## **Chapter 1: The Solid State**

## **Solids**

Solids are the chemical substances which are characterised by define shape and volume, rigidity, high density, low compressibility. The constituent particles (atoms, molecules or ions) are closely packed and held together by strong interparticle forces

## **Types of Solids**

The solids are of two types : Crystalline solids and amorphous solids.

## **Distinction Between Crystalline and Amorphous Solids**

S.No Crystalline solid	Amorphous solids
1 These have definite and regular arrangement of the constituent particles in space.	These doesn't have any regular arrangement of the constituent particles in space.
2 These are true solids.	Theseare super cooled liquids or pseudo soilds.
3 These have long order arrangement of the particles.	These have short order arrangement of particle.
4 These are anisotropic in nature, i.e., their physical properties are different in different directions.	These are isotropic in nature i.e., their physical properties are same in all the directions.
5 They have sharp melting points.	They melt over a certain range of temperature.
6 They undergo a clean cleavage when cut.	They undergo irregular cleavage when cut.

rays are diffracted. If the waves are in phase after reflection, the difference in distance travelled by the two rays ti.e., path difference) must be equal to an integral number of Wavelength,  $n\lambda$  for constructive.



Thus, path difference = WY + YZ

= XY  $\sin \theta$  + xy  $\sin \theta$ 

= 2 XY sin  $\theta$  = 2d sin  $\theta$ 

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

This equation is called Bragg's equation.

Where, n = 1. 2, 3... (diffraction order)

 $\lambda$  = wavelength of X·rays incident on crystal

d = distance between atomic planes

 $\theta$  = angle at which interference occurs.

## **Unit Cell**

The smallest geometrical portion of the crystal lattice which can be used as repetitive unit to build up the whole crystal is called unit cell.

#### **Types of Unit Cell**

#### ) Simple or primitive Unit cell

In which the particles are present at the corners only.





**Number of Particles Per Unit Cell** 

	No. of part			
Unit cell	Corner	- Face	Centre	lotal
Simple cubic	$8 \times \frac{1}{8}$	1	3 <u>—</u> 8	1
Face centred	$8 \times \frac{1}{8}$	$6 \times \frac{1}{2}$	-	4
Body centred	$8 \times \frac{1}{8}$	-	1	2
End centred	$8 \times \frac{1}{8}$	$2 \times \frac{1}{2}$	-	2

#### Seven Crystal Systems

There are about 230 crystal forms, which have been grouped into 14 types of space lattices, called Bravais Lattices, on the basis of their symmetry and seven different crystal systems on the basis of interfacial angles and axes.

	1	Parameters of unit cell			
	Crystal system	intercepts/axes	Angles		
1.	Cubic	a = b = c	$\alpha = \beta = \gamma = 90^{\circ}$		
2.	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^{\circ}$		
З.	Rhombohedral	a = b = c	$\alpha = \beta = \gamma \neq 90^{\circ}$		
4.	Orthorhombic	a≠b≠c	$\alpha = \beta = \gamma = 90^{\circ}$		
5.	Monoclinic	a≠b≠c	$\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$		
6.	Triclinic	a≠b≠c	$\alpha \neq \beta \neq \gamma \neq 90^{\circ}$		
7,	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$		

#### Seven Crystal Systems

#### **Packing Fraction**

High pressure increases CN and high temperature decreases the CN.

## **Close Packing in Crystals**

## **Two Dimensional Packing of Constituent Particles**

#### ) Square close packing

Space occupied by spheres is 52.4%.



## i) Hexagonal close packing

Space occupied by spheres is 60.4%.Hence. It is more efficient.



**Three Dimensional Packing of Constituent Particles** 

- (i) ABAB arrangement gives hexagonal close packing (hcp).
- (ii) ABCABC arrangement gives cubic close packing or face centred CUbIC packing (ccp or fcc).
- In both these arrangements 740/0 space is occupied
- Coordination number in hop and ccp arrangement is 12 while in bcc arrangement, it is 8.
- Close packing of atoms in cubic structure = fcc > bcc > sc.
- All noble gases have ccp structure except He (hcp structure).

## Void or Space or Holes

• Empty or vacant space present bet veen spheres of a unit cell, is called void or space or hole or interstitial void. When particles are closed packed resulting in either cpp or hcp structure, two types of voids are generated:

• **Tetrahedral voids** are holes or voids surrounded by four spheres Present at the corner of a tetrahedron. Coordination number of a tetrahedral void is 4.

