

## SOLID STATE

### Density, Bragg's Equation, Crystal Defects and Properties of solids

1. Density of unit cell,

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

Where, z = No. of atoms present per unit cell,

M = Atomic mass of element.

a = Edge of the cube crystal in pm,

$N_0$  = Avogadro number,

$a^3$  = volume of the unit cell

### X – RAY STUDY OF CRYSTAL STRUCTURE – BRAGG'S METHOD

#### BRAGG'S EQUATION – X – RAY DIFFRACTION STUDIES

X- Rays produce diffraction pattern with crystalline substances because the interatomic distance in a crystal is in the same order as the wave length of x – rays ( $1 \text{ \AA}$ ).

- i. In case of constructive interference, Resultant wave amplitude =  $2E_0$ , path difference =  $n\lambda$  ( $n = 1, 2, 3, \dots$  etc).
- ii. In case of destructive interference, Resultant wave amplitude =  $E_0 - E_0 = 0$ ,

$$\text{Path difference} = \left( (2n+1) \frac{\lambda}{2} \right)$$

iii. Bragg's equation:  $2d\sin\theta = n\lambda$ , Where d = distance between successive atomic planes

$\theta$  = angle of the incident X-rays with the crystal surface,  $\lambda$  = wavelength of the X-rays used

$n = 1, 2, 3, \dots$  Called the order of diffraction maxima. As n value increases ' $\theta$ ' increases

iv: The diffracted beam makes an angle of  $2\theta$  with the direction of the incident beam.

v. In rotating crystal method a large single crystal is to be taken with well developed planes.

vi. In NaCl crystal the 'd' values are in the ratio of 1:0.703:1.134. It confirms the f.c.c structure of NaCl.

#### DEFECTS IN CRYSTALS

Stoichiometric compounds are called Daltonides, non-stoichiometric compounds are called Berthollides.

Point defects are the irregularities or deviations from ideal arrangement around a point or an atom in a crystalline substance

## TYPES OF CRYSTAL DEFECTS

**INTRINSIC DEFECTS:** These are seen in pure crystals

**EXTRINSIC DEFECTS:** These are due to the impurities in the solids

**POINT DEFECTS:** These occur at the lattice points or sites in the crystals

**EXTENDED DEFECTS:** These are present in one or more dimensions

Properties like density, entropy and heat capacity are influenced by crystal defects to a lesser extent.

The properties like mechanical strength, electrical conductivity and chemical activity of the solids are influenced by crystal defects to a greater extent.

Thermodynamically all solids possess a tendency to acquire defects because defects result in disorder and hence increase the entropy of the system

Electron microscope is used to know the defects in a solid crystal

### STOICHIOMETRIC DEFECTS

They are also called intrinsic or thermodynamic defects.

#### a) SCHOTTKY DEFECT

It is a vacancy defect in ionic solids. The crystal is said to have vacancy defect when some of the lattice points are vacant. In order to maintain electrical neutrality, the number of missing cations and anions are equal. Schottky defect was observed in ionic substances in which cation and anion are of similar size. This was shown by ionic crystals of high coordination number (6 or 8).

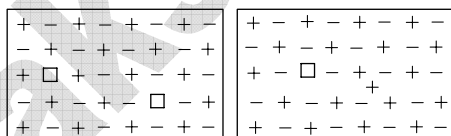
Eg. Include NaCl, KCl, CsCl, AgBr, etc.

As a result of Schottky defect density decreases and conductivity increases.

#### b) FRENKEL DEFECT

It is a combined effect of vacancy and interstitial defects. This is also called dislocation defect. Generally the smaller cation is dislocated from its normal site to an interstitial site (i.e either tetrahedral void or Octahedral void). Frenkel defect is shown by ionic substance in which there is a large difference in the size of ions. It is observed in ionic substances of low coordination number (usually 4 or 6). Examples include ZnS, AgCl, AgBr, AgI, etc.

