Solid State

Introduction

i.   Matter is divided into solids, liquids and Gases.

ii.   Random motion and weak intermolecular forces are characteristic of gases.

iii.   In liquid state, free movement of the molecules is limited due to cohesive forces.

iv.   In solid state atoms, ions or molecules are arranged orderly in a three dimensional manner due to strong binding forces. Thus Solids have generally high density, low compressibility, very slow or no diffusion. The vapour pressure of solids is generally much less than that of liquids at a definite temperature.

I. **Types of Solids**:   Solids are of two types – crystalline and amorphous solids.

A crystalline solid is one in which the component structural units are arranged in a definite geometrical order which is   characteristic of the substances. (Long range order)

Amorphous solids do not have regular and orderly arrangement of the building units of the substances. (Short range order)

II. Properties of solids

Sl. No.	Property	Crystalline solids	Amorphous solids
1	Condition of formation	Slow cooling without disturbing the liquid or disturbance	Rapid cooling with churning
2	Rigidity and hardness	Rigid and hard	Rigid and hard

3	Shape	Definite geometrical configuration	Particles are arranged not in regular order or arranged in short range order
4	Melting points	Sharp	Not sharp and melts over a range of temperature
5	Plane *surfaces*	Possess plane surfaces	Not bound by plane surfaces
6	X-ray diffraction	Characteristic X– ray diffraction	Diffraction bands are not given experiment bands are given bands are given.
7	Examples	KCl; CuSO$_4$. 5H$_2$O; KNO$_3$	Fused silica, glass, pitch, gelatinous

When Quartz is melted and rapidly cooled an amorphous solid result, in which SiO$_4$ chains are irregular.

I. Amorphous solids can be moulded or blown into articles of different shapes.

II. Amorphous solids have a tendency to flow, but very slowly. Hence, they are also called 'pseudo solids' or 'super cooled liquids'. Amorphous solids are 'isotropic' i.e. their physical properties are same in all directions.

III. Crystalline solids are 'anisotropic' i.e. some of their physical properties like electrical resistance or   refractive index show different values when measured along different directions.

IV. Amorphous solids are used in domestic constructions or appliances like photo voltaic cells, where the sunlight is transformed into electricity.

III. Classification of crystalline Solids: These are classified into ionic, covalent, metallic and molecular solids according to the nature of the building units, chemical bonding and the intermolecular forces in the crystal.

The characteristics of various types of solids are given in the table.

Type of solid	Constituent particles	Bonding or attractive forces	Examples	Physical nature	Electrical conductivity	Melting point
Molecular solids (i) Non polar	Molecules	London or Dispersion forces	$I_2, CO_2(s)$, $Ar(s)$	Soft		Very low
(ii) Polar		Dipole - dipole interactions	$HCl(s)$, $SO_2(s)$	Soft	Extremely low	Low
(iii) Hydrogen bonded		Hydrogen bonding	H_2O (ice)	Soft		Low
Ionic solids	Ions	Coulombic or electrostatic	$NaCl, MgO$, ZnS, CaF_2	Hard but brittle	Insulators in solid state but conductors in molten state and in aqueous solutions	High
Metallic solids	Positive ions in a sea of delocalised electrons	Metallic bonding	Fe, Cu, Ag, Mg, Sn, Au	Hard but malleable and ductile	Conductors in solid state as well as in molten state	Moderate to high
Covalent or network solids	Atoms	Covalent bonding	SiO_2(quartz), SiC, AlN, BN, C (diamond) C (graphite)	Very hard, except graphite	Insulators, except graphite	Very high High

IV. Coordination Number of Crystals: The coordination number of an atom or ion in solid is the number of nearest neighbours for that atom or ion

Eg:

1) In NaCl crystal, coordination number of Na^+ ion as well as Cl^- ion is 6.

2) Coordination number of C in diamond is 4

3) In Silica, coordination number of 'Si' is 4 while that of oxygen atom is 2

4) In metal lattices the coordination number of a metal atom is usually 8 or 12.

5) In ZnO, coordination number of Zn^{+2} ion as well as O^{-2} ion is 4.

6) In CsCl crystal, coordination number of Cs^{+} ion as well as Cl^{-} ion is 8.

