SOLID STATE

Preface

It is a branch of physical chemistry that deals with study of crystals, their classifications, properties & structure. In this Chapter, you will learn different types of solids, space lattice and unit cell, elements of symmetry and crystal system. After successful completion of the topic, you will be able to know about different crystal, types of packing, imperfections and Bragg's Law.

This book consists of theoretical & practical explanations of all the concepts involved in the chapter. Each article followed by a ladder of illustration. At the end of the theory part, there are miscellaneous solved examples which involve the application of multiple concepts of this chapter.

Students are advised to go through all these solved examples in order to develope better understanding of the chapter and to have better grasping level in the class.

Total No.of questions in **Solid State** are -

In chapter Examples 06

Solved Examples 15

Total No. of questions 21

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.

1.1 Properties of solids

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

(b) They have definite shape and volume.

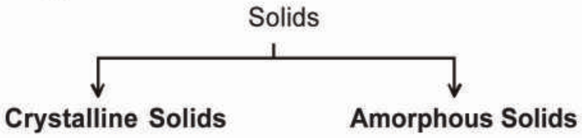
(c) Solids have high density .

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

(e) They are almost incompressible.

(f) They show very slow diffusion.

1.2 Types of Solids



1.2.1 Crystalline solids

(a) In this type of solids the atoms or molecules 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 Ice, Quartz, diamond etc.

1.2.2 Amorphous Solids

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

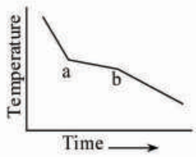
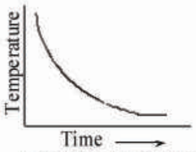
(b) They are regarded as super cooled liquids with high viscosity in which the force of attraction holding the molecules together are so great, that the material becomes rigid but there is no regularity in structure.

(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 glass, Rubber, plastics, wax, paper, wood etc.

1.3 Difference between crystalline and amorphous solids

S.No.	Property	Crystalline solids	Amorphus solids
1	Shape	They have definite and regular geometrical 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.  Amorphous substances cooling curve
6	Isotropy and Anisotropy	They are anisotropic.	They are isotropic.

2. STUDY OF CRYSTALS

2.1 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.

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

2.3 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.

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

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

2.6 Corner : A corner is formed by intersection of two or more edges.

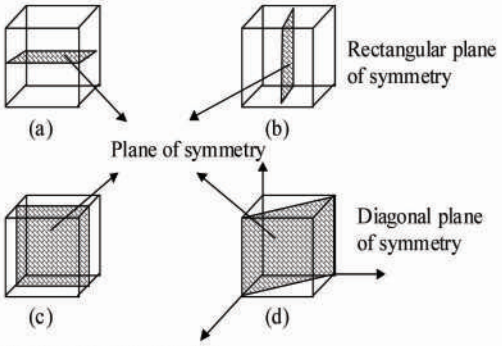
2.7 Interfacial angles : The angle between the perpendiculars two intersecting faces called interfacial angles.

3. TYPES OF SYMMETRY

A crystal possesses following three types of symmetry.

3.1 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.



3.2 Axis of symmetry

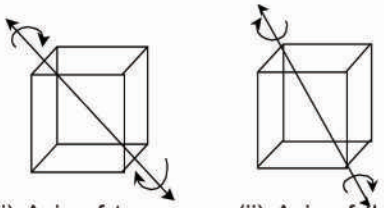
(a) It is an imaginary line about which the crystal may be rotated so that it presents the same appearance more than once in a complete rotation through 360°.

(b) The axes of symmetry are called diad, triad, tetrad and hexad respectively. It is the original appearance and is repeated twice (180°), thrice (120°), four times (90°) and six times (60°) in one rotation.

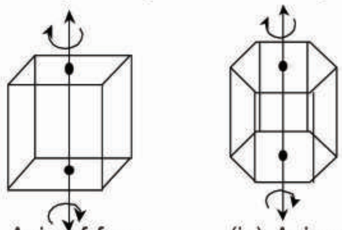
(c) These axes of symmetry are also called as two fold, three fold, four fold and six fold respectively.

(d) Five fold symmetry is not found in crystals.

