

## IMPERFECTIONS IN SOLIDS

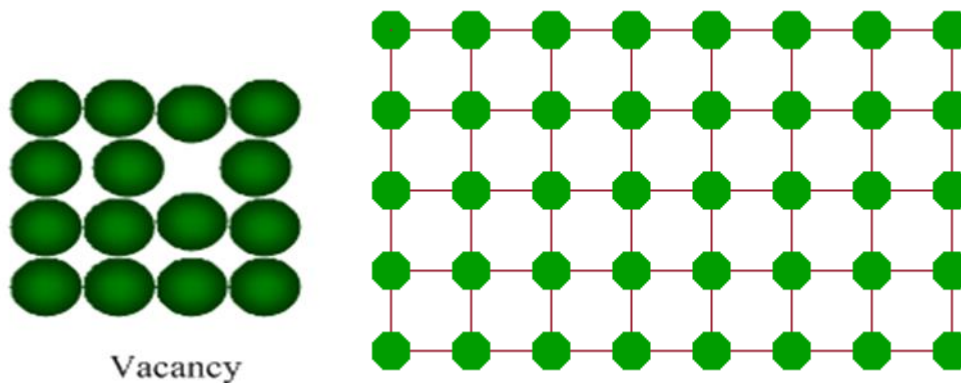
Kumud Bala

Ionic crystal has well-defined order of the constituent ions. “An ionic crystal which has the same unit cell containing the same lattice points throughout the whole Crystal is known as ideal crystal”. Such ideal crystals exist only at absolute zero (0K) temperature. At any temperature above zero kelvin, the crystals have some departure from the complete order arrangement. Any deviation from completely order arrangement in a crystal and may have some additional defects due to the presence of some impurities called imperfection or disorder. These imperfections will not only change the properties of the crystals but also give rise to new properties. There are two types of imperfections- (i) electronic imperfection (ii) atomic imperfection or point defects.

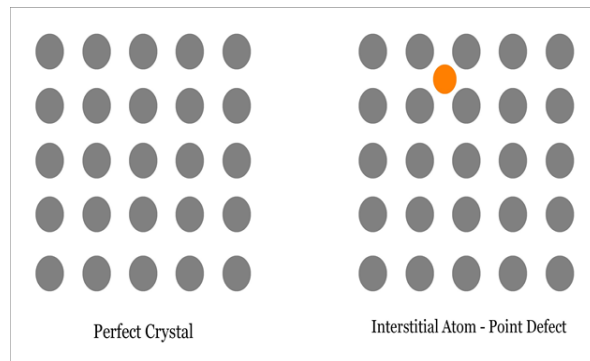
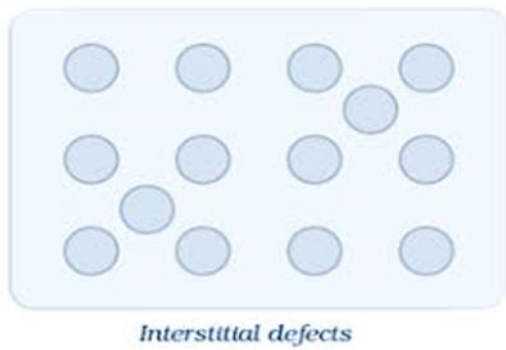
**Electronic imperfections:** These correspond to defects in ionic crystals due to the electrons. The perfectly ionic or covalent crystal at 0K have electrons present in fully occupied lowest energy states. But at higher temperature (above 0K), some of the electrons may occupy higher energy states, depending upon the temperature. For example, in crystals of pure silicon, some electrons are released thermally from covalent bonds at temperature above zero kelvin. These electrons become free to move and therefore, they are responsible for electrical conductivity. The bonds from which electrons have been removed become electron deficient and these are referred to as holes. The holes also give rise to electrical conductivity, but the direction of motion of holes in an electric field is opposite to that of the electrons. Free electrons and holes in crystals are considered to be electronic imperfections.

**Point defects or atomic imperfection:** “The Defects which arise due to the irregularity or deviations from ideal arrangement of atoms around a point or an atom in a crystalline substance are called point defects or atomic imperfections”. The point defects arise due to any one of the following causes:

(i) **Vacancy Defect:** When some of the lattice sites are vacant, the crystal is said to have vacancy defect. The unoccupied positions are called vacancies. This defect results in decrease in density of the substance. This type of defect may also develop when a substance is heated.

