THE SOLID STATE

TOPIC-4
CRYSTAL DEFECTS, ELECTRICAL AND MAGNETIC PROPERTIES OF CRYSTALS

VERY SHORT ANSWER QUESTIONS

1. **What are point defects in crystal structures?**

Ans: When deviations exist from the regular (or periodic) arrangements around an atom or a group of atoms in a crystalline substance, the defects are called point defects.

Type of point defects – point defects in a crystal may be classified into three types

(a) Stoichiometric defects

(b) Non – stoichiometry defects

(c) Impurity defects

2. **Explain Ferro magnetic solid materials?**

Ans: **Ferromagnetic substances:** Substances which show permanent magnetism even in the absence of the magnetic field are called Ferromagnetic substances. e.g. Fe Ni. CO, CrO_2 show Ferromagnetism. Such substances remain permanently magnetised, once they have been magnetised. This type of magnetism arises due to spontaneous alignment of magnetic moment due to unpaired electrons in the same direction.

3. **What are Daltonide and Berthollide compounds?**

Ans: The stoichiometric compounds are called Daltonide compounds. The Non-stoichiometric compounds with variable compositions are called Berthollides.

SHORT ANSWER QUESTIONS

1. **What are crystal defects? Explain**?

Ans: **Atomic imperfections / point defects:**

When deviations exist from the regular (or periodic) arrangements around an atom or a group of atoms in a crystalline substance, the defects are called point defects.

Type of point defects – point defects in a crystal may be classified into three types

(a) Stoichiometric defects

(b) Non – stoichiometry defects

(c) Impurity defects

2. What are Schottky Defects? Explain?

Ans: **Schottky defect:** If in an ionic crystal of the type $A^+ B^-$, equal number of cations and anions are missing from their lattice. It is called Schottky defect.

This type of defect is shown by highly ionic compounds which have

(i) High Co – ordination number and

(ii) Small difference in the sizes of cations and anions

A few examples of ionic compounds exhibiting Schottky defect are NaCl, KCl, KBr and CsCl.

CONSEQUENCES OF SCHOTTKY DEFECT

(a) As the number of ions decreases as a result of this defect, the mass decreases whereas the volume remains the same. Hence density of the solid decreases

(b) The crystal begins to conduct electricity to a small extent by ionic mechanism

(c) The presence of too many voids lowers lattice energy and the stability of the crystal

3. What are Frenkel Defects? Explain?

Ans: **Frenkel defect:** If an ion is missing from its correct lattice sites (causing a vacancy or a hole) and occupies an interstitial site, electrical neutrality as well as stoichiometry of the compounds are maintained. This type of defect is called **Frenkel** defect. Since cations are usually smaller it is more common to find the cations occupying interstitial sites.

This type of defect is present in ionic compounds which have

(i) Low co ordinations number

(ii) Larger difference in size of cation and anions

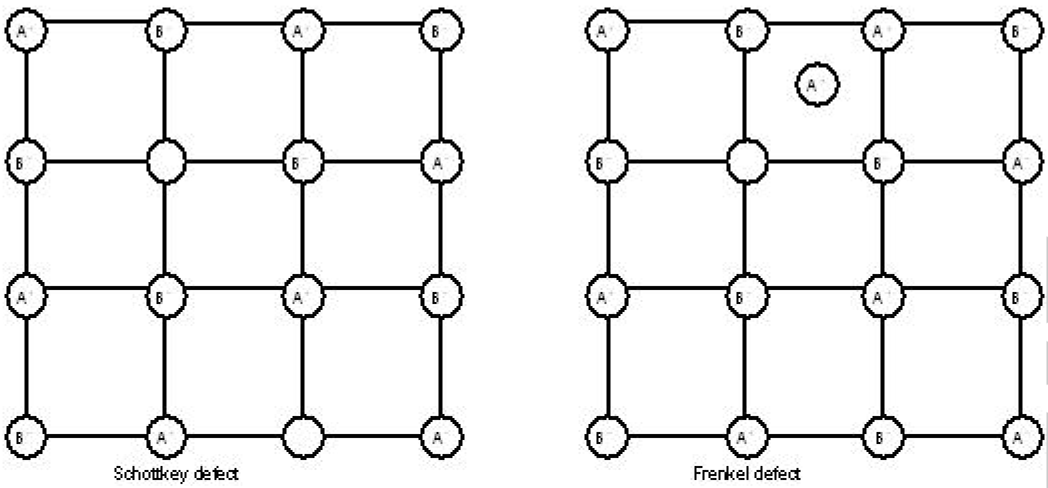
(iii) Compounds having highly polarising cation and easily polarisable anion. A few examples of ionic compounds exhibiting this defect are AgCl, AgBr, AgI, ZnS etc.