(e)



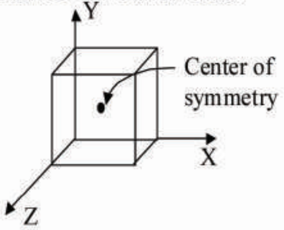
(i) Axis of two fold symmetry. (ii) Axis of three fold symmetry.



(iii) Axis of four fold symmetry. (iv) Axis of six fold symmetry.

3.3 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.

4. ELEMENTS OF SYMMETRY

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

(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 (A) = 1

Total symmetry = 23

5. CRYSTAL SYSTEM

(a) On the basis of geometrical consideration theoritically there can be 32 different combinations of elements of symmetry of crystal.

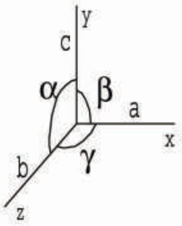
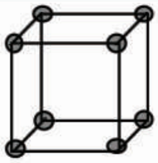
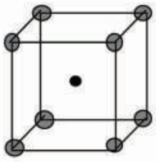
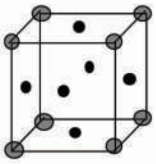
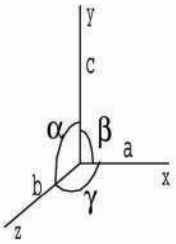
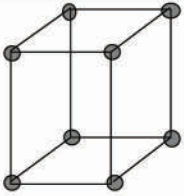
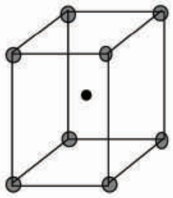
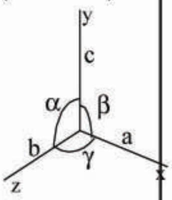
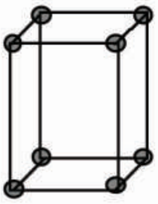
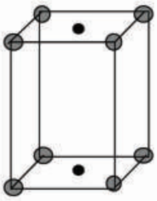
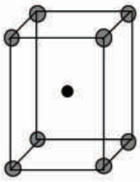
(b) But on the other hand Bravais showed that there are only seven types of crystal system.

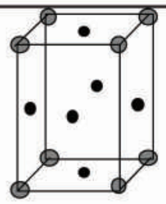
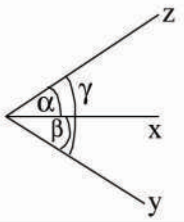
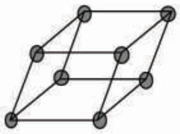
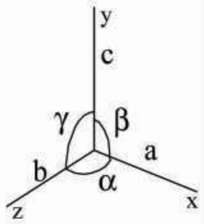
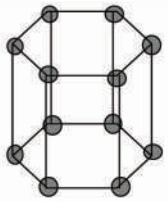
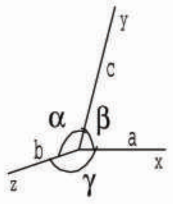
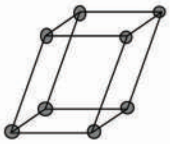
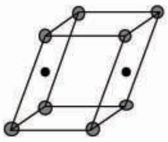
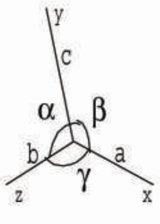
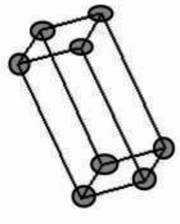
These are :–

(a) Cubic
(b) Tetragonal
(c) Orthorhombic
(d) Rhombohedral
(e) Hexagonal
(d) Monoclinic
(e) Triclinic

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

The Bravais Lattices

S. No.	Crystal system	Axial distance	Axial angles	Space lattice	Unit cell
1.	Cubic  	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	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 centres.	
2.	Tetragonal  	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	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 (Rhombic)  	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	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 at two face centres 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 	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	j. Simple : – Points at the eight corners of the unit cell.	
5.	Hexagonal 	$a = b \neq c$	$\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	k. Simple : – i. Points at the twelve corners of the unit cell out lined by thick line.	
6.	Monoclinic 	$a \neq b \neq c$	$\alpha = \beta = 90^\circ \neq \gamma$	l. Simple : – Points at the eight corners of the unit cell. m. End centered : – Point at the eight corners and at two face centres opposite to the each other.	 
7.	Triclinic 	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	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_2O, 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.	Hexagonal	Simple	ZnO, PbI_2,CdS, HgS, Graphite, Ice, Beryl, Mg, Zn, Cd.
6.	Monoclinic	Simple	$Na_2\ SO_4.\ 10\ H_2O$, $Na_2\ B_4O_7.\ 10\ H_2O$, $CaSO_4\ .\ 2H_2\ O$, Monoclinic sulphur
7.	Triclinic	Simple	$CaSO_4\ .\ 5H_2O$, $K_2Cr_2O_7$, H_3BO_3.