V. Limiting Radius ratio:

The shape of ionic crystal and Co-ordination number depends on cation to anion radius ratio (i.e. r_c/r_a value) called 'Limiting Radius Ratio'

Limiting radius ratio	Coordination number	Shape or structure
< 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 centred

Ex.1. The r_c/r_a for NaCl is 0.52. Thus NaCl has F.C.C Lattice

2. The r_c/r_a for CsCl is 0.93. Thus CsCl has b.c.c Lattice

VI. Metallic Bonding: Metallic bond is neither ionic nor covalent in nature. Three theories are familiar in explaining bonding in metallic solids.

1. Electron sea model of Drude and Lorentz

2. Valence bond theory of Linus Pauling

3. Molecular orbital theory of Hund and Mulliken

(1) Electron Sea Model

According to this in a metallic solid all metal atoms lose their valence electrons to form positive metal ions (called Kernels) and a sea of electrons (called delocalised or mobile electrons). As a result an electrostatic force of attraction develops between Kernels and free electrons which is called metallic bond. It explains electrical conductivity and metallic luster.

Defects: Failed to explain quantitative calculations for the lattice energies of ionic compounds.

(2) Valence Bond Theory or Resonance theory: According to this theory,

The metallic bond is essentially a polar or a non polar covalent bond.

The covalent bond involves resonance between a number of structures having one electron and electron pair bonds. Resonance occurs due to the possibility of insufficient valence electrons for the formation of electron pair bonds with each atom of the metal. Resonance involves both covalent and ionic linkages.

Defects: It does not explain the conduction of heat in solids and their lustre. It does not explain the retention of metallic properties in liquid state.

VII. Close Packing in Three Dimensions

(i) Simple Cubic Arrangement

In this arrangement the spheres can be arranged in a layer such that each metal atom is in touch with four other atoms. A second layer of spheres is superposed on the first layer such that the spheres of the second layer are exactly above the spheres of first layer.

* Coordination number of each sphere is 6.

*In this structure the percentage space occupied is 52% & the remaining 48% space is void.

Eg: Polonium

(ii) Hexagonal Close Packed (HCP) Arrangement

It is also called as AB AB AB ...... type arrangement.

In any layer of spheres every sphere is in contact with six other spheres.

The vacant spaces between the spheres known as holes or voids

If the second layer of spheres is arranged by placing these spheres over the holes in the first layer, three of the six holes formed are only covered by the spheres. Out of the six holes; only three are covered by the spheres. Third layer of spheres can be superposed on the spheres of this layer directly over the spheres of the first layer. i.e. third layer is the repetition of the second layer.

In HCP each sphere is in contact with 6 spheres in its own layer. It also touches '3' spheres in the above layer and 3 spheres in the below layer. Thus the co-ordination number is 12.

In this arrangement atoms occupy 74% of the available space and thus have 26% vacant space.

E.g. Be, Mg, Tl, Cd, Co, Zn, Ce, Ti, Os, Ru, etc.

(iii)   Body Centered Cubic (BCC) Arrangement

This arrangement is obtained when the spheres in the first layer are slightly opened up, ie. None of the spheres touches each other. I n the second layer, the spheres are placed at the top of hollows in the first layer. In the third layer, spheres are placed exactly above the first layer. Each sphere in this system of packing is in contact with eight spheres, four in the lower layer and four in the upper layer. Thus the co-ordination number is 8.

In this arrangement atoms occupy 68% of the available space and thus have 32% vacant space.

This lattice is quite common for Alkali metals.

Eg. Na, K, Rb, Cs, Ba, Cr, Mo, W

(iv)   Face Centered Cubic (FCC) Arrangement or Cubic Closed Packing

This type of arrangement is known as ABC ABC ABC ...... arrangement.

In this arrangement, the spheres of the   second layer are placed in the holes formed by the first layer and the spheres in the third layer may be placed in the hollows of the second layer such that the sphere is not exactly above the sphere in the first layer.

* Coordination number of each sphere is 12.

In this arrangement atoms occupy 74% of the available space and thus have 26% vacant space.

Eg: - Al, Cu, Au, Pb, Pt, Pd, Ni and Ca.

