle of reflection and

(b) the incident ray, the reflected ray and the normal to the reflecting plane are coplanar.

By using a monochromatic X-ray beam and nothing the angles of strong reflection, the interplaner spacing d and several informations about the structure of the solid can be obtained.

PROPERTIES OF SOLIDS

Electrical properties of solids :

On the basis of electrical conductivity, solids are classified into three types.

i. metals   ii. semi-conductors   iii. insulators

Electrical conductivity of metals is very high and is of the order of $10^6 – 10^8$ ohm^{-1} cm^{-1}.

Electrical conductivity of solids is due to the movement of electrons and positive holes or through the motion of ions.

The conduction through electrons is called n-type conduction and through positive ions is called p-type conduction.

Pure ionic solids, where conduction takes place only through motion of ions, are insulators.

The presence of defects in the crystal structure increases their conductivity.

The solids whose conductivity lies between those of metallic conductors and insulators are called semiconductors.

Semi - conductors have conductivity which lies in the range of $10^2 - 10^{-9}$ ohm^{-1} cm^{-1}.

The solids which do not allow the passage of electric current through them are called insulators.

Eg: Wood, rubber, sulphur, phosphorus etc..

The conductivity of semi conductors and insulators. is mainly due to the presence of interstial electrons and positive holes in the solids due 10 imperfections.

The conductivity of semi conductors and insulators increases with increase in temperature while that of metals decreases.

Magnetic properties of solids :

The substances which are weakly repelled by magnetic field are called **diamagnetic** substances.

Eg : TiO_2, NaCI, benzene etc..

Diamagnetism arises when all the electrons are paiTed.

The substances which are weakly attracted by magnetic field are called **paramagnetic substances**.

Atoms,-ions or molecules with unpaired electrons exhibit paramagnetism.

Paramagnetic substances lose their magnetism in the absence of magnetic field.

Eg : TiO, VO_2' CuO etc.

The substances which are strongly attracted by magnetic field are called **ferromagnetic substances**.

Ferromagnetic substances show permanent magnetism even in the absence of magnetic field.

Eg : Iron, cobalt, nickel, CrO_2 etc.

Ferromagnetism arises due to spontoneous alignment of magnetic moments in the same direction.

Anti ferromagnetism arises due to the alignment of magnetic moments in opposite direction in a compensatory manner and resulting in a zero magnetic moment.

Eg : MnO, MnO_2, Mn_2O_3.

Ferrimagnetism arises due to alignment of magnetic moments in opposite directions resulting in a net magnetic moment.

Eg : Fe_3O_4, $M^{2+}Fe_2O_4$; (M = Mg, Cu, Zn etc.)

Ferromagnetic and ferrimagnetic substances change into paramagnetic substances at higher temperatures due to randomisation of spins.

Dielectric Properties :

A dielectric is a substance in which an electric field gives rise to no net flow of electric charge. The electrons in a dielectric are tightly held by individual atoms.

Due to shift in charges, dipoles are created which result into polarisation.

The dipoles may align in an ordered manner such that there is some resultant dipole moment in the crystals.

The dipoles may align in such a way that the dipole moments cancel each other and resultant dipole moment is zero.

There may be no dipoles in the crystal but only ions are present.

Depending upon the alignment of the dipoles, the properties of crystals are:

i. Piezoelectricity   ii. Ferroelectricity
iii. Anti-ferroelectricity   iv. Pyroelectricity

When these crystals are subjected to a pressure or mechanical stress, electricity is produced. These crystals are used as pickups in record players by the application of pressure.

ii. Ferroelectricity :

The solids, in which dipoles are spontaneously aligned in a particular direction, even in the absence of electric field, are called ferroelectric substances and the phenomenon is called ferroelectricity.

The direction of polarisation in these substances can be changed by applying electric field.

The examples are barium titanate ($BaTiO_3$), sodium potassium tartrate (Rochelle salt) and potassium dihydrogen phosphate (KH_2PO_4).

iii. Anti-ferroelectricity :

If the alternate dipoles are in opposite direction, then the net dipole moment will be zero and the crystal is called anti-ferroelectric and the phenomenon is **antiferroelectricity**.

iv. Pyroelectricity :

Some of the polar crystals when heated produce small electric current. This phenomenon is called **pyroelectricity**.

SUPER CONDUCTING MATERIALS

* Super conducting materials are those which offer no resistance to the passage of electricity. Electrical resistance decreases with decrease in temperature and becomes almost zero near the absolute zero.

* In this state, the materials become' diamagnetic and are repelled by- the magnets.

* Most metals become super conducting at very 10w temperatures (2-5K).

* The highest temperature at which superconductivity was known is 23K in alloys of niobium (Eg. Nb_3Ge).

* Some organic compounds also become super conducting at temperatures below 5 K.

* Some complex metal oxides passess super conductivity at higher temperatures.

Super conductors are used in electronics, building magnets, power transmission, levitation transportation, (trains which move in air without rails).