6. 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.

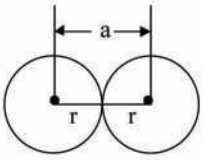
(c) **Face Centered Cubic (FCC) :** Atoms are arranged at the corners and at the centre of the each face.

6.1 Atomic radius

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

(a) Simple cubic structure (S.C.)

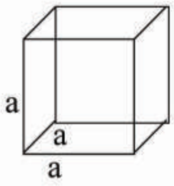
Radius of atom 'r' = $\frac{a}{2}$



(b) Face centered cubic structure (FCC) 'r' = $\frac{a}{2\sqrt{2}}$

(c) Body centered cubic structure (BCC)

'r' = $\frac{\sqrt{3}\,a}{4}$



a = b = c

$\alpha = \beta = \gamma = 90°$

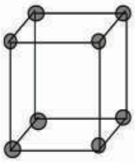
6.2 Number of atoms per unit cell / unit cell contents

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)

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

$\therefore \ z = 8 \times \frac{1}{8} = 1$

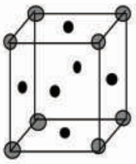


(b) Face centered cubic structure (fcc)

(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 centered 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 centered 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

6.3 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 C.N. = 6.

(d) For bcc C.N. = 8.

(e) For fcc C.N. = 12.

6.4 Density of cubic unit cell

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

(b) Density of cubic unit cell =

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

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

6.5 Packing fraction (P.F.)

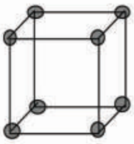
It is defined as ratio of the volume of the unit cell that is occupied by spheres of the unit cell to the total volume of the unit cell.

(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 $\qquad r = \frac{a}{2}$

therefore, $\qquad \text{P.F.} = \dfrac{\frac{4}{3}\pi r^3}{(2r)^3} = 0.52$

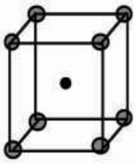
% P.F. = 52%

% of void = 100 – 52 = 48 %

(b) Body centered cubic unit cell

Number of atoms per unit cell = $8 \times \frac{1}{8} + 1 = 2$

$r = \frac{\sqrt{3}a}{4}$

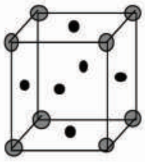


$$P.F. = \frac{2 \times \frac{4}{3}\pi r^3}{\left(\frac{4r}{\sqrt{3}}\right)^3} = 0.68$$

% P.F. = 68 %

% 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 %

Crystal Structure of Some Cubic Ionic Solids

Crystal Structure Units	Brief description and Examples	Co-ordination Number	No. of formula per Unit cell
1. Rock Salt (NaCl - type)	Cl^- ions in C.C.P, Na^+ ions occupy all the octahedral voids. **Example :** Halides of Li, Na, K and Rb, AgCl, AgBr, NH_4Cl etc.	$Na^+ - 6$ $Cl^- - 6$	4
2. CsCl - type	Cl^- ions at the corner of cube and Cs^+ ions at the body centre Example : CsCl, CsBr, CsI etc.	$Cs^+ - 8$ $Cl^- - 8$	1
3. Zinc. Blende (ZnS type)	S^{-2} ions in C.C.P., Zn^{+2} ions occupy alternate tetrahedral voids i.e. only half of the total number of tetrahedral voids are occupied **Examples :** ZnS, CuCl, CuBr, CuI, AgI etc.	$Zn^{+2} - 4$ $S^{-2} - 4$	4
4. Flourite (CaF_2 – type)	Ca^{+2} ions (+ve ions) in C.C.P. and F^- ions (-ve ions) in all the tetrahedral voids. Example : CaF_2, SrF_2, BaF_2, $BaCl_2$ etc.	$Ca^{+2} - 8$ $F^- - 4$	4
5. Anti-flourite Structure (Li_2O – type)	Negative ions means O^{-2} in CCP and Positive Li^+ ions in all the tetrahedral voids. Example : Na_2O	$Na^+ - 4$ $O^{-2} - 8$	4

7. 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.