VIII. Unit Cell in Two Dimensional &Three Dimensional Lattices

(i) Space Lattice: The pattern of points which indicates the arrangement of particles in the crystal is known as space lattice.

Ex. The space lattice of sodium chloride is obtained by joining the space lattices of Na^+ and Cl^- ions.

(ii)Unit Cell: - The smallest three dimensional portion of the space lattice which when repeated again and again in different directions produces the complete space lattice is called the unit cell.

Types of unit cells:

i) Primitive or simple unit cell: The unit cell without a point inside is known as 'primitive unit cell' i.e., the particles are present only at the corners of the unit cell.

Ii) Centered unit cell: Contains a point inside is known as centered unit cell. Eg. F.C.C, B.C.C, End face centered unit cell.

 a) In face-centered unit cell: in addition to the particles at the corners, there is one particle present at the centre of every face.

It has 14 lattice points (8 corners and 6 face centers)

 b) In End face centered unit cell: in addition to the particles at the corners, there is one particle in the centre of two opposite faces.

It has 10 lattice points (8 corners and 2 face centers)

c) In body-centered unit cell: in addition to the particles at the corners, there is one particle present within the body of the unit cell.

It has 9 lattice points (8 corners + 1 body centre)

IX. Crystal Systems

On the basis of symmetry and set of crystallographic parameters crystals are classified into 14 types of crystal lattices (Bravais lattices) and 7 different types of crystal systems.

The intercepts on the X,Y and Z axes are designated as a, b and c respectively. The angle between the Y and Z axes is, that between X and Z axes is and that between X and Y axes is .

Seven primitive cells and their possible variations as centred unit cells

Crystal system	Possible variations	Axial distances or edge lengths	Axial angles	Examples
1. Cubic	Primitive, f.c.c, Body-centered	a = b = c	$\alpha = \beta = \gamma = 90°$	NaCl, Zinc blend, Cu
2.Tetragonal	Primitive, Body-centered	a = b≠ c	$\alpha = \beta = \gamma = 90°$	White tin, SnO_2 TiO_2, $CaSO_4$
3.Orthorhombic	Primitive, Body-centered, Face-centered End-centered	a ≠b≠c	$\alpha = \beta = \gamma = 90°$	Rhombic sulphur KNO_3, BaSO_4
4.Hexagonal	Primitive	a = b ≠c	$\alpha = \beta = 90°$ $\gamma = 120°$	Graphite, ZnO, CdS

5. Rhombohedral or Trigonal	Primitive	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	Calcite ($CaCO_3$), HgS (cinnabar),$KMnO_4$,Bi,As,Sb
6.Monoclinic	Primitive End-centered	$a \neq b \neq c$	$\alpha = \gamma = 90°$ $\beta \neq 120°$	$Na_2SO_4.10H_2O$ monoclinic sulphur,
7.Triclinic	Primitive	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	$K_2Cr_2O_7$, $CuSO_4.5H_2O$

*Ice & Quartz may give hexagonal or trigonal crystals

Space lattices of crystal system

S.No.	Crystal system	Number. of Bravais lattices	Common names of the lattices
1	Cubic	3	Simple cubic, face centered and body centered cubes
2	Tetragonal	2	Simple cubic and body centered tetragonal prisms
3	Rhombic	4	Rectangular, body centered, face centered and end centered rhombic prisms
4	Hexagonal	1	Hexagonal prism
5	Trigonal	1	Rhombohedral
6	Monoclinic	2	Primitive and edge centered
7	Triclinic	1	Triclinic primitive

X. characteristics of a crystal lattice

      a) Each point in a lattice is called lattice point or lattice site.

      b) Each point in a crystal lattice represents one constituent particle which may be an atom, a molecule or an ion.

      c) Lattice points are joined by straight lines to bring out the geometry of the lattice.

XI. Position of ions in cubic unit cell and contribution to unit cell

| Position of ion in unit cell	Number of unit cells sharing	Contribution of ion to each unit cell
Centre of the body	1	1
Centre of the face	2	1/2
Edge of a face	4	1/4
Corner of cube	8	1/8

Effective Number of Atoms (Z) In Unit Cell:

IN SIMPLE CUBIC IS 1, B.C.C IS 2 AND F.C.C IS 4

XIII. Interstitial Voids:

    The empty spaces between the three dimensional layers are known as voids or holes. There are two types of common voids possible. They are called tetrahedral and octahedral voids. These are also called interstices.

