The Solid State - Part 3

Objectives

After going through this lesson, the learners will be able to understand the following:

- Types of defects in solids
- Difference between line and point defect
- Stoichiometric, impurity and non-stoichiometric defects
- Effect of defects on density of solids

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- Introduction
- Imperfections in Solids
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  - Stoichiometric Defects
  - Impurity Defects
  - Non-Stoichiometric Defects
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Introduction

In the previous modules, you have studied that the solids can be classified as crystalline solids and amorphous solids based on the regularity in the arrangement of their constituent particles. In the crystalline solids, the particles are arranged in a definite pattern which is repeated throughout the crystals. In this module, you will be studying the different types of irregularities that can occur in the arrangement of constituent particles and the effect of these defects on the properties of the crystals.

Imperfections in Solids

Although crystalline solids have long range order in the arrangement of their constituent particles, yet crystals are not perfect. A crystal which has the same unit cell containing the same lattice points throughout the crystal is known as an ideal crystal. Ideal crystals exists only at absolute zero (0 K) Temperature. At any temperature above 0 K, the crystals have some deviation from a perfectly ordered arrangement. In actual practice it is very difficult to grow a perfect or an ideal crystal lattice. Usually a solid consists of an aggregate of large number of small crystals. Single crystals are formed when the process of crystallisation occurs at an extremely slow rate. Even these crystals are not free of defects.

The defects are irregularities in the arrangement of constituent particles. These irregularities are also called *crystal defects*. The imperfection will not only change the properties of the crystals but also give rise to new properties. The defects can be broadly classified as **point defects** and **line defects.**

Point defects are the irregularities or deviations from ideal arrangement around a point or an atom in a crystalline substance.

Line defects are the irregularities or deviations from ideal arrangement in the entire rows of lattice points.

The crystalline defects can be summarized as shown in Fig.1.

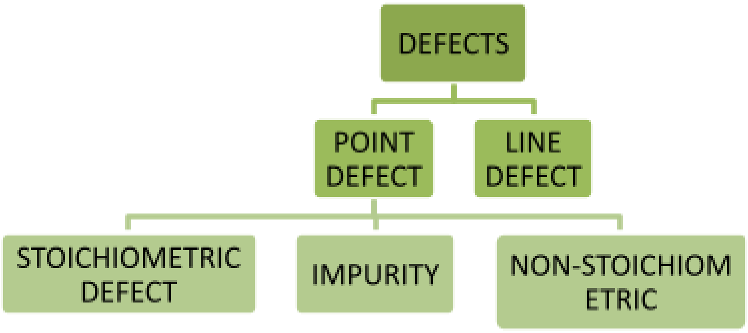


Fig. 1: Classification of defects

In this module, we shall confine our discussion to point defects only.

Point Defects

There are three types of point defects :

- Stoichiometric defects
- Impurity defects
- Non-stoichiometric defects

Stoichiometric Defects

These are the point defects that do not disturb the stoichiometry of the solid. They are also called intrinsic or thermodynamic defects. Basically these are of two types, namely, vacancy defects and interstitial defects.

- *Vacancy defect:* When some of the lattice sites are vacant, the crystal is said to have vacancy defect (Fig. 2) . The unoccupied positions are called vacancies. This defect results in a decrease in density of the substance. This type of defect may also develop when a substance is heated.

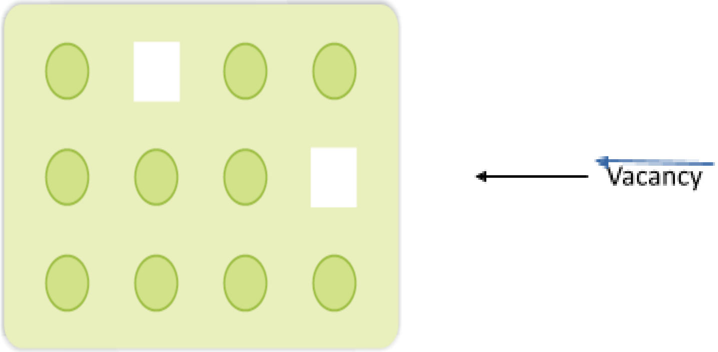


Fig.2: Vacancy defects

- *Interstitial defect:* When some constituent particles (atoms or molecules) occupy interstitial sites (vacant places between the lattice sites), the crystal is said to have interstitial defect (Fig. 3). This defect increases the density slightly.

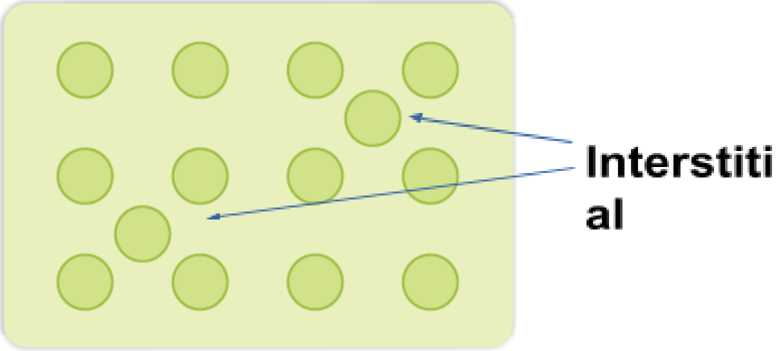


Fig.3: Interstitial defects

- It may be noted that vacancy and interstitial defects are shown by non-ionic solids. Since the ionic solids must always maintain electrical neutrality they do not show simple vacancy or interstitial defects. However, they show these defects as Frenkel and Schottky defects. The classification of stoichiometric defects can be summarized as shown in Fig. 4.