Consequences of Frenkel defect

(a) As no ions are missing from the crystal lattice as a whole, therefore density of the solid remains the same

(b) The closeness of like charges tends to increases the dielectric constant of the crystal

(c) The crystal conducts electricity to a small extent by ionic mechanism

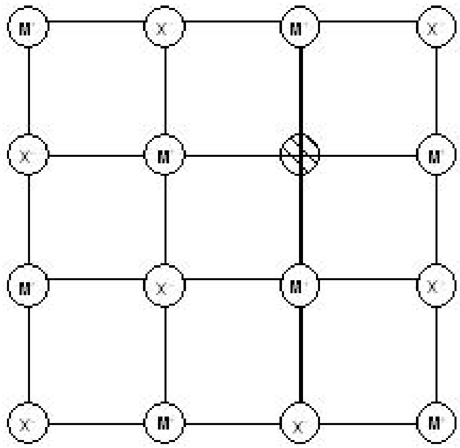


4. What are non-stoichiometric defects/ explain?

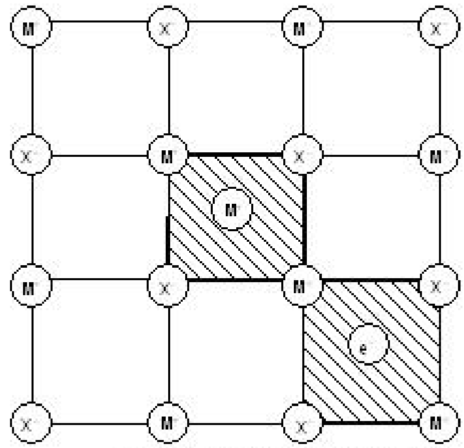
NON – STOICHIOMETRIC DEFECTS

If as a result of imperfection, the ratio of number of cation to anion becomes different from that indicated by the ideal chemical formula; the defects are called non – stoichiometric defects. These defects arise either due to excess of metal atoms or non metal atom or presence of impurities / foreign particle.

(a) **Metal excess defects due to anion vacancies**: - A compound may have excess metal ion if a negative ion is absent from its lattice site leaving a hole which is occupied by electron to maintain neutrality. The holes that are occupied by electrons are called ‘F’ centres (or colour centres) and are responsible for the colour of the compound and many interesting properties.



Metal excess – due to anion vacancies



Metal excess defect – due to interstitial cation

(ii) **Metal excess defects due to interstitial cations:** Metal excess may also be caused by an extra cation (positive ion) present in an interstitial site. Electrical neutrality is maintained by presence of an electron in another interstitial site. This defect is similar to Frenkel defect and is found in crystals having Frenkel defects.

(iii) **Metal deficiency due to cation vacancies: The** non-stoichiometric compounds may have metal deficiency due to the absence of a metal from its lattice site. The charge is balanced by an adjacent ion having higher positive charge. These types of defects are generally shown by compounds of transition elements.

(c) **Point defects due to the presence of foreign atoms**: These defects arise when foreign atoms are present at the lattice site (in place of host atoms) or at the vacant interstitial sites. In the former case, we get substitutional solid solutions. The formation of former depends upon the electronic structure of impurity while that of later on the size of impurity.

LONG ANSWER QUESTIONS

1. **How many types of semi-conductors are known? Explain the influence of doping on the conductivity of crystalline solids?**

Semi conductors: The solids with intermediate conductivities at the room temperature. Semi conductors allow a portion of electric current to flow through them.

Actually semi conductors are those solids which are perfect insulators at absolute zero, but conduct electric current at room temperature.

(1) **Intrinsic semi conductors** (semi-conductors due to thermal defects)

At zero Kelvin pure substance silicon and germanium act as insulators because electrons fixed in covalent bonds are not available for conduction. However at higher temperature some of the covalent bonds are broken and the electrons so released become free to move in the crystal and thus conduct electric current. This type of conduction is known as intrinsic conduction as it can be introduced in the crystal without adding an external substance.