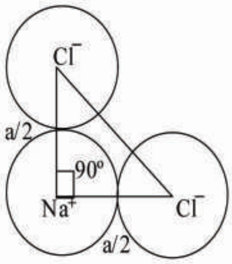
Let, cube of edge length 'a' having cations and anions say NaCl structure.

Then

$$r_C + r_a = a/2$$

Where r_c and r_a are radius of cation and anion.

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



For body centered lattice say CsCl.

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

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	4	Square planar
0.414 – 0.732	6	Octahedral
0.732 – 0.999	8	Body-centered cubic or cubical viod

Examples based on characteristics of cubic system

Ex.1 A metallic element exists as cubic lattice. Each edge of the unit cell is 2.88 Å . The density of the metal is 7.20 g cm^{-3}. How many unit cell will be present in 100 g of the metal-

(A) 6.85×10^2 (B) 5.82×10^{23}
(C) 4.37×10^5 (D) 2.12×10^6

Sol. (B) The volume of the unit cell = $(2.88\ Å)^3$

$= 23.9 \times 10^{-24}$ cm^3.

The volume of 100 g of the metal

$$= \frac{m}{\rho} = \frac{100}{7.20}$$

$= 13.9$ cm^3.

Number of unit cells in this volume

$$= \frac{13.9\ cm^3}{23.9 \times 10^{-24}\ cm^3}$$

$= 5.82 \times 10^{23}$

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

(A) $\frac{\pi}{2}$ (B) $\frac{\sqrt{3}\pi}{8}$

(C) $\frac{\sqrt{2}\pi}{6}$ (D) $\frac{\pi}{6}$

Sol. **(D)**

In a simple cubic system, number of atoms in a unitcell is one and a = 2r

∴ Packing fraction

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

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

8. CLASSIFICATION OF CRYSTALS

According to attractive forces which hold crystal together thus crystal can be classified into five types :

8.1 Ionic Crystals

(a) The lattice 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.

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

eg. NaCl → $Na^+ + Cl^-$

8.2 Covalent Crystals

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

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

eg. Diamond, Graphite.

8.3 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.

8.4 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.

Examples based on Types of crystals

Ex.3 Iodine crystal is -

(A) Metallic Solid (B) Ionic solid
(C) Molecular solid (D) Covalent solid

Sol. **(C)**

Molecular solids are the substances having molecules as constituent units having interparticle forces such as Vander Waal's forces or hydrogen bonds.

Ex.4 Which of the following is molecular crystal-

(A) Noble gases (B) Ice
(C) A and B both (D) None of these

Sol. Correct answer is **(C)**

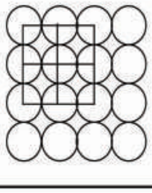
9. PACKING OF CONSTITUENTS IN CRYSTALS

It is of two types

9.1 Close packing in two dimensions

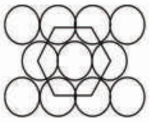
The two possible arrangements of close packing in two dimensions.(uni-layer packing)

9.1.1 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.

9.1.2 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

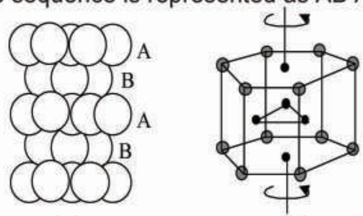
1. Hexagonal close packing is more dense than square close packing.
2. In hexagonal close packing about 60.4% of available space is occupied by spheres. Whereas, square close packing occupies only 52.4% of the space by spheres.
3. In square close packing the vacant spaces (voids) are between four touching 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.

9.2 Close packing in three dimensions (multi-layer packing)

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

9.2.1 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 .....