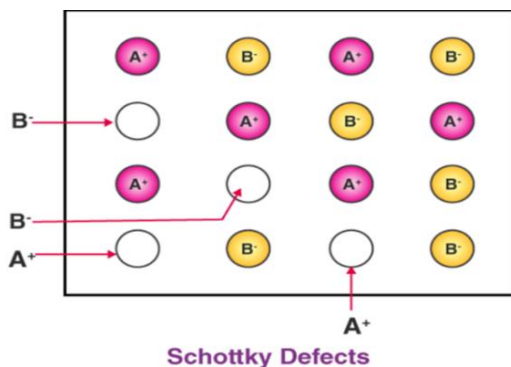


(ii) **Interstitial Defect:** when some constituent particles (atoms and molecules) occupy vacant interstitial position, the crystal is said to have interstitial defect. This defect increases the density slightly. It may be noted that vacancy and interstitial defects are shown by non- ionic solids. On the other hand, ionic solids must always maintain electrical neutrality. The point defects in ionic crystals may be classified as: (a) defects in stoichiometric crystals, (b) defects in non-stoichiometric crystals, (c) impurity defects

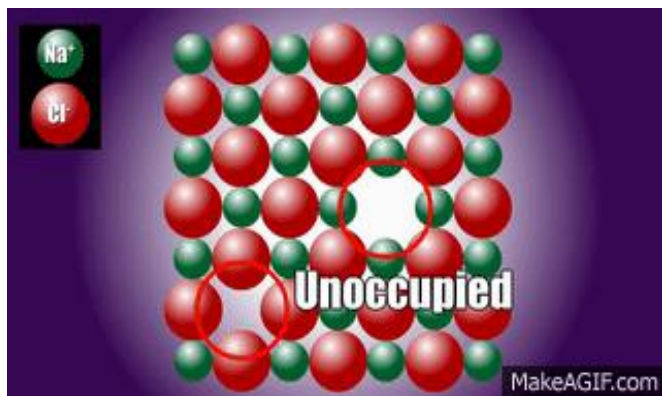


**Point defects in stoichiometric crystals:** Stoichiometric compounds are those in which the number of positive and negative ions are exactly in the ratios indicated by their chemical formulae. For simplicity, we can consider the compounds of the type AB having equal number of A<sup>+</sup> and B<sup>+</sup> ions. The defects in these types of compounds are called stoichiometric defects. In these compounds two types of defects are generally observed. These are: 1. Schottky defect and 2. Frankel defect.

**1. Schottky defect:** This effect was discovered by German scientist Schottky in 1930. It arises if some of the atoms or ions are missing from their normal lattice sites. The lattice sites which are unoccupied called lattice vacancies or holes. Since the crystal is to remain electrically neutral, equal number of cations and anions are missing. The Ideal AB crystal is shown in figure. The existence of two holes one due to a missing cation and other due to a missing anion is shown in the figure. This is basically a vacancy defect in ionic solids.

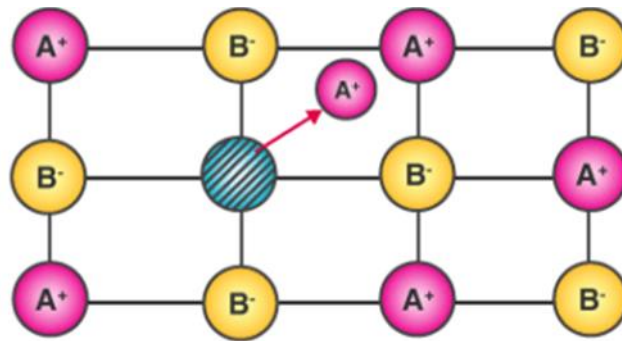


Here two cations (A<sup>+</sup>) and anions (B<sup>-</sup>) are missing from the lattice



**Conditions causing Schottky defects:** This type of defect is usually observed in strongly ionic compounds having (i) high coordination number and (ii) ions (cations and anions) of almost similar sizes. For example, NaCl, KCl, KBr, CsCl and AgBr ionic solids have Schottky defects. It has been observed that in NaCl, there are about  $10^6$  Schottky pairs per  $\text{cm}^3$  at room temperature. In one  $\text{cm}^3$  there are about  $10^{22}$  ions. This means, there will be one Schottky defect per  $10^{16}$  ions in sodium chloride. Because of the presence of large number of vacancies in crystals, its density is markedly lowered.

**2. Frankel defect:** This defect was discovered by a Russian scientist Frankel in 1926. It arises when an ion is missing from its normal position and occupies an interstitial site between the lattice points. The existence of one hole due to a missing cation from its normal position and occupying an interstitial position is shown in figure. In this case also, the crystal remains electrically neutral because the number of anions and cations remains the same. This defect is also known as interstitial defect. It creates a vacancy defect at its original position and an interstitial defect in its new location.