As a result of Frenkel defect, the density does not change, but the conductivity increases. \*It may be noted that silver bromide (AgBr) shows both Schottky and Frenkel defects. Stability of the crystal decreases in stoichiometric defect.



**SCHOTTKY DEFECT      FRENKEL DEFECT**

**C) Non - stoichiometric defects:** The non - stoichiometric defects may be metal excess or metal deficient.

**I. Metal excess defects:** These defects may arise in two ways.

Metal excess due to anion vacancies

i) A negative ion may be missing from its lattice site, leaving a hole which is occupied by an electron.

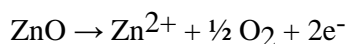
ii) The electrons trapped in anion vacancies are referred to as 'F' centres (F = Farben in German means colour).

iii) This defect is rather similar to Schottky defect and is found in crystals which are known to have Schottky defects.

- iv) For example when NaCl is treated with sodium vapours, a yellow coloured non-stoichiometric form of NaCl is obtained in which there is an excess of sodium ions.
- v) Sodium atom removes chloride ion from the anionic lattice site leaving its electron trapped in the vacancy and makes the lattice contain excess of sodium ions.
- vi) Similarly, excess of potassium in KCl makes the crystal to appear violet and excess lithium in LiCl makes it pink.
- vii) The electrons trapped in anionic vacancies absorb energy of the white light, giving yellow colour to NaCl, pink colour to LiCl and violet colour to KCl.

### II. Metal excess due to extra cations:

- i) In this case, the excess metal occurs when an extra positive ion occupies an interstitial position in the lattice.
- ii) The free electron is trapped in another interstitial site close to the vicinity of the interstitial cation. This electron helps to maintain the electrical neutrality.
- iii) For example, when zinc oxide is heated at high temperatures, it loses oxygen reversibly and turns yellow in colour.



- iv) The excess metal ion is accommodated in the interstitial site giving rise to electrons trapped in the neighbourhood.
- v) The higher electrical conductivity of the non-stoichiometric ZnO is due to these electrons.
- vi) Crystals with either type of metal excess defects contain free electrons and if these migrate, they conduct electricity.
- vii) The free electrons in each crystal can be excited to higher energy levels giving absorption spectra and as a consequence the compounds acquire colour.
- viii) ZnO is yellow when hot and white when cold.

### III) Metal deficiency defects:

- I) These defects occur in metals with variable oxidation states, i.e. the transition metals.
- ii) A cation may be missing from its lattice site but the electrical neutrality is maintained when the adjacent metal ion acquires higher oxidation state.

### IV) Impurity defects:

These defects arise due to the presence of foreign atoms or ions at the lattice sites. Thus depending upon the nature of impurity, two types of impurity defects are possible.

#### Impurity defect due to ions:

- i) This defect is brought about by adding impurity ions to ionic solid.
- ii) If the impurity ions are in different valence state from that of the host ions, vacancies are created.
- iii) For example, addition of CdCl<sub>2</sub> to AgCl (SrCl<sub>2</sub> or MgCl<sub>2</sub> to NaCl) yields solid solutions where the divalent cation Cd<sup>2+</sup> (or Sr<sup>2+</sup>, Mg<sup>2+</sup>) occupies the Ag<sup>+</sup> (or Na<sup>+</sup>) sites and produces cation vacancies equal in number to that of the divalent ions.
- iv) The SrCl<sub>2</sub> doped NaCl has much higher electrical conductivity than that of pure NaCl.

### PROPERTIES OF SOLIDS:

There is a close relationship between the properties of a solid and its structure and composition. Some of these properties are:

- I) Electrical properties
- II) Magnetic properties

Based on their electrical conductivity, solids can be broadly classified into three types:

- a) Metals (conductors)
- b) Insulators or Non-conductors
- c) Semi-conductors

Metals are conductors and have conductivity of the order of  $10^3$  to  $10^8 \text{ ohm}^{-1}\text{cm}^{-1}$

Insulators have very low conductivity of the order of  $10^{-10}$  to  $10^{-22} \text{ ohm}^{-1}\text{cm}^{-1}$

The solids whose conductivity lies between those of Metallic conductors and insulators are called semi-conductors. The order of conductivity of semi - conductors is  $10^{-6}$  to  $10^4 \text{ ohm}^{-1}\text{cm}^{-1}$

The electrical conductivity that is observed is usually related to defects in the crystal.