(2) **Extrinsic semi conductors:** (semi conductors due to impurity defects)

The conductivity of pure silicon and germanium is very low at room temperature. The conductivity of silicon and germanium can be increased by doping with impurities producing n-type semiconductors or p – type semi conductors.

2. What do you mean by imperfections in solids? Write an essay on crystal defects. ?

Ans: **IMPERFECTIONS IN SOLIDS: DEFECTS IN CRYSTALS**

Atomic imperfections / point defects: When deviations exist from the regular (or periodic) arrangements around an atom or a group of atoms in a crystalline substance, the defects are called point defects. Type of point defects – point defects in a crystal may be classified into three types

(a) Stoichiometric defects

(b) Non – stoichiometry defects

(c) Impurity defects

Stoichiometry defect: The compounds in which the number of cation and anions are exactly in the same ratio as represented by their chemical formula are called stoichiometric compounds. The defects that do not disturb the ratio of cations and anions are called stoichiometric defect. These are of two types:

1. Schottky defect: If in an ionic crystal of the type $A^+ B^-$, equal number of cations and anions are missing from their lattice. It is called Schottky defect. This type of defect is shown by highly ionic compounds which have

(i) High Co – ordination number and

(ii) Small difference in the sizes of cations and anions

A few examples of ionic compounds exhibiting Schottky defect are NaCl, KCl, KBr and CsCl.

CONSEQUENCES OF SCHOTTKY DEFECT

(a) As the number of ions decreases as a result of this defect, the mass decreases whereas the volume remains the same. Hence density of the solid decreases

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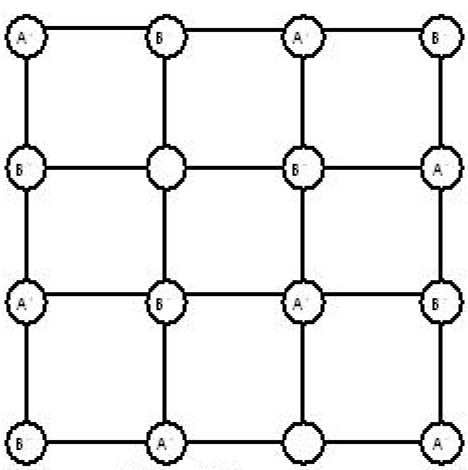
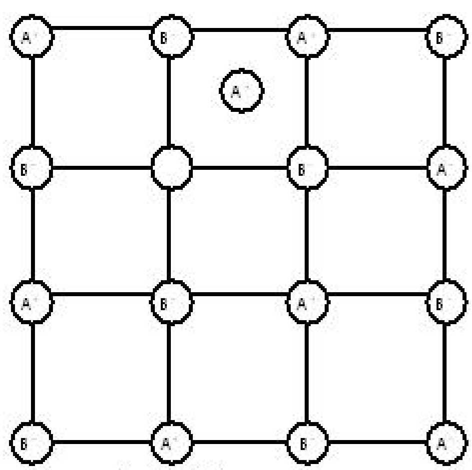


Schottkey defect

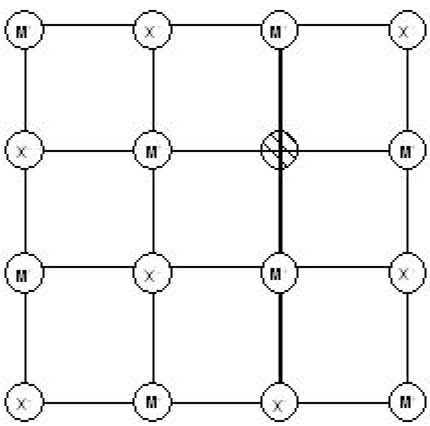


Frenkel defect

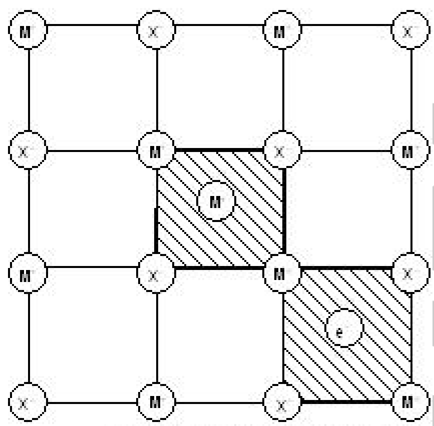
NON – STOICHIOMETRIC DEFECTS: If as a result of imperfection, the ratio of number of cation to anion becomes different from that indicated by the ideal chemical formula; the defects are called non – stoichiometric defects. These defects arise either due to excess of metal atoms or non metal atom or presence of impurities / foreign particle.