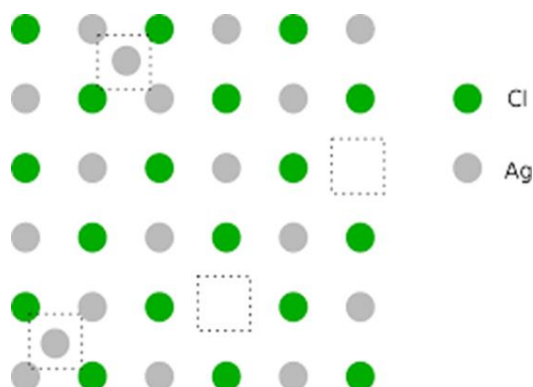


## Frenkel Defect

**Conditions causing Frenkel defects:** This defect generally occurs in compound in which (i) coordination number is low; (ii) anions are much larger in size than the cations. In pure alkali metal halide, defects are not very common because the ion cannot get into interstitial position due to their large sizes. These defects can be found in the silver halide such as AgCl, AgBr, AgI, ZnS, etc. Because of the small size of the  $\text{Ag}^+$  ion and  $\text{Zn}^{2+}$  ion, these ions can go into the interstitial sites. We observe that vacancies or holes present in crystal with Frenkel defects do not affect the density of the crystal. In certain ionic solids such as Silver Bromide both Schottky and Frenkel defects occur.

### Consequences of Schottky and Frenkel defects:

- 1. Electrical conductivity-** Electrical conductivity of crystal increases due to presence of these defects. When we apply an electric field, a nearby electron moves from its lattice site to occupy a hole. This results in creating a new hole and another nearby ion moves into it and so on. This process continues and a hole, thereby, moves from one end to another end. Thus, it conducts electricity across the whole of the crystal.
- 2. Density:** Density decreases only for the crystals having Schottky defects due to the presence of holes. In Frenkel defects, density of the crystal remains same.
- 3. Stability of the crystal:** Lattice energy or stability of the crystal decreases due to the presence of hole and may cause a partial collapse of the lattice.
- 4. Dielectric constant:** The closeness of similar charges in Frankel defects tends to increase the dielectric constant of the crystal

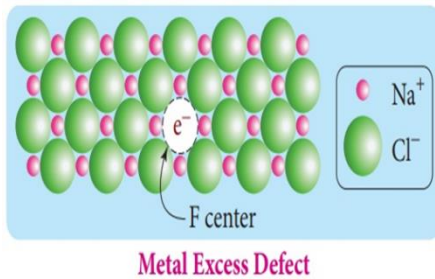


**Point defects in non-stoichiometric crystal:** “The compounds in which the ratio of positive and negative ions present in the compound differs from that required by ideal chemical formula of the compound are called non-stoichiometric compounds”. The defects in these compounds are called non-stoichiometric defects. For example -

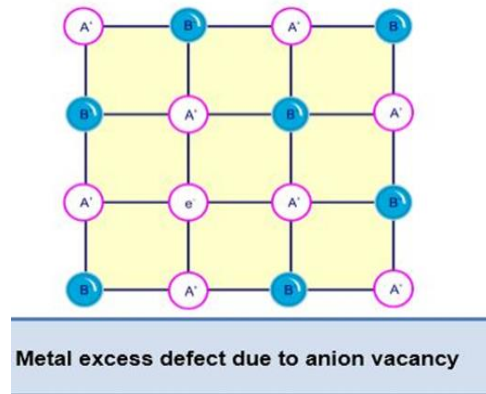
- (i) vanadium oxide,  $\text{VO}_x$  where  $x$  lies between 0.6 to 1.3 .
- (ii) iron oxide,  $\text{FeO}$  (ideal composition), but it is difficult to obtained. Normally, we get  $\text{Fe}_{0.95}\text{O}$  sample of more oxygen atoms than iron atoms. But it may range from  $\text{Fe}_{0.93}\text{O}$  to  $\text{Fe}_{0.96}\text{O}$ .
- (iii) zinc oxide ( $\text{ZnO}$ ) usually has excess of Zn atoms than oxygen atoms. In each case, the electrical neutrality of the crystal is maintained. Non-stoichiometric behavior is most commonly found for transition metal compounds. It is also found for some lanthanoids and actinides. There are two types of defects: (i) metal excess defects (ii) metal deficiency defects

(i) **Metal excess defects:** In these defects, the positive ions are in excess. These may arise due to two ways: (a) Anionic vacancies, (b) Presence of extra cation in interstitial sites.