Density of unit cel1 = mass of unit cell / volume of unit cell

 $d = Z * M / a^3 = ZM / a^3 * NA$ 

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

where, d = density of unit cell

M = molecular weight

Z = no. of atoms per unit cell

 $N_A$  = Avogadro number

a = edge length of unit cell.

## The Structure of Ionic Crystals

The ionic radius ratios of cation and anion, play a very important role in giving a clue to the nature of the crystal structure of ionic substances.

Radius Ratio and Crystal Structure

S. No.	Radius tatio	Coordination number	Shape	Crystal structure	Example
1.	< 0.225	2 or 3	Linear or triangular	Linear or triangular	B <sub>2</sub> O <sub>3</sub>
2.	0.225-0.414	4	Tetrahedral	ZnS type	CuCl, CuBr, HgS, BaS
3.	0.414-0.732	. 6	Octahedral	NaCl type	MgO, NaBr, CaS, KBr, CaO
4.	0.732 or more	8	Cube	CsCl type	Csl, CsBr, NH <sub>4</sub> Br

Ionic crystals may be of two types

(i)AB type and

(ii)  $A_2B$  or  $AB_2$ 

Structure of Ionic Crystals

Point defects are the irregularities or deviations from ideal arrangement around a point or an atom in a crystalline substance Point defects can be classified into three types : (1) psychometric defects (2) impurity defects (3) non-stoichiometric defects

#### . Stoichiometric Defect

These are point defects that do not disturb' the -stoichiometric of the solid. They are also called intrinsic or thermodynamic defects. In ionic solids, basically these are of two types, Frankel defect and Schottky defect

11 A A A	Schottky defect	Frenkel defect
1.	It is due to equal number of cations and anions missing from the lattice sites.	It is due to the missing of ions (usually cations) from the lattice sites and they occupy the interstitial sites.
2.	This results in the decrease in density of crystal.	It has no effect on the density of crystal.
3.	This type of defect is found in highly ionic compounds with high coordination number, e.g., NaCl, CsCl, etc.	This types of defect is found in crystal, where the difference in the size of cations and anions is very large, e.g., AgCI, ZnS, etc.

AgBr has both Schottky and Frenkel defects. Frenkel defects are not found in pure alkali metal halides because cations are of large size.

#### . Impurity Defect

• It arises when foreign atoms or ions aloe present in the lattice. In case of ionic compounds, the impurity 1S also ionic in nature. When the impurity has the same charge as the host ion. it just substitutes some of the host ions.

• Impurity defects can also be introduced by adding impurity ions having different charge than host ions. e.g. molten NaCl containing a little amount of SrCI2 is crystallised. In such cases,

• Cationic vacancies produced = [number of cations of higher valence \* Difference in valence of the host cation and cation of higher valence

## . Non-Stoichiometric Defect

Non-stoichiometric crystals are those which do not obey the law of constant proportions. The numbers of positive and negative ions present in such compounds are different from those expected from their ideal chemical formulae. However, the crystal as a whole in neutral.



[The electricity produced on heating a polar crystal is called 'pyroelectricity'.] When mechanical stress is applied on polar crystals, electricity produced due to displacement of ions is called 'piezoelectricity'

#### Semiconductors

Electronic conductors having electrical conductivity in the range of  $10^4 - 10^7 \Omega^{-1} \text{ cm}^{-1}$  are known as semiconductors. Examples Si, Ge Sn (grey), Cu<sub>2</sub>O, SiC and GaAs.

#### **Intrinsic Semiconductors**

Pure substances that are semiconductors are known as Intrinsic Semiconductors e.g., Si, Ge

#### **Extrinsic Semiconductors**

Their conductivity is due to the presence of impurities. They are formed by doping. It is defined as addition of impurities to a semiconductor to increase the conductivity. Doping of Si or Ge is carried out with P, As, Sb, B, Al or Ga.

(i) n-type semiconductors Silicon doped with 15 group elements like phosphorus is called ntype semiconductor. The conductivity is due to the presence of negative charge (electrons),

(ii) p-type semiconductors Silicon doped with 13 group element like gallium is called p-type semiconductor. The conductivity is due to the presence of positive holes.