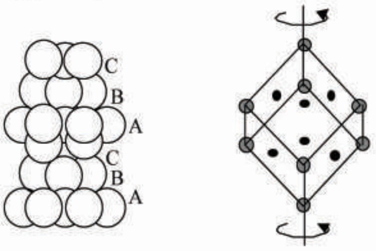


(a) (b)

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

9.2.2 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, is represented as ABC ABC ABC .... This arrangement possesses cubic close packing (CCP).

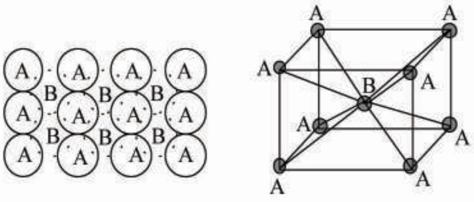


(a) (b)

9.2.3 Body centred cubic 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)

10. IMPERFECTIONS IN SOLID

Any deviation from the perfectly ordered arrangement constitutes a defect or imperfection. These defects are 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.

10.1 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 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.

10.2 Atomic imperfection

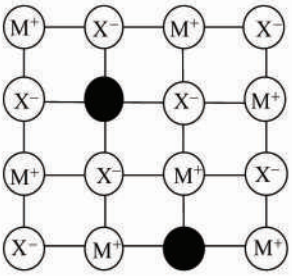
The compounds in which the number of irregularity present in the arrangement of atoms or ions are called atomic imperfections. It is of two types -

10.2.1. 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. NaCl (1 : 1)

These solids show following types of defects :

(a) Schottky defect



Schottky Defect

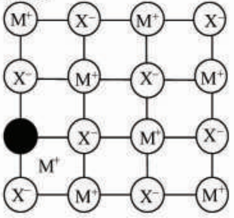
This type of defect is created when same number of positive ion and negative ion are missing from their respective positions leaving behind a pair of holes. Schottky defect is more common in ionic compounds with high co-ordination number and where the size of positive and negative ions are almost equal.

The presence of large number of schottky defects in crystal results in significant decrease in its density. Eg. NaCl, KCl, CsCl, KBr etc.

(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



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 and negative ions.

Eg. ZnS, AgCl, AgBr, AgI etc.

10.2.2 Non Stoichiometric Defect

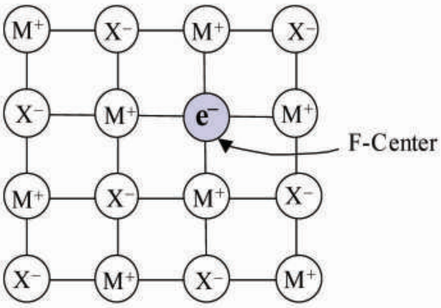
There are many compound in which the ratio of positive and negative ions present in the compound differs from that required by ideal formula of the compound. Such compounds are called Non-stoichiometric compounds.

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



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.

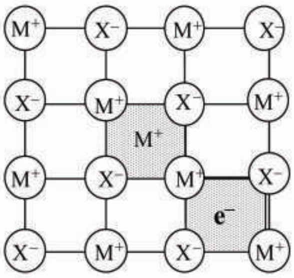
The holes occupied by electrons are called F-centres and are responsible for the colour of the compound.

Eg.

- The excess sodium in NaCl makes the crystal appears yellow.
- Excess potassium in KCl makes it voilet.
- Excess lithium in LiCl 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



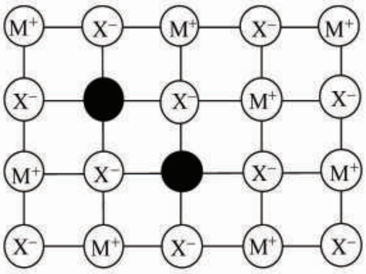
Metal excess defects
due to interstitial cations

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.

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



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.

This type of defects are generally shown by compounds of transition metals.