(a) **Anion vacancies:** In this case, negative ions may be missing from their lattice site leaving holes in which electrons remain entrapped to maintain the electrical neutrality. Evidently, there is an excess of

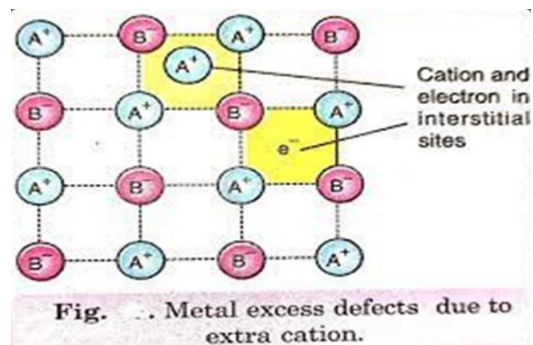


positive (metal) ions although, the crystal as a whole is electrically neutral. This type of defect is observed in those crystals which are likely to form Schottky defects. In alkali halides, anion vacancies are produced when alkali metal halide crystal are heated in the atmosphere of alkali metal vapours. For example, when crystal of sodium chloride is heated

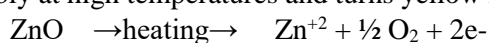


in an atmosphere of sodium vapours, the excess of sodium atoms is deposit on the surface of the crystal. The  $\text{Cl}^-$  ions diffuse to the surface of the crystal and combine with sodium atoms to give sodium chloride. This happens by the loss of electrons by sodium atoms to form  $\text{Na}^+$  ion. The electrons, thus produced by the ionization of sodium atoms diffuse into the crystal and get trapped at the anion vacancies. The electron trapped in anion vacancies are referred to as F-Centre (from German word farbenzenter meaning colour Centre). They impart yellow colour to the crystal of  $\text{NaCl}$ . The color results by excitation of these electrons when they absorb energy from the visible light falling on the crystals. Similarly, excess of potassium in  $\text{KCl}$  makes the crystal appear violet, excess of lithium in  $\text{LiCl}$  makes the crystal appear pink.

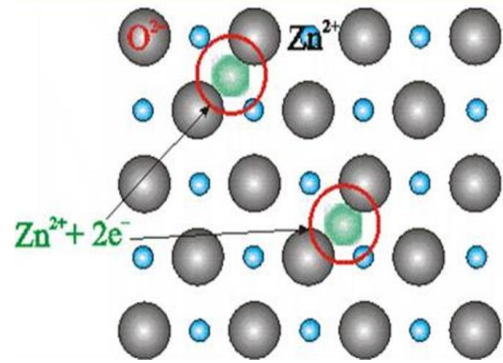
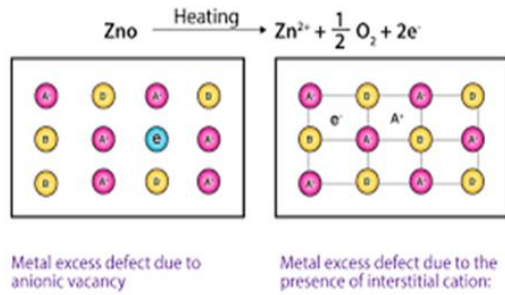
(b) **Excess cations occupying interstitial sites:** In this case, there are extra positive ions occupying interstitial sites and the electrons in another interstitial sites to maintain electrical neutrality. The defect may be visualized as the loss of non -metal atoms which leave their electrons behind. The excess metal ions occupy interstitial positions.



This type of defect is found in crystals which are likely to develop Frankel defect. The common example is zinc oxide. Zinc oxide ( $\text{ZnO}$ ) is white in colour at room temperature. On heating it loses oxygen reversibly at high temperatures and turns yellow in colour.



The excess  $\text{Zn}^{+2}$  ions are trapped in interstitial sites and equal number of electrons are trapped in the neighborhood to balance the electrical charge. These electrons give rise to enhanced electrical conductivity.