Solved Examples

Ex.1 Calculate the distance between 111 planes in a crystal of Ca. Repeat the calculation for the 222 planes. (a = 0.556nm)

Sol. We have,

$$d = \frac{a}{\sqrt{h^2 + k^2 + \ell^2}}$$

$$d_{111} = \frac{0.556}{\sqrt{1^2 + 1^2 + 1^2}} = 0.321 \text{ nm}$$

and $d_{222} = \dfrac{0.556}{\sqrt{2^2 + 2^2 + 2^2}} = 0.161$ nm

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

Ex.2 Fraction of total volume occupied by atoms in a simple cube is -

[1] $\dfrac{\pi}{2}$ [2] $\dfrac{\sqrt{3}\pi}{2}$ [3] $\dfrac{\sqrt{2}\pi}{6}$ [4] $\dfrac{\pi}{6}$

Sol. In a simple cubic system, number of atoms a = 2r

∴ Packing fraction

$$= \frac{\text{Volume occupied by one atom}}{\text{Volume of unit cell}}$$

$$= \frac{\frac{4}{3}\pi r^3}{a^3} = \frac{\frac{4}{3}\pi r^3}{(2r)^3} = \frac{\pi}{6}$$

Ex.3 In a crystal both ions are missing from normal sites in equal number. This is an example of -

[1] F-centres   [2] Interstitial defect

[3] Frenkel defect   [4] Schottky defect

Sol. Schottky defects are arised when one positive ion and one negative ion are missing from their respective position leaving behind a pair of holes. These are more common in ionic compounds with high coordination number and having almost similar size of cations and anions.

Ex.4 Xenon crystallizes in face centre cubic lattice and the edge of the unit cell is 620 PM, then the radius of Xenon atom is -

[1] 219.20 PM   [2] 438.5 PM

[3] 265.5 PM   [4] 536.94 PM

Sol. For fcc lattice

$4r = \sqrt{2}\ a$ where a = 620 PM

or $r = \dfrac{1}{2\sqrt{2}}$ x a = $\dfrac{1}{2\sqrt{2}}$ x 620 PM = 219.20 PM.

Ex.5 The edge length of cube is 400 PM. Its body diagonal would be -

[1] 500 PM [2] 693 PM

[3] 600 PM [4] 566 PM

Sol. Since in body centre cubic, the body diagonal

$= \sqrt{3}\ a$

$= \sqrt{3}$ x 400 PM

= 692.82 PM or say 693 PM

Ex.6 What is the simplest forkuma of a solid whose cubic unit cell has the atom A at each corner, the atom B at each face centre and C atom at the body centre

[1] AB_2C [2] A_2BC

[3] AB_3C [4] ABC_3

Sol. An atom at the corner of a cube is shared among 8 unit cells. As there are 8 corners in a cube, number

of corner atom [1] per unit cell = 8 x $\dfrac{1}{8}$ = 1.

A face-centred atom in a cube is shared by two unit cellls. As there are 6 faces in a cube, number of

face-centred atoms [2] per unit cell = 6 x $\dfrac{1}{2}$ = 3.

An atom in the body of the cube is not shared by other cells.

∴ Number of atoms [3] at the body centre per unit cell = 1

Hence, the formula of the solid is AB_3C.

Ex.7 A compound alloy of glod and copper crystallizes in a cube lattice in which the gold atoms occupy the lattice points at the coruers of cube and copper atoms occupy the centres of each of the cube faces. The formula of this compound is -

[1] AuCu [2] $AuCu_2$

[3] $AuCu_3$ [4] None

Sol. One-eighth of each corner atom (Au) and one half of each face centered atom (Cu) are contained with in the unit cell of the compound.

Thus, the number of Au atoms per unit cell = 8 x $\dfrac{1}{8}$

= 1 and

the number of Cu atoms per unit cell = 6 x $\dfrac{1}{2}$ = 3.

The formula of the compound is $AuCu_3$.

Ex.8 Lithium borohydride ($LiBH_4$), crystallises in a orthorhombic system with 4 molecules per unit cell. The unit cell dimensions are : a = 6.81 Å, b = 4.43 Å, c = 717Å. If the molar mass of $LiBH_4$ is 21.76 g mol^{-1}. The density of the crystal is -

[1] .668 g cm^{-3} [2] .585 g cm^2

[3] 1.23 g cm^{-3} [4] None

Sol. We know that,

$\rho = \dfrac{ZM}{NV}$

$= \dfrac{4\times(21.76\,g\,mol^{-1})}{(6.023\times10^{23}\,mol^{-1})(6.81\times4.43\times7.17\times10^{-24}\,cm^3)}$

$= 0.668\,g\ cm^{-3}$

Ex.9 The unit cell of a metallic element of atomic mass 10^8 and density 10.5 g/cm^2 is a cube with edge length of 409 PM. The structure of the crystal lattice is -

[1] fcc [2] bcc [3] hcp [4] None

Sol. $\rho = \dfrac{Z\times M}{N\times a^3}$

Here, M = 108, N_A = 6.023 x 10^{23}

Put on these values and solving we get -

a = 409 PM = 4.09 x 10^{-8}cm, ρ = 10.5 g/cm^2

n = 4 = number of atoms per unit cell

So, The structure of the crystal lattice is fcc.

Ex.10 Copper metal has a face-centred cubic structure with the unit cell length equal 0.361 nm. Picturing copper ions in contact along the face diagonal. The apparent radius of a copper ion is -

[1] 0.128 [2] 1.42

[3] 3.22 [4] 4.22

Sol. For a face-centred cube, we have

Radius = $\dfrac{\sqrt{2}a}{4} = \dfrac{\sqrt{2}\times 0.361}{4}$ nm = 0.128.