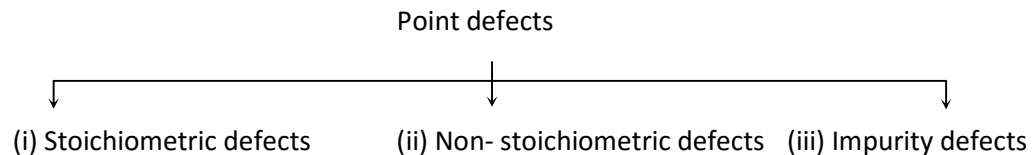


Defects or Imperfections in Solids.

Any deviation from the perfectly ordered arrangement constitutes a defect or imperfection. These defects sometimes called thermodynamic defects because the number of these defects depend on the temperature. Crystals may also possess additional defect due to the presence of impurities. Imperfection not only modify the properties of solids but also give rise to new properties. Any departure from perfectly ordered arrangement of atoms in crystals called imperfections or defects.

(1) Electronic imperfections: Generally, electrons are present in fully occupied lowest energy states. But at high temperatures, some of the electrons may occupy higher energy state depending upon the temperature. For example, in the crystals of pure Si or Ge some electrons are released thermally from the covalent bonds at temperature above 0 K. these electrons are free to move in the crystal and are responsible for electrical conductivity. This type of conduction is known as intrinsic conduction. The electron deficient bond formed by the release of an electron is called a hole. In the presence of electric field the positive holes move in a direction opposite to that of the electrons and conduct electricity. The electrons and holes in solids gives rise to electronic imperfections.

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



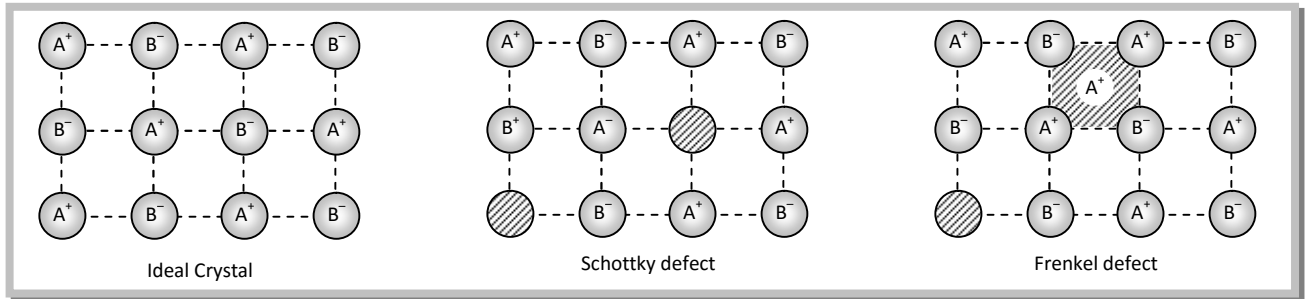
(i) Stoichiometric defects: The compounds in which the number of positive and negative ions are exactly in the ratios indicated by their chemical formulae are called stoichiometric compounds. The defects do not disturb the stoichiometry (the ratio of numbers of positive and negative ions) are called stoichiometric defects. These are of following types:

(a) Schottky defects: This type of defect when equal number of cations and anions are missing from their lattice sites so that the electrical neutrality is maintained. This type of defect occurs in highly ionic compounds which have high co-ordination number and cations and anions of similar sizes. e.g., NaCl, KCl, CsCl and KBr etc.

(b) Interstitial defects: This type of defect is caused due to the presence of ions in the normally vacant interstitial sites in the crystals.

(c) Frenkel defects: This type of defect arises when an ion is missing from its lattice site and occupies an interstitial position. The crystal as a whole remains electrically neutral because the number of anions

and cations remain same. Since cations are usually smaller than anions, they occupy interstitial sites. This type of defect occurs in the compounds which have low co-ordination number and cations and anions of different sizes. e.g., ZnS, AgCl and AgI etc. Frenkel defect are not found in pure alkali metal halides because the cations due to larger size cannot get into the interstitial sites. In AgBr both Schottky and Frenkel defects occurs simultaneously.



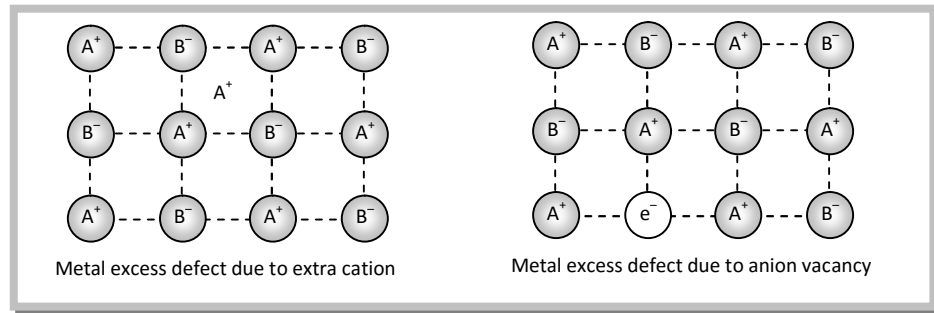
Consequences of Schottky and Frenkel defects: Presence of large number of Schottky defect lowers the density of the crystal. When Frenkel defect alone is present, there is no decrease in density. The closeness of the charge brought about by Frenkel defect tends to increase the dielectric constant of the crystal. Compounds having such defect conduct electricity to a small extent. When electric field is applied, an ion moves from its lattice site to occupy a hole, it creates a new hole. In this way, a hole moves from one end to the other. Thus, it conducts electricity across the crystal. Due to the presence of holes, stability (or the lattice energy) of the crystal decreases.