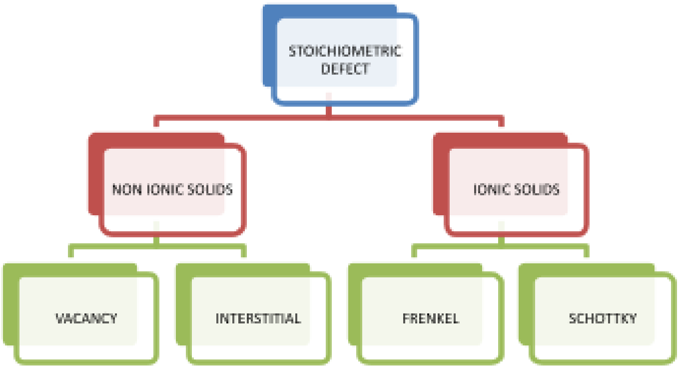


Fig. 4: Classification of stoichiometric defects

- *Schottky defect:* This defect was discovered by German scientist Schottky in 1930. It arises if some of the ions are missing from their normal lattice sites. This is basically a vacancy defect in ionic solids. The lattice sites which are unoccupied are called lattice vacancies or holes. Since the crystal has to remain electrically neutral, **an equal number of cations and anions are missing** (Fig. 5). This type of defect is usually observed in ionic compounds having cations and anions of almost similar sizes. For example; NaCl, KCl, KBr, CsCl and AgBr which are ionic solids, show Schottky defects. The number of such defects in ionic solids is quite significant. For example; in NaCl there are approximately 10^6 Schottky pairs per cm^3 at room temperature. In 1 cm^3 there are about 10^{22} ions. Thus, there is one Schottky defect per 10^{16} ions. **Because of the presence of large no. of vacancies in crystals, its density is markedly lowered.**

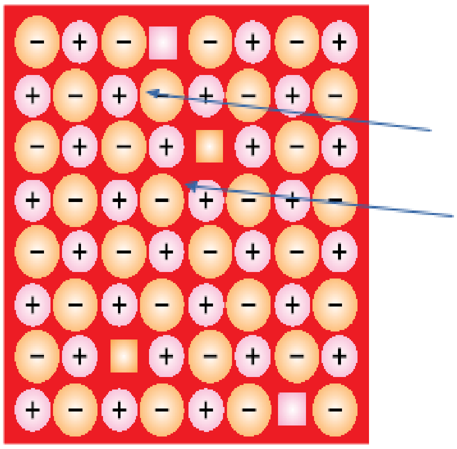


Fig. 5: Schottky defect

- *Frenkel Defect*: This defect was discovered by a Russian scientist Frenkel in 1926. **It arises when an ion is missing from its normal position (causing a vacancy or a hole) and occupies an interstitial site between the lattice points**. The smaller ion (usually cation) is dislocated from its normal site to an interstitial site (Fig. 6). It creates a vacancy defect at its original site and an interstitial defect at its new location, that's why also known as *dislocation defect*. The crystal remains electrically neutral because the number of cations and anions remains the same. Frenkel defect is generally shown when the coordination number is low and the size of anion is much larger than the size of cation. These defects can be in AgCl, AgBr, AgI and ZnS because of the small size of Ag^+ and Zn^{2+} ions. It may be noted that AgBr shows both, Frenkel as well as Schottky defects.

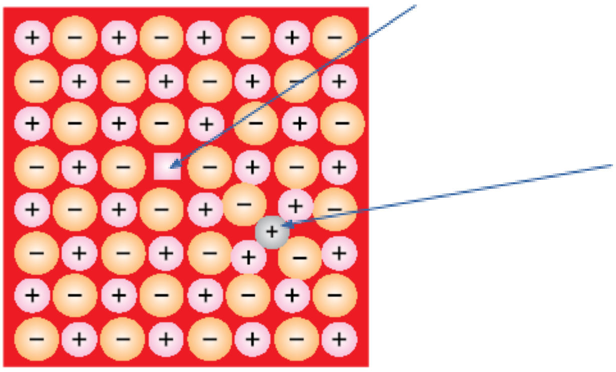


Fig. 6: Frenkel defect

Table 1: Comparison between Schottky and Frenkel defects

Schottky defect	Frenkel defect
It is produced because of missing ions from their normal crystal sites.	It is produced when some ions are displaced from their normal sites and occupy interstitial sites.
The presence of Schottky defect lowers the density of the crystal.	It does not affect the density of the crystal.
It is generally shown by ionic solids having high coordination number and cations and anions of similar sizes. For example, NaCl, CsCl.	It is generally present in ionic solids having low coordination number and larger anions than cations. For example, AgCl, ZnS.