    Tetrahedral void: A hole formed by three spheres of a layer in contact with each other and also with a sphere on the top or bottom layer is a hole between four spheres. The spheres are arranged at the vertices of a regular tetrahedron**.** Such a hole is called tetrahedral void.

*Radius ratio of tetrahedral void= 0.225X Radius of atom
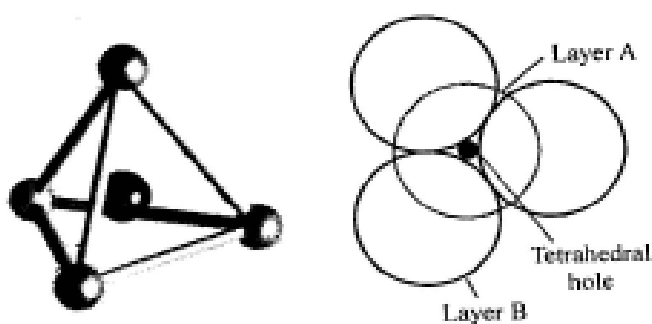
Octahedral void: A hole formed by three spheres of a hexagonal layer and another three spheres of the adjacent layer is a hole between six spheres. The spheres are arranged at the vertices of a regular octahedron. Such a hole is called octahedral void.
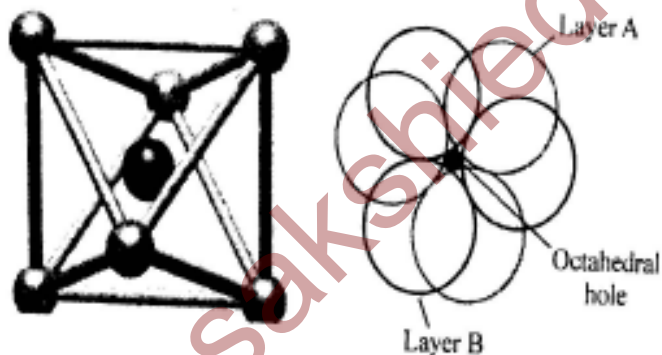
*Radius ratio of octahedral void,= 0.414X Radius of atom

If there are 'n' atoms present in the unit cell of close packed structure the number of tetrahedral voids are '2n' and the number of octahedral voids are 'n'.

XIV. Relation between atomic radius and the edge of the Unit cell. (For elements)

   i) **In simple cubic structure:** edge length (a) = 2r

                  Distance between nearest neighbours (d) = 2r = a

                  Atomic radius (r) = a/2.

ii)   In body centered cubic lattice

Body diagonal length = 4r = $\sqrt{3}$ a

Distance between nearest neighbours (d) 2r = $\frac{\sqrt{3}}{2} \times a$ = 0. 866 a

Atomic radius (r) = $\frac{\sqrt{3}}{4} \times a$ = 0. 433 a

iii)   In face centered cubic lattice: - face diagonal length (4r) = $\sqrt{2}\,a$

Distance between nearest neighbours (d) = 2r = $\frac{a}{\sqrt{2}}$ = 0.707 a

Atomic radius (r) = $\frac{a}{2\sqrt{2}}$ = 0.3535 a

XV.   Packing Efficiency: The percentage of total space filled by the particles in a solid is called packing efficiency.

Packing efficiency = packing fraction X 100.

Packing fraction = $\frac{Volume\,occupied\,by\,all\,the\,spheres\,in\,the\,unit\,cell}{Total\,volume\,of\,\,the\,unitcell}$

In both H.C.P and C.C.P structures

Packing efficiency = $\frac{\pi\sqrt{2}}{6} \times 100$ =0.74X 100 = 74%

In B.C.C structure packing efficiency= $\frac{\pi\sqrt{3}}{8} \times 100$ = 0.68X 100 = 68%

In simple cubic lattice: Packing efficiency = $\frac{\pi}{6} \times 100$ = 0.524 X 100 = 52.4%

* Hexagonal close – packing and cubic close – packing are more efficient than any other sort of arrangement.