Examples based on Imperfections in solid

Ex.5 In a crystal both ions are missing from normal sites in equal number. This is an example of-

(A) F-centres (B) Interstitial defect

(C) Frenkel defect (D) Schottky defect

Sol. (D)

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

Ex.6 Frenkel defect is noticed in-

(A) AgBr (B) ZnS

(C) AgI (D) All

Sol. (D)

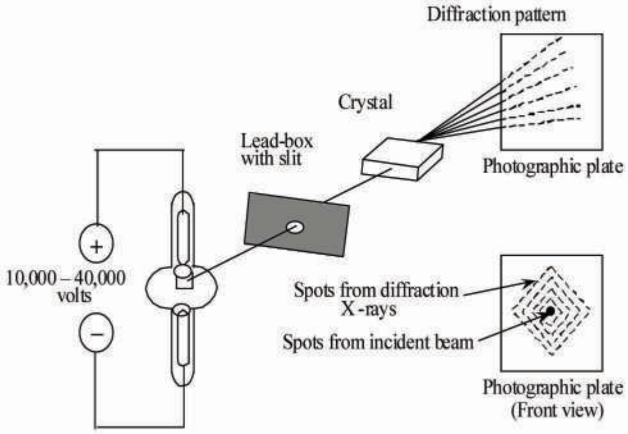
Frenkel defect is arised when the cations are missing from their lattice sites and occupy interstitial sites. As a result of Frenkel defect, density remains unchanged but dielectric constant increases.

11. EXPERIMENTAL METHOD OF DETERMINING CRYSTAL STRUCTURE :

Crystal structure has been obtained by studying on the diffraction of X-rays by solids.

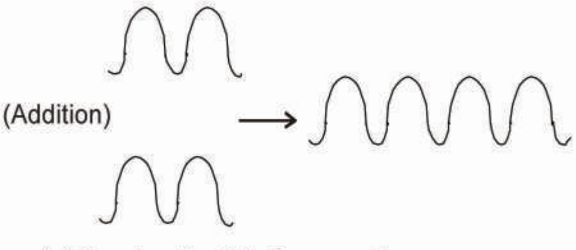
A crystal, having constituents particles arranged in planes at very small distances in three dimension array, acts as diffraction grating for X-rays which have wavelengths of the same order as the spacing in crystal.

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

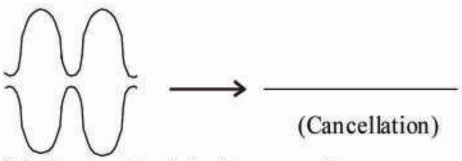


When a beam of X - rays passes through a crystalline solid, each atom in the beam scatters some of the radiations. If waves are on same phase means if their peak and through coincides they add together to give a wave of greater amplitude. This enhancement of intensity is called constructive interference.

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



(a) Constructive interference of waves

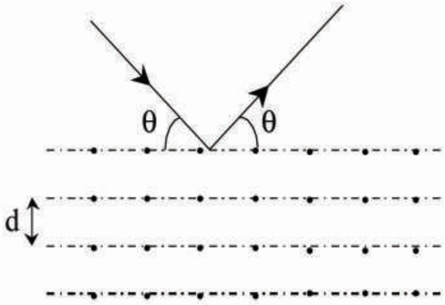


(b) Destructive interference of waves

11.1 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 on a solid, making an angle θ 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 shows that there will be a strong reflected X - ray beam only if

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

where, 'n' is an integer. For monochromatic X - rays is fixed and there are some specific angles θ_1, θ_2, θ_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.

12. MAGNETIC PROPERTIES OF CRYSTALS

	Properties	Information	Magnetic Alignment	Example	Application
1.	Diamagnetic	Repelled weakly in magnetic field. Such solids have only paired electrons.	⥮⥮⥮⥮⥮	Benzene NaCl, TiO_2, V_2O_5, etc.	Insulators
2.	Paramagnetic	Have unpaired electrons; weakly attracted in magnetic field. They cannot be permanently magnetised.	↖↙→↑↘↗	O_2, VO, CuO, TiO	Electronic devices
3.	Ferromagnetic	Also, have unpaired electrons. Strongly attracted in magnetic field. Such solids can be permanently magnetised. On heating to a temperature called Curie Point, these solids change to paramagnetic solid.	↑↑↑↑↑↑↑	Fe, Ni, Co, CrO_2	CrO_2 is used in audio, video tapes.
4.	Antiferro-magnetic	In these solids change electrons align themselves in such a way that resultant magnetic moment is zero.	⇅ ⇅ ⇅ ⇅	Cr_2O_3, CoO, Co_3O_4, Fe_2O_3 MnO, MnO_2	Used in the instruments of magnetic susceptibility measurement
5.	Ferrimagnetic	unpaired electrons align themselves in such way that there is a net magnetic moment.	↑↓↓ ↑ ↓↓↑ ↓↓ OR ↑↑ ↓↓↓ ↑↑ ↓↓↓ ↑↑ and so on	Fe_3O_4, ferrites	–