(ii) Non-Stoichiometric defects: The defects which disturb the stoichiometry of the compounds are called non-stoichiometry defects. These defects are either due to the presence of excess metal ions or excess non-metal ions.

(a) Metal excess defects due to anion vacancies: A compound may have excess metal anion if a negative ion is absent from its lattice site, leaving a 'hole', which is occupied by electron to maintain electrical neutrality. This type of defects are found in crystals which are likely to possess Schottky defects. Anion vacancies in alkali metal

halides are reduced by heating the alkali metal halides crystals in an atmosphere of alkali metal vapors. The 'holes' occupy by electrons are called F-centers (or colorcenters).

(b) Metal excess defects due to interstitial cations: Another way in which metal excess defects may occur is, if an extra positive ion is present in an interstitial site. Electrical neutrality is maintained by the presence of an electron in the interstitial site. This type of defects are exhibit by the crystals which are likely to exhibit Frenkel defects e.g., when ZnO is heated, it loses oxygen reversibly. The excess is accommodated in interstitial sites, with electrons trapped in the neighborhood. The yellow color and the electrical conductivity of the non-stoichiometric ZnO is due to these trapped electrons.



Consequences of Metal excess defects:

The crystals with metal excess defects are generally colored due to the presence of free electrons in them.

The crystals with metal excess defects conduct electricity due to the presence of free electrons and are semiconductors. As the electric transport is mainly by “excess” electrons, these are called n-type (n for negative) semiconductor.

The crystals with metal excess defects are generally paramagnetic due to the presence of unpaired electrons at lattice sites.

Note: ColorCenters: Crystals of pure alkali metal halides such as NaCl, KCl, etc. are white. However, alkali metal halides becomes colored on heating in excess of alkali metal vapor. For example, sodium chloride becomes yellow on heating in presence of sodium vapor. These colors are produced due to the preferential absorption of some component of visible spectrum due to some imperfections called colorcenters introduced into the crystal.

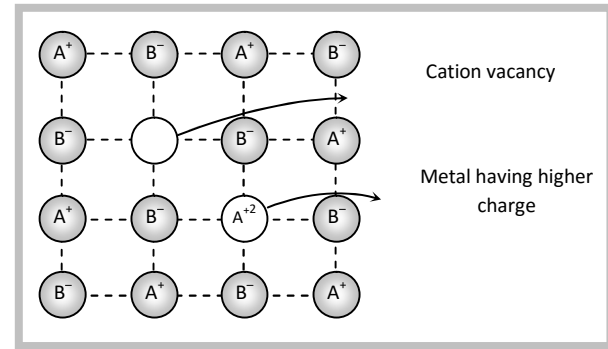
When an alkali metal halide is heated in an atmosphere containing an excess of alkali metal vapor, the excess alkali metal atoms deposit on the crystal surface. Halide ions then diffuse to the surface where they combine with the metal atoms which have become ionized by losing valence electrons. These electrons diffuse back into the crystal and occupy the vacant sites created by the halide ions. Each electron is shared by all the alkali metal ions present around it and is thus a delocalized electron. When the crystal is irradiated with white light, the trapped electron absorbs some component of white light for excitation from ground state to the excited state. This gives rise to color. Such points are called F-centers. (German word Farbe which means color) such excess ions are accompanied by positive ion vacancies. These vacancies serve to trap holes in the same way as the anion vacancies trapped electrons. The colorcenters thus produced are called V-centers.

(c) Metal deficiency defect: These arise in two ways

By cation vacancy: in this a cation is missing from its lattice site. To maintain electrical neutrality, one of the nearest metal ion acquires two positive charge. This type of defect occurs in compounds where metal can exhibit variable Valency. e.g., Transition metal compounds like NiO, FeO, FeS etc.

By having extra anion occupying interstitial site: In this, an extra anion is present in the interstitial position. The extra negative charge is balanced by one extra positive charge on the adjacent metal ion. Since anions are usually larger it could not occupy an interstitial site. Thus, this structure has only a theoretical possibility. No example is known so far.

Consequences of metal deficiency defects: Due to the movement of electron, an ion A^+ changes to A^{2+} ions. Thus, the movement of an electron from A^+ ion is an apparent of positive hole and the substances are called p-type semiconductor



Impurity defect: 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 while in the latter case, we get interstitial solid solution. The formation of the former depends upon the electronic structure of the impurity while that of the later on the size of the impurity.

Important Tips

Berthallides is a name given to non-stoichiometric compounds.

Solids containing F- centers are paramagnetic.

When NaCl is dopped with MgCl₂ the nature of defect produced is schottky defect.

AgBr has both Schottky & Frenkel defect.