The mechanism of electrical conductivity may be given in terms of

a) Vacancy Mechanism   b) Interstitial Mechanism and   c) Interstitialcy Mechanism

- i. The Magnitude of electrical conductivity strongly depends on the number of electrons available to participate in the conduction process.
- ii. In Metals the conductivity depends on the number of valence electrons present per atom.
- iii. when a large number of atoms unite their wave functions interact. This results in a large number of molecular orbitals or energy levels, some Bonding and some antibonding. These energy levels are closely spaced energy levels and are known as bands. The number of energy levels is equal to the number of Atomic orbitals interacting. One half of these resulting orbitals have lowered energy levels and are known as bonding orbitals. They are of similar energies and form a continuous band of orbitals.  
The other halves of resultant orbitals have raised energy levels are known as Antibonding energy levels or orbitals.
- iv. At all real temperatures the band has a large number of half filled energy levels. Electrons can flow readily through these bands only when the band is incompletely filled with electrons or when electronic band (filled energy levels) is very close to vacant molecular orbitals.
- v. At laboratory temperatures the conductivity of the metals is nearly independent of impurities and the lattice defects.
- vi. At low temperatures the mobility due to vibrations in the lattice is quite negligible and as a result the conductivity becomes infinitely large.
- vii. The conductivity of metals generally decreases with an increase in temperature. This is probably due to increased vibrations in the lattice points the resistance to the flow of electrons increases. The impurities in the metal and the imperfections in the lattice also contribute to the conductivity.
- viii. Measurement of the resistance of the metal as resistance ratio  $\rho_{300K} / \rho_{4.2K}$  explains the purity of the metal.

#### **Semi conductors:**

- i. Semi conductor's conductivities increase with increase in temperature. This is due to the fact that the electrons from the valence band jump to the conduction band.
- ii. Pure semi conductors which exhibit this property are known as intrinsic semi conductors.
- iii. The temperature zone where the conductivity depends on the thermal electrons and the holes in the lattice of the semi conductors is known as intrinsic region.  
At low temperature the conductivity is mainly determined by the concentrations of the electron donors and the acceptors. This region is known as extrinsic region.

#### **Doping: -**

- i. Addition of Boron (IIIA group) or P or As (VA group) element to alter the conductivity of Si or Ge is called as doping. In doping, VA (or) IIIA group element is called as dopant
- ii. Pure Si or Ge is intrinsic semiconductors
- iii. In doping, group IIIA element behaves as electron acceptor and group VA element behaves as donor.

- iv. When VA (or) 15<sup>th</sup> group element is added to Si, the crystal lattice does not change, but few Si atoms are replaced by group VA (or) 15<sup>th</sup> group elements, it forms covalent bonds with the fifth electron is delocalised, therefore becomes electrical conductor. Silicon doped with VA (or) 15<sup>th</sup> group element is known as 'n' type semi conductor (n = negatively charged electrons are responsible for conductivity)
- v. When IIIA (or) 13<sup>th</sup> group element like B (or) Ga or is added to Si, the substitution of few Si atoms by IIIA group takes place IIIA group element has only 3 valence electrons. One more electron is required; IT is left as a vacant place on the atom. This is called as electron vacancy or a hole. This electron vacancy in the crystal structure migrates from one atom to another. This is responsible for electrical conductivity of Si. 'Si' doped with IIIA (or) 13<sup>th</sup> group element is called p – type semiconductor
- vi. n – type and p – type semi conductors both are used in electronic devices  
Example : Diode, pnp or npn type semiconductors are used in transistors. These transistors are used to detect (or) amplify radio or audio signals In the conversion of radiant energy into electrical energy solar cell (p – n type ) is used