• Some typical 13-15 compounds are InSb, AlP and GaAs and SOme typical 12-16 compounds are ZnS, CdS. CdSe and HgTe.

• These exhibit electrical and optical properties of great use in electronic industry.

#### **Magnetic Properties of Solids**

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xample: iron, copper, diamond, graphite etc.

olids: The arrangement of constituent particles is an irregular xample: Glass, plastics, rubber etc.





olids e solids:

finite characteristic geometrical shape.

g range order.

arp melting point.

tropic in nature i.e. their physical properties show different values d along different directions in the same crystal.

finite and characteristic heat of fusion.

true solids.

a sharp edged tool, they split into two pieces and the newly generated ain and smooth. photo bonabi

regular shape.

ort range order.

soften over a range of temperature.

opic in nature i.e. their physical properties are the same in all

a sharp edged tool, they cut into two pieces with irregular surfaces. ve definite heat of fusion.

l pseudo solids or super cooled liquids. This is because they have a *w*, though very slowly.

ds:

tuent	Bonding/	Electrical	Physical	Melting	Examples
es	Attractive	conductivity	nature	point	
	Forces				
ıles	Dispersion or	Insulator	Soft	Very	Ar, CCl4,
	London forces			low	H2, I2,
					CO2
ıles	Dipole- dipole	Insulator	Soft	Low	HCl, solid
	interactions				solid NH3
ıles	Hydrogen	Insulator	Hard	Low	H20 (ice)
	bonding				

s: Molecules

s: Ions

es: Atoms

- Forces: Covalent bonding
- rity: Conductors in solid state as well as in molten state
- rd but malleable and ductile
- y high
- artz), SiC, C (diamond), C(graphite)



arrangement of constituent particles in three dimensions is called



sites:



Parameters which characterise a unit cell

 $\gamma = 90^{\circ}, a = b = c$   $\beta = \gamma = 90^{\circ}; a = b \neq c$   $\alpha = \beta = \gamma = 90^{\circ}; a \neq b \neq c$   $\gamma = 90^{\circ}, \beta \neq 90^{\circ}; a \neq b \neq c$   $\beta = 90^{\circ}, \gamma = 120^{\circ}; a = b \neq c$ or trigonal:  $\alpha = \beta = \gamma \neq 90^{\circ}; a = b = c$  $\beta \neq \gamma \neq 90^{\circ}; a \neq b \neq c$ 

ple unit cells have constituent particles only at its corners.

Ils are those unit cells in which one or more constituent particles are tions in addition to those present at the corners.

ells:

nit cell:

ne constituent particle present at the centre of each face in addition to t the corners.

nit cell:



icles at corner is unit cells Open structure

Space-filling structure Actual portions of atoms

Figure representing a primitive cubic unit cell

resent at the centre of the face, it is shared by two unit cells. So, only a ctually belongs to the unit cell.



esent at the body centre, it is not shared by any other unit cell. So, that letely belongs to the same unit cell.



Figure representing a body centric cubic unit cell

resent at the edge centre, it is shared by four unit cells. So, only one

ways:

packing and ii) Hexagonal close packing.

in three dimensions: They can be obtained by stacking the two vers one above the other. It can be obtained in two ways:

packed layers and ii) Hexagonal close packed layers.

f the second row are placed exactly above those of the first row. This re aligned horizontally as well as vertically. The arrangement is AAA ion number is 4.



# g:

f the second row are placed above the first one in a staggered manner its spheres fit in the depression of the first row. The arrangement is rdination number is 6.



Three dimensional close packing from two dimensional square close packed layers

e packing from two dimensional hexagonal close packed layers: There as:

d layer over the first layer

layer over the third layer

r over the first layer:

al layer is considered as A, the second layer which is placed above the way that the spheres of the second layer (considered as B) are placed of the first layer. This gives rise to two types of voids: tetrahedral voids s.

over the third layer:

bilities:

trahedral voids:

al voids of the second layer may be covered by the spheres of the third ise to ABABAB type pattern. The three dimensional structure is called e packed structure. The coordination number is 12. Examples: Mg, Zn.



tahedral voids:

C

al voids of the second layer may be covered by the spheres of the third rise to ABCABCABC type pattern. The three dimensional structure is se packed structure or face centred cubic structure. The coordination fxample: Cu, Ag.



