Program Bachelor of Science: T. Y. B.Sc
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Section A

Welcome students. I will be discussing Unit 1 of Inorganic solid-state chemistry.
Module name: Defects in solids ,Point defects,Schottky and Frenkel defects.
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Outline of today's module:

Defects in solids,
Types of point defects
Stoichiometric defects
Schottky defect
Frenkel defect.

Learning outcomes:

At the end of this module, students will be able to;
List down defects in solids.
Explain points defect.
Clarify stoichiometric defects.
Compare Schottky and Frenkel defects.
Discuss consequences of Schottky and Frenkel defects.

Defects in solids.

What are defects in solids?

Defects in molecule of a solid can be understood by considering the ideal crystal.

An ideal crystal or perfect crystal is one which has the same unit cell and contain all the same lattice points throughout the crystal or constituent's molecules, atoms or ions are arranged in completely regular 3D dimensional pattern as shown in this figure.

However, irregularities or deviations from ideal arrangement of an atom around an atom or ion or point in a crystal arises due to considerable degree of thermal vibration and these irregularities are called defects or atomic imperfection.

In this figure, one of the lattice point is missing, introducing defect in the crystal.

Defects in solids are basically divided into:
Electronic defects,
Point or atomic defects and
Line or dislocation defect.

In this session, we are going to discuss about the Point or atomic defects.

Point defect is the simplest defect in solid, in which an atom is missing or an impurity is in place of a normal atom. Such a structurally defects are called point defects.

Point or atomic defects are further classified into stoichiometric defects and non-stoichiometric defects. Which is based on the ratio of different kind of atoms present in the crystal.

There is still one more type of point defect called as impurity defect.

In this session, we are going to discuss about stoichiometric defects, which are :

1. Non- ionic defects, are two types: vacancy defect and interstitial defect.

2nd type of stoichiometric defects is ionic defect. Which consists of Schottky defect and Frenkel defect.

Now, we are going to see in detail about stoichiometric defects,

What are stoichiometric defects?

Stoichiometric defects are observed in the compound in which ratio of number of different types of atoms or ions presents are exactly in the ratio as indicated in their molecular formula as shown in the figure.

The figure shows a crystal of sodium chloride, in which the sodium ion and chloride ion are in stoichiometric ratio of 1 :1.

The stoichiometric defects, as discussed earlier is of two type non-ionic and ionic defects. The non-ionic

defects are basically two types.

1. Vacancy defects, which is observe or arise when some lattice sites or atoms are vacant or absent from normally occupied position in pure crystal.

The second type of non-ionic defect is interstitial defect, in which atoms occupies a normally unoccupied site that is interstitial site in the crystal structure.

The second type of stoichiometric defect is ionic defect. To understand ionic defects, we should know the crystal lattice once again.
At absolute temperature, all ionic crystals show well-ordered arrangement of ion in the crystal lattice as represented in the sodium chloride crystal.
However, with the rise in temperature, some of the lattice sites may remain unoccupied by the ions, constituting defects in the ionic crystal.

The ionic crystals are two types: Schottky and Frenkel defects.

Schottky Ionic defect, also known as Schottky- Wagner defect, which arises if some of the ions,that is positive ion and negative ions (cation and anion) are missing from their normal lattice sites resulting in lattice vacancy or hole as depicted in the figure, introducing Schottky defect.

Thus, a Schottky defect consists of a pair of “holes” in the crystal lattice.

The number of Schottky defects formed per cm^3, represented by n_s at a particular temperature T, is given by equation.

$$ns = Ne^{\frac{-ws}{2kT}}$$

Where,

N= Total number of sites per cm^3 left vacant
W_s= Work requires to produce a defect
k = Gas constant
T= Absolute temperature

Schottky defects occurs in ionic compound where :

- Cations and anions are with similar size. In other words, we can say the radius ratio $\mathbf{r^+/r^- \approx 1.}$
- Atom with high coordination number, i.e. usually 8 and 6 coordination number will show Schottky defect
- Example of compound which shows Schottky defects are sodium chloride, potassium chloride, KBr and caesium chloride.

Let us see the consequences of Schottky defects.

- Due to the Schottky defect, the holes are present in the crystal. This decreases the density of crystal. So, due to presence of holes in the crystal, density decreases.
- Compounds with Schottky defect results in the electric conductivity, due to migration of either one type of holes or both holes. However, at low temperature, migration of cations are favoured.

- Stability or lattice energy of the crystals decreases.

Next, defect is Frenkel defect: which arises when ion is missing from their normal lattice sites and occupies and interstitial site between lattice site.

Figure depict the Frenkel defect, wherein the cation occupied interstitial position.

Frenkel defects occur in ionic compounds where:

- Cations are much smaller in size than anion, that is when the radius ratio r+/r- = low
- Atoms with low coordination number, that is 4 and 6.

Examples: Silver chloride, silver bromide, silver iodide and zinc sulfide.

The number of Frenkel defects formed per cm^3 (n_f) is given by

$$n_f = \sqrt{NN'}exp^{(\frac{-W_f}{2KT})}$$

Where,

N= Number of sites per cm^3 that could be left vacant
N'= Number of alternative interstitial position per cm^3
W_f= Work necessary to form a Frenkel defect
T= The absolute temperature

Consequences of Frenkel defect:

- Dielectric constant of the crystal increases due to proximity of like charges at the interstitial position.
- Conduct electricity to a small extent through ionic mechanism, resulting intrinsic semiconduction.
- Density of the crystal is not affected; however, lattice may distort or expand and increase the unit cell dimension.
- Schottky defect appears more often than *Frenkel defect*, as energy needed to form a

Schottky defect is much less than that of *Frenkel defect*.

In summary, we can picturize two types of defects: Schottky defect and Frenkel defect.

Schottky defect can be represented by missing of pair of cation and anion.

And Frenkel defects, represented by positive cation occupying an interstitial position.

Here are some of the references for further reading,

Thank you.