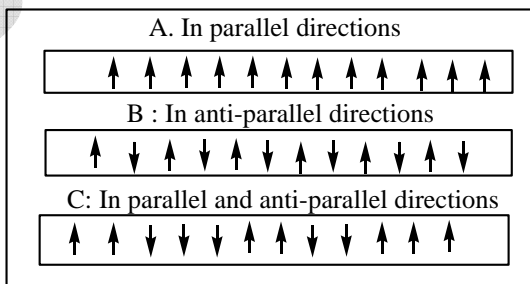
Transition metal oxides shows wide variation in these electrical properties. Metal sulphides of transition elements also exhibits wide variation in their electrical properties.

### MAGNETIC-PROPERTIES

Property	Information	Example	Applications
Diamagnetic	Repelled weakly in magnetic field. Such solids have only paired electrons.	C <sub>6</sub> H <sub>6</sub> , NaCl, TiO <sub>2</sub> , V <sub>2</sub> O <sub>5</sub> , ZrO <sub>2</sub>	Insulators
Paramagnetic	Have unpaired electrons and weakly attracted in magnetic field. They cannot be permanently magnetised.	O <sub>2</sub> , NO, Na atom, Ti <sub>2</sub> O <sub>3</sub> , VO <sub>2</sub> , VO, CuO, TiO	Electronic devices
Ferromagnetic	Also, have unpaired electrons. Strongly attracted in magnetic field. Such solids can be permanently magnetised.	Fe, Ni, Co, CrO <sub>2</sub>	CrO <sub>2</sub> is used in audio and video tapes
Antiferromagnetic	Unpaired electrons align themselves in such a way that resultant magnetic moment is zero.	Cr <sub>2</sub> O <sub>3</sub> , CoO, Co <sub>3</sub> O <sub>4</sub> , Fe <sub>2</sub> O <sub>3</sub> , MnO, MnO <sub>2</sub>	Used in the instruments of magnetic susceptibility measurement
Ferrimagnetic	Unpaired electrons align themselves in such a way that there is a net magnetic moment	Fe <sub>3</sub> O <sub>4</sub> , Ferrites	--

\*All the magnetically ordered solids transforms to the paramagnetic state at elevated temperatures due to the randomization of spins

Ex : V<sub>2</sub>O<sub>3</sub> changes antiferromagnetic to paramagnetic at 150 K and NiO at 523 K



“A’ represents alignment in Ferromagnetic, B represents alignment in Anti Ferromagnetic &”C” represents alignment in Ferri magnetism

### **DIELECTRIC PROPERTIES**

I.A dielectric is a substance in which an electric field gives rise to net flow of electric charge.Under the influence of applied field; dipoles are developed in these substances.

ii. These dipoles align in two different ways

a) In such a way that there is a net dipolemoment (non - compensatory way)

b) In such a way that there is no net dipolemoment (compensatory way)

iii. The crystals in which there is a net dipolemoment when subjected to a stress or pressure produce electricity. It is called piezoelectricity or pressure electricity.

iv. In some piezoelectric solids, dipoles are spontaneously aligned in a particular direction, even in the absence of electric field. They are called ‘ferroelectric substances’.

Eg: Barium titanate ( $\text{BaTiO}_3$ ), sodium potassium tartarate, potassium hydrogen phosphate ( $\text{KH}_2\text{PO}_4$ ) etc.

V. In some crystals, the dipoles align in opposite directions, then there is no net dipolement. They are called ‘antiferro electric substances’ eg: lead zirconate ( $\text{PbZrO}_3$ )

Vi. If electricity is produced on heating the crystal then it is called pyroelectricity.

**Applications:** Piezoelectric crystals are used in microphones, ultrasonic generators, sonar detectors, transducers etc.