

Solid state

Part – 2

chemistry

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Content:



Crystal defects

Crystal defects

Defect or Imperfection:-

- Any departure from perfectly ordered arrangement of the constituent particles in the crystal called imperfection or defect.
- The defects in the crystal are arises when crystallization takes place at the fast or moderate rates because the constituent particles does not get sufficient time to arrange in perfect order.

There are mainly two types of defects:-

1. **Point defect**:-When the deviation or irregularities exists from ideal arrangement around a point or an atom in a crystalline substance the defect is called the point defect.
2. **Line defect**:- When the deviation from the ideal arrangement exists in the entire row of lattice points the defect is called as line defect.

Types of the point defects:

1. Stoichiometric defects
2. Non stoichiometric defects
3. Impurity defects

Stoichiometric defect:-

If imperfection in the crystal are such that the ratio between cation and anions remains same. Stoichiometry of substance do not disturbed defect is called stoichiometric defect these defects are of the following types.

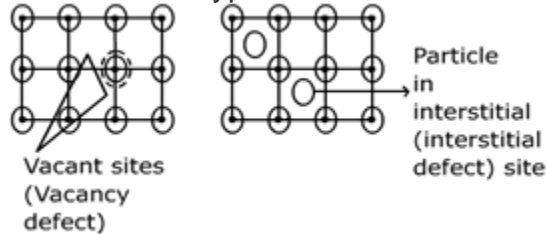
1. Vacancy defect:-

When is in a crystalline substance, some of the lattice sites are vacant the crystal is said to have vacancy defect it results in decrease of density of substance.

2. Interstitial defect:-

- When some extra constituent particles are present in the interstitial site the crystal is said to be have interstitial defect.
- This defect increases density of the crystal

- These above types of defects are shown only by non – ionic solids.



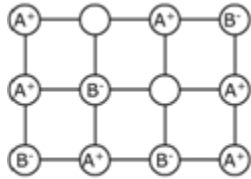
3. Schottky defect:-

- If in an ionic crystal of the type A^+B^- equal number of cations and anions are missing from the lattice site. So that electrical neutrality is remained is called schottky defect. Compounds exhibiting schottky defect are NaCl, KCl
- Which compounds have small difference in size of cation and anions show defect.

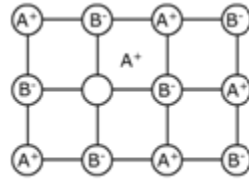
Frenkel defect:- If an ion is missing, from its lattice site and is occupies the interstitial site, electrical neutrality as well as Stoichiometry of the compound are maintained this type of defect is called frenkel defect. It is also called dislocation defect.

Example:-

(AgCl, AgBr, AgI, ZnS) shows this defect which have a large difference in size of cations and anions.



Schottky defect



Frenkel defect

Main points of difference between Schottky and Frenkel defect

Schottky defect	Frenkel defect
<ol style="list-style-type: none">1. It is due to equal no. of cations and anions missing from lattice sites.2. It results in decrease in density of crystal3. This is found in the highly ionic compounds with having cations and anions of same sizes NaCl, CaCl	<ol style="list-style-type: none">1. It is due to missing of ions [usually cations] from the lattice sites and these occupies interstitial sites.2. It has no defect on the density of crystal.3. This is found in crystal with low coordination no. Example:- AgI, ZnS etc.

Non stoichiometric defects:-

If a result of the imperfections in the crystal the ratio, of the cations and anions becomes difference from that indicated by ideal chemical formula. The defects are called non-stoichiometric defects.

They are of two types:-

i. Metal excess defects:-

- A negative ion may be missing from its lattice site, leaving a hole which is occupied by an electron, there by maintain the electrical neutrality.
- The interstitial sites containing the electron thus trapped in the anion vacancies are called the F – centers. They are responsible for imparting colour to the crystals.

Example:- When NaCl is heated in an atmosphere of Na vapours. The excess of Na atoms deposition the surface of NaCl crystal Cl⁻ ions then diffuse to the surface where the combine with Na⁺ ions which becomes due to losing electrons.

- These electrons lost by Na atom are diffuse back into the crystal and occupy the vacant site created by Cl⁻ ions and imparts Yellow colour to NaCl crystal

ii. By presence of extra cation in interstitial sites:-

- • Metal excess may also be caused by an extra cation occupying the interstitial site. For example when ZnO is heated it loses oxygen and turns yellow due to following $\text{ZnO} \rightarrow \text{Zn}^{+2} + (1/2)\text{O}_2 + 2e^-$
The excess interstitial sites and the electrons in neighbouring interstitial sites.

- **Metal deficiency defect:-** This defect occurs when the metal shows the variable valency. Due to metal deficiency the compounds obtained are non stoichiometric. For example it is difficult to prepare ferrous oxide with ideal composition because ferum exists as both Fe⁺² and Fe⁺³ ions thus we obtain Fe_{0.95}O or Fe_xO with x = 0.93 to 0.96

Impurity defects:-

These defects are arises when foreign atoms are present at the lattice site in place of the host atom. Or it is present at the vacant interstitial site example n – type semi conductor, p – type semi conductor.

The process of adding impurities to the crystalline is called as doping.

In case of ionic solids the impurities are introduced by adding impurity of ions. If the impurity ions are in different valence state from that of host ions. Vacancies are created if mole ten NaCl containing a little impurity of SrCl₂ and is allowed to cool. The vacancies of Na⁺ ions are created and these are occupied by Sr²⁺ ions.

Introducing Impurity in covalent solids:-

i. Doping with electron rich impurities (formation of n – type semi conductor):-

- Group IV elements like silicon or germanium has 4 electrons in valence shell. Thus it forms four covalent bonds with neighbouring atoms. When it is doped by group 15 element like P or As, the silicon or germanium atom at some lattice sites are substituted by P or As.
- Now doped atom has 5 valence electrons after forming four covalent bonds. The fifth free electron is delocalized. This increases conductivity of silicon.
- As conductivity increases due to electrons thus the germanium crystal doped with electron-rich impurity are called n – type semi conductors.

ii. Doping with electron deficit impurities:- (P – type semi conductor)

- If group 14 element like silicon are doped with 3 valance electron containing 13 group elements like Al or Ga.
- Due to three valance electron all atom forms 3 valance bond with 3 silicon atoms. Thus a hole is get created at the site of fourth electron is missing. This is called electron hole or electron vacancy.
- If an electron jump from neighbouring site to fill this hole a another hole is generated at that site and it continues.
- Thus if electric field is applied the electrons move towards +vely charged plate and electron holes move towards negative charged plate as they carry +ve charge. Thus a semiconductor with increased conducting is formed and called P – type semiconductor.