ds



backing or cubic close packing arrangement, the octahedral and present. The number of octahedral voids present in a lattice is equal to acked particles. The number of tetrahedral voids is twice the number

packed particles = n esent in octahedral voids = n articles present in tetrahedral voids = 2n

of total space occupied by constituent particles (atoms, molecules or

 $= \frac{\text{Volume occupied by spheres}}{\text{Total volume of unit cell}} \times 100\%$ Face centred unit cell = 74%

oody centred cubic unit cell =68%

simple cubic unit cell = 52.4%

cell: a  $\mathbb{Z} 2\sqrt{2r}$ cell: a =  $\frac{4r}{\sqrt{3}}$ = (edge length)<sup>3</sup> = a<sup>3</sup> ell: Volume =  $(2r)^3$ rell: Volume  $\mathbb{Z} (2\sqrt{2r})^3$ cell: Volume =  $\left(\frac{4r}{\sqrt{3}}\right)^3$ unit cell (z): hit cell: z = 1 hit cell: z = 4 nit cell: z = 2

sically irregularities in the arrangement of constituent particles.

the irregularities or deviations from ideal arrangement around a point ystalline substance.

he irregularities or deviations from ideal arrangement in entire ints.

nt defects:

or intrinsic or thermodynamic defects

oint defects that do not disturb the stoichiometry of the solid.

chiometric defects for non- ionic solids

have vacancy defect when some of the lattice sites are vacant. This crease in density of the substance.



have interstitial defect when some constituent particles (atoms or an interstitial site. This defect results in increase in density of the



Interstitial defect chiometric defects for jonic solids

smaller ion (usually cation) is dislocated from its normal site to an creates a vacancy defect at its original site and an interstitial defect at t does not change the density of the solid. Frenkel defect is shown by which there is a large difference in the size of ions. It includes ZnS, I.



Frenkel defects -stoichiometric defects:

is due to excess of metal cations.

have an extra metal ion if the negative ion is absent from its lattice ttice site is called a hole. To maintain electrical neutrality this site is lectron. The hole occupied by an electron is called f-centre or re. The F- centre is responsible for the colour of the compound. ations:

d to have extra cations if a cation is present in the interstitial site. ent in the interstitial site to maintain the electrical neutrality. s based on their electrical conductivities:

conductivities ranging between  $10^4$ to $10^7$ ohm $^{-1}$ m $^{-1}$ are called

ls with very low conductivities ranging between  $10^{-20}$ to $10^{-10}$ 

## rs

s with conductivities in the intermediate range from  $10^{-6}$  to  $10^4$ 

zed by a band structure. The highest filled band is called valence unoccupied band is called conduction band. The gap between the rbidden band.

ent types of solids based on their electrical conductivity ors, the valence band and conduction band overlap.

nductors, forbidden gap is small. Therefore, some electrons may on band and show some conductivity. Electrical conductivity of acreases with rise in temperature, since more electrons can jump band.

ors:

luctors

semiconductors in which the forbidden gap is small. Only some onp to conduction band and show some conductivity. They have very luctivity. Example: Silicon, germanium.

ductors

riate impurity is added to an intrinsic semiconductor, it is called ductors. Their electrical conductivity is high.

ng an appropriate amount of suitable impurity to increase the onductors is known as doping.

e formed by the combination of group 12 and group 16 compounds. age valency of 4. Examples - ZnS, CdS, CdSe and HgTe.

ls:

e formed by the combination of group 13 and group 15 compounds. age valency of 4. Examples - InSb, AlP and GaAs.

some magnetic properties associated with it. The origin of these electrons.

om behaves like a tiny magnet. Its magnetic moment originates from (i) its orbital motion around the nucleus and (ii) its spin around its

ances based on their magnetic properties:

stances

ubstances which are weakly attracted by the magnetic field. It is due e or more unpaired electrons.

tances

stances are weakly repelled by a magnetic field. Diamagnetism is substances in which all the electrons are paired and there are no s.

bstances

ubstances which are attracted very strongly by a magnetic field.

c substances

number of parallel and antiparallel magnetic dipoles resulting in a oment.

ostances

al number of parallel and antiparallel magnetic dipoles resulting in a nt.