13. ELECTRICAL PROPERTIES OF CRYSTALS

	Properties	Information	Dipolar Property	Example	Application
1.	Piezoelectricity	When a crystal of dielectrics is subjected to mechanical stress, then small magnitude current is produced. It is called direct Piezoelectric effect.	Development of charge in some part of crystal	Quartz and Rochelle salt	Used in mechanical electric transducer, e.g., in record player Transmission of direct signals, sounding of sea depths.
2.	Anti piezoelectricity	In some solids, electric field developes mechanical effect.	Crystal suffers elastic deformation in an electric field	–	
3.	Ferroelectricity	Piezoelectric crystals having permanent dipoles are said to possess ferroelectricity	↑↑↑↑↑↑	$BaTiO_3$, KH_2PO_4 Rochelle salt	Electromagnetic appliances.
4.	Anti ferroelectricity	Piezoelectric crystals with zero dipole are said to posses anti ferroelectrictity.	⇅ ⇅ ⇅	$PbZrO_3$ Lead zirconate	
5.	Pyroelectricity	Some polar crystals produce electric impulse on heating.	–	Crystals of tartaric acid.	Used in fire alarms, thermostat.

SOLVED EXAMPLES

Ex.1 Graphite in an example of-

(A) Ionic solid

(B) Covalent Solid

(C) Vander waal's Crystal

(D) Metallic crystal

Sol. **(B)**

Graphite is a covalent solid having sp^2 hybridised carbon atoms.

Ex.2 Which is amorphous solid -

(A) Rubber (B) Plastic

(C) Glass (D) All

Sol. **(D)**

Amorphus solids neither have ordered arrangement (i.e. no definite shape) nor have sharp melting point like crystals, but when heated, they become pliable until they assume the properties usually related to liquid. It is therefore they are regarded as super cooled liquids.

Ex.3 Xenon crystallizes in face centre cubic lattice and the edge of the unit cell is 620 PM, then the radius of Xenon atom is-

(A) 219.20 PM (B) 438.5 PM

(C) 265.5 PM (D) 536.94 PM

Sol. **(A)**

For fcc lattice ; $\boxed{r = \frac{1}{2\sqrt{2}} \times a}$

where a = 620 PM

On solving r = 219.20 PM.

Ex.4 The edge length of cube is 400 PM. Its body diagonal would be-

(A) 500 PM (B) 693 PM

(C) 600 PM (D) 566 PM

Sol. **(B)**

Since in body centre cubic, the body diagonal

$$= \sqrt{3}\,a$$

$$= \sqrt{3} \times 400 \text{ PM}$$

$$= 692.82 \text{ PM or say } 693 \text{ PM}$$

Ex.5 What is the simplest formula of a solid whose cubic unit cell has the atom A at each corner, the atom B at each face centre and a C atom at the body centre-

(A) AB_2C (B) A_2BC

(C) AB_3C (D) ABC_3

Sol. **(C)**

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 (A) per unit cell $= 8 \times \frac{1}{8} = 1$.

A face-centered atom in a cube is shared by two unit cells. As there are 6 faces in a cube, number of face-centered atoms (B) per unit cell $= 6 \times \frac{1}{2} = 3$.

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

∴ Number of atoms (C) at the body centre per unit cell = 1.

Hence, the formula of the solid is AB_3C.

Ex.6 A compound alloy of gold and copper crystallizes in a cube lattice in which the gold atoms occupy the corners of a cube and the copper atoms occupy the centres of each of the cube faces.The formula of this compound is-

(A) AuCu (B) $AuCu_2$

(C) $AuCu_3$ (D) None

Sol. **(C)**

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 $= 8 \times \frac{1}{8} = 1$ and the number of Cu atoms per unit cell $= 6 \times \frac{1}{2} = 3$. The formula of the compound is $AuCu_3$.

Ex.7 Select the correct statement (s)-

(a) The C.N. of cation occupying a tetrahedral hole is 4.

(b) The C.N. of cation occupying a octahedral hole is 6.