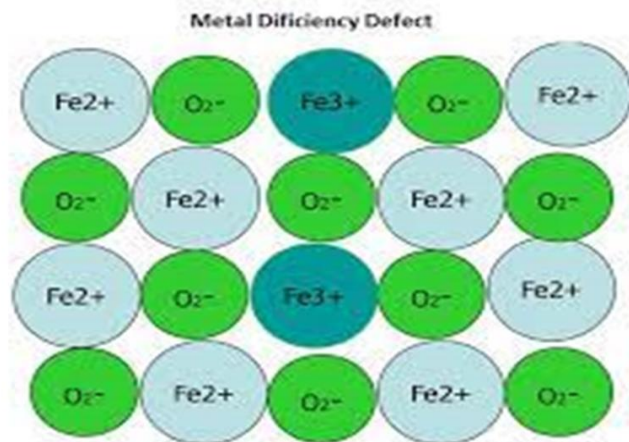
**Consequences of metal excess defects:**

1. The crystal with metal excess defects conduct electricity due to the presence of free electrons. However, the conductivity is very low because of the number of defects and therefore, the number of free electrons is very small. Because of low conductivity as compared to conductivity of metal, these are called semiconductors. These compounds are also called n-type semiconductors since the current is carried by the electron in the normal way.
2. The crystals with metal excess defects are generally colored. For example, non-stoichiometric sodium chloride is yellow, non-stoichiometric potassium chloride is violet.

**Metal deficient defects:** These defects contain a smaller number of positive ions than negative ions. These arise due to two ways: (i) cation vacancies and (ii) extra anions occupying interstitial sites.

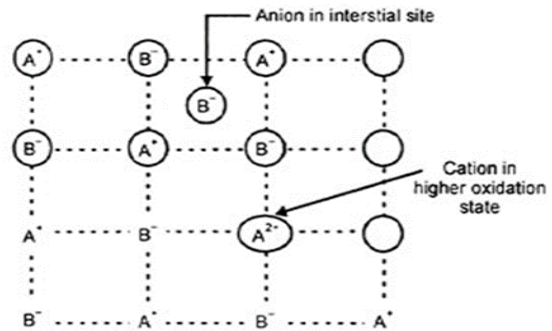
**Cation vacancies:** In some cases, the positive ions may be missing from their lattice sites. The extra negative charge may be balanced by some nearby metal ion acquiring two positive charges instead of one. This type of defect is possible in metals which show variable oxidation states. The common examples of compounds having this defect are ferrous oxide, ferrous sulphide, nickel oxide etc. In case of iron pyrite (FeS), for example, two out of three ferrous ions in a lattice may be converted into  $Fe^{+3}$  state and the third  $Fe^{+2}$  ion may be missing from its lattice site. Therefore, the Crystal contains  $Fe^{+2}$  and  $Fe^{+3}$  ions. This gives rise

to exchange of electrons from one  $Fe^{+2}$  to  $Fe^{+3}$  ion in which  $Fe^{+2}$  changes to  $Fe^{+3}$  and  $Fe^{+3}$  changes to  $Fe^{+2}$  ion. As a results, the crystal has metallic luster. Because of the natural colour of iron pyrite and metallic luster some samples of minerals shine like gold and have been nicknamed as fool's gold. Similarly, FeO is mostly found with a composition of  $Fe_{0.95}O$ . It may actually range from  $Fe_{0.93}O$  to  $Fe_{0.96}O$ . In crystals of FeO, some  $Fe^{+2}$  ions are missing and the loss of positive charge is made up by presence of required number of  $Fe^{+3}$  ions. Moreover, since there is exchange of electrons, the substances become conductors.



In crystals of FeO some  $Fe^{2+}$  cations are missing and the loss of positive charge is made up by the presence of required number of  $Fe^{3+}$  ions.

**Extra anions occupying interstitial sites:** In this case, the extra anions may be occupying interstitial positions. The extra negative charge is balanced by the extra charges (oxidation of equal number of cations to higher oxidation states) on the adjacent metal ions. Such type of defect is not common because of the negative ions are usually very large and they cannot easily fit into the interstitial sites.



**Consequences of metal deficient defects:** Crystal with metal deficiency defects are semiconductors. The conductivity is due to the movement of electron from one ion to another. For example, when an electron moves from ion A<sup>+</sup>, it changes to A<sup>2+</sup>. The substances are called p-type semi-conductors.

**3. Impurity defects:** These defects in ionic crystals arise due to the presence of some impurity ions at the lattice sites (in place of host ions) or at the vacant interstitial sites. For example, if molten sodium chloride containing a little amount of Strontium chloride (SrCl<sub>2</sub>) is allowed to crystallize, some of the sites of Na<sup>+</sup> ions are occupied by Sr<sup>2+</sup> ions. For each Sr<sup>2+</sup> ion introduced, two sodium ions are removed to maintain electrical neutrality. One of these lattice sites is occupied by Sr<sup>2+</sup> ion and the other remain vacant. Therefore, these vacancies result in increased electrical conductivity of the solid. Similar, defect and behaviour is observed when cadmium chloride (CdCl<sub>2</sub>) is added to Silver chloride (AgCl).