Consequences of Schottky and Frenkel defect: Schottky and Frenkel defects in crystals lead to some interesting consequences. These are given below:

- The electrical conductivity of crystals increases due to the presence of these defects. When an electrical field is applied, a nearby ion moves from its lattice site to occupy a "hole". This results in creating "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.

- Due to the presence of holes in the crystal having Schottky defects, the density decreases.
- The presence of 'holes' also decreases the lattice energy or the stability of the crystal. The presence of too many holes may cause a partial collapse of the lattice.
- The closeness of similar charges in Frenkel defects tends to increase the dielectric constant of the crystals.

Impurity Defects

It is an extrinsic defect which occurs when a foreign particle (atom or ion) is introduced in the crystal lattice. The impurity particle can occupy the interstitial or it may replace the particle from the lattice site. If molten NaCl containing a little amount of $SrCl_2$ is crystallised, some of the sites of Na^+ ions are occupied by Sr^{2+}. Each Sr^{2+} replaces two Na^+ ions to maintain electrical neutrality. It occupies the site of one Na^+ ion and the other site remains vacant. The cationic vacancies thus produced are equal in number to the number of Sr^{2+} ions. Another example is the solid solution of $CdCl_2$ and AgCl.

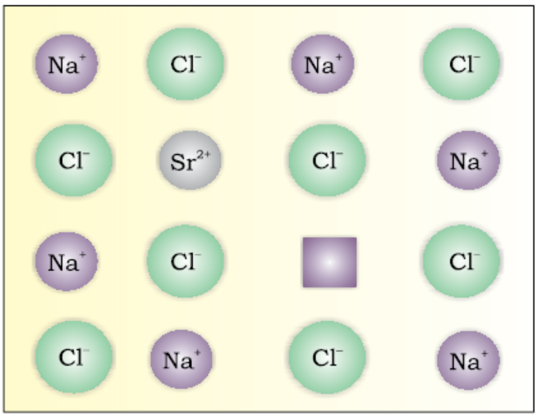


Fig. 7: Impurity defect

Solved Example 1

During the crystal formation of KCl some $CaCl_2$ was present as impurity. What will be the effect on the density of KCl crystals formed?

Solution:

In KCl crystal, the Ca^{2+} ion from $CaCl_2$ will replace K^+ ions. Since one Ca^{2+} ion will replace two K^+ ion in order to make the system electrically neutral. Thus, the density of KCl crystal will decrease.

Non-Stoichiometric Defects

The compounds in which the ratio of positive and negative ions present in the compound differs from that required by the ideal chemical formula of the compound are called **non-stoichiometric compounds**.

The defects in these compounds are called non-stoichiometric defects. For example; vanadium oxide has the formula VO_x where x lies between 0.6 and 1.3. Similarly, iron(II) oxide of ideal composition FeO is difficult to obtain. Normally, we get samples of more oxygen atoms than iron atoms (composition of $Fe_{0.95}$ O but it may range from $Fe_{0\cdot 93}O$ to $Fe_{0\cdot 96}0$). ZnO usually has more zinc atoms than oxygen atom. The electrical neutrality of the crystal is maintained. The non-stoichiometric behaviour is the most commonly found for transition metal compounds. It is also found for some lanthanides and actinides.

These are of two types depending upon whether positive ions are in excess or negative ions are in excess. These are also known as **metal excess defects and metal deficiency defects,** respectively. The classification of non-stoichiometric defects can be summarized as shown in Fig. 8.

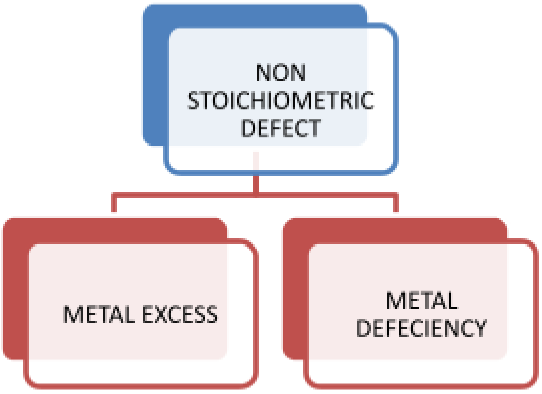


Fig. 8: Classification of non-stoichiometric defects

Metal excess defects: In these defects, the positive ions are in excess. These may arise due to the following two ways :

- Anionic vacancies
- Presence of extra cations in interstitial sites.

- *Anionic Vacancies*: In this case, negative ions may be missing from their lattice sites leaving holes in which the electrons remain entrapped to maintain the electrical neutrality. This is shown in Fig. 9. Evidently, there is an excess of positive (metal) ions all though the crystal as a whole is electrically neutral. This type of defect is observed in those crystals which are likely to form Schottky defects. When alkali metal halides crystals are heated in the atmosphere of the alkali metal vapour, anion vacancies are produced. For example, when the crystals of NaCl are heated in