(c) In schottky defects, density of the lattice decreases.

(A) a, b (B) b, c

(C) a, b, c (D) a, c

Sol. **(C)**

Since tetrahedral holes are surrounded by 4 nearest neighbours. So, the C.N. of cation occupying tetrahedral hole is 4. Since octahedral hole is surrounded by six nearest neighbours. So, C.N. of cation occupying octahedral is 6. In schottky a pair of anion and cation leaves the lattice. So, density of lattice decreases.

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

(A) .668 g cm^{-3} (B) .585 g cm^{-3}

(C) 1.23 g cm^{-3} (D) None

Sol. **(A)**

We know that,

$$\rho = \frac{ZM}{NV} \text{ ; where } V = a \times b \times c$$

$$= \frac{4 \times (21.76\,\text{g}\,\text{mol}^{-1})}{(6.023 \times 10^{23}\,\text{mol}^{-1})\,(6.81 \times 4.43 \times 7.17 \times 10^{-24}\,\text{cm}^3)}$$

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

Ex.9 The unit cell of a metallic element of atomic mass 10^8 and density 10.5 g/cm^3 is a cube with edge length of 409 PM. The structure of the crystal lattice is -

(A) fcc (B) bcc

(C) hcp (D) None of these

Sol. **(A)**

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

Here, M = 108, $N_A = 6.023 \times 10^{23}$

Put on these values and solving we get-

a = 409 PM = 4.09×10^{-8} cm,

ρ = 10.5 g/cm^3

n = 4 = number of atoms per unit cell

So, The structure of the crystal lattice is fcc.

Ex.10 Among the following types of voids, which one is the largest void-

(A) Triangular system

(B) Tetragonal system

(C) Monoclinic system

(D) Octahedral

Sol. **(D)**

The vacant spaces between the spheres in closed packed structure is called void. The voids are of two types, tetrahedral voids and octahedral voids. Also radius of tetrahedral voids and octahedral voids are $r_{void} = 0.225 \times r_{sphere}$ and $r_{void} = 0.411 \times r_{sphere}$ respectively. Thus, octahedral void is larger than tetrahedral void.

Ex.11 Close packing is maximum in the crystal which is-

(A) Simple cube (B) bcc

(C) fcc (D) None of these

Sol. **(C)**

The close packing in the crystal is 0.52, 0.68 and 0.74 for simple cubic, bcc, and fcc respectively.

i.e the close packing is maximum is fcc.

Ex.12 Bragg's equation is-

(A) $n\lambda = 2\theta \sin \theta$ (B) $n\lambda = 2d \sin\theta$

(C) $2n\lambda = d \sin \theta$ (D) $\lambda = (2d/n) \sin \theta$

Sol. **(B)**

Bragg's equation is $n\lambda = 2d \sin \theta$.

Ex.13 Copper metal has a face-centred cubic structure with the unit cell length equal to 0.361 nm. Picturing copper ions in contact along the face diagonal, The apparent radius of a copper ion is-

(A) 0.128 (B) 1.42

(C) 3.22 (D) 4.22

Sol. **(A)**

For a face-centred cube, we have,

$$\text{radius} = \frac{\sqrt{2}\,a}{4} = \frac{\sqrt{2} \times 0.361}{4}\text{nm} = 0.128.$$

Ex.14 The rank of a cubic unit cell is 4. The type of cell as-

(A) Body centred (B) Face centred

(C) Primitive (D) None

Sol. **(B)**

The number of atoms present in sc, fcc and bcc unit cell are 1, 4, 2 respectively.

Ex.15 At room temperature, sodium crystallises in a body centred cubic cell with a = 4.24 Å. The theoretical density of sodium is –(Atomic mass of sodium = 23.0 g mol^{-1})

(A) 2.05 g cm^{-3} (B) 3.45 g cm^{-3}

(C) 1.00 g cm^{-3} (D) 3.55 g cm^{-3}

Sol. **(C)**

The value of Z for a bcc unit cell is 2.

Volume V = $(4.24 \text{ A})^3$

$$\therefore \rho = \frac{ZM}{NV} = \frac{2 \times 23}{(6.023 \times 10^{23}) \times (4.24 \times 10^{-8})^3}$$

$$= 1.00 \text{ g / cm}^3$$