(a) **Metal excess defects due to anion vacancies**: - A compound may have excess metal ion if a negative ion is absent from its lattice site leaving a hole which is occupied by electron to maintain neutrality.

The holes that are occupied by electrons are called 'F' centres (or colour centres) and are responsible for the colour of the compound and many interesting properties.



Metal excess – due to anion vacancies



Metal excess defect – due to interstitial cation

(ii) **Metal excess defects due to interstitial cations:** Metal excess may also be caused by an extra cation (positive ion) present in an interstitial site. Electrical neutrality is maintained by presence of an electron in another interstitial site. This defect is similar to Frenkel defect and is found in crystals having Frenkel defects.

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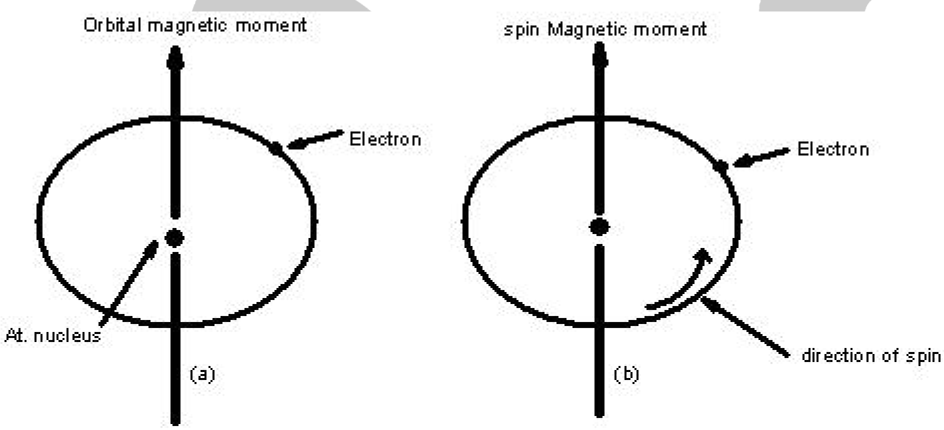
3. Explain the magnetic properties of solids?

MAGNETIC PROPERTIES: The magnetic properties of different materials are studies in terms of their magnetic moments which arise due to the orbital motion and spinning motion of the electron. As electron is charged particle, the circular motion of the electric charge causes the electron to act as a tiny electro magnet. The magnetic moment of the magnetic field generated due to orbital motion of the electron is along the axis of rotation. The electron also possesses magnetic moment due to the spin which is directed along the spin axis.

Thus, magnetic moment of the electron is due to travelling in closed path (orbital motion) about the nucleus and spinning on its axis. For each electron spin magnetic moment is $\pm\mu_B$ where μ_B, Bohr Magneton is the fundamental unit of magnetic moment and is equal to 9.27×10^{-24} em^2. The magnetic moment due to orbital motion is equal to $M_l\mu_B$ where M_l is the magnetic quantum number of the electron.

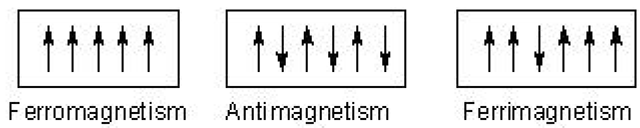


As magnetic moment is a vector quantity, the net magnetic moment of an electron may be represented by an arrow. Thus a material may be considered to contain a number of magnetic dipoles (similar to a bar magnet with north and south poles). Due to the magnetic moment of the electrons different substances behave differently towards the external applied magnetic field. Based on the behaviour in the external magnetic field, the substances are divided into different categories as explained below.

(i) **Diamagnetic substance:** Substances which are weakly repelled by the external magnetic fields are called diamagnetic field e.g. TiO_2, NaCl, benzene etc. Diamagnetic substances have all their electrons paired.

(ii) **Paramagnetic substances:** Substances which are weakly attracted by magnetic field are called paramagnetic substances. These substance have permanent magnetic dipoles due to the presence of some species (atoms, ions or molecules) with unpaired electron. The paramagnetic substances lose their magnetism in the absence of magnetic field. For e.g. TiO, VO_2 and CuO, O_2, Cu^{+2}, Fe^{+3} etc.

(iii) **Ferromagnetic substances:** Substances which show permanent magnetism even in the absence of the magnetic field are called Ferromagnetic substances. e.g. Fe Ni. CO, CrO_2 show Ferromagnetism. Such substances remain permanently magnetised, once they have been magnetised. This type of magnetism arises due to spontaneous alignment of magnetic moment due to unpaired electrons in the same direction.



(iv) **Anti Ferromagnetic substance:** Substances which are expected to possess paramagnetism or Ferromagnetism on the basis of unpaired electron but actually they posses zero net magnetic moment are called anti Ferromagnetic substances e.g. MnO, Mn_2O_3, MnO_2.

Anit Ferromagnetism is due to presence of equal number of magnetic moments in the opposite direction.

(v) **Ferrimagnetic substances:** Substance which are expected to posses large magnetism on the basis of the unpaired electrons but actually have small net magnetic moments are called Ferrimagnetic substances e.g. Fe_3O_3

(3) **Dielectric properties:** A dielectric substance is, in which an electric field gives rise to no net flow of electric charge. This is due to the reason that electrons in dielectric substances are tightly held by individual atoms. However when electric field is applied, Polarization takes place because nuclei are attracted to one side and the electron cloud to the other side. In addition to these dipoles, there may also be permanent dipoles in the crystal.

The alignment of these dipoles may be in compensatory way i.e. the net dipole moment is zero or non compensatory way i.e. has a net dipole moment. The net dipole moment leads to certain characteristic properties to solids.

(a) **Piezoelectricity (or pressure electricity):** When mechanical stress is applied on crystals so as to deform them, electricity is produced due to displacement of ions. The electricity thus produced is called piezoelectricity and the crystals are called piezoelectric crystals. Conversely, if electric field is applied to such crystals, atomic displacement takes place resulting into mechanical strain. This is sometimes called **Inverse piezoelectric effect.**

The crystals are used as pick – ups in record players where they produce electrical signals by application of pressure. Examples of piezoelectric crystals include titanates of barium and lead, lead zirconate ($PbZrO_3$), ammonium dihydrogen phosphate ($NH_4H_2PO_4$) and quartz. They are also used in microphones, ultrasonic generators and sonar detectors.

(b) **Pyroelectricity:** Some piezoelectric crystals when heated produce a small electric current. The electricity thus produced is called pyroelectricity.

(c) **Ferroelectricity:** In some of the piezoelectric crystals, the dipoles are permanently polarized even in the absence of the electric field. However on applying electric field, the direction of polarization changes e.g. Barium titanate ($BaTiO_3$) sodium potassium tartarate (Rochelle salt) and potassium dihydrogen phosphate (KH_2PO_4). All ferroelectric solids are piezoelectric but the reverse is not true.

(d) **Anti Ferroelectricity:** In some crystals, the dipoles align themselves in such a way, that alternately; they point up and down so that the crystal does not posses any net dipole moment. Such crystal are said to be anti Ferroelectric e.g. Lead zirconate ($PbZrO_3$)

IMPOTANT QUESTIONS

I . Very short answer questions.

1. Name an element that forms mono clinic crystals?

2. What are point defects in crystal structure?

3. Do amorphous solids have unit cell in them?

4. What will be magnitude of the vapour pressure of these ionic crystals?

5. Which group and period of the periodic table does polonium occupy?

II. Short answer questions.

1. Derive bragg's equation**?**

2. What are octahedral holes? How are they formed?

3. Expalin Schottky defect in solids?

4. Define Co-ordination number in a crystalline solid. What is the co-ordination number in a body centered cubic lattice?

III. Long answer questions.

1. What do you know about amorphous substances? Discuss.

2. Describe Bragg's method for determination of structure of a regular solid?

3. Derive Bragg's equation for X-rays of wavelength (λ) and a diffraction angle (Θ) for nth order reflection?

4. How many types of semi-conductors are known? Explain the influence of doping on the conductivity of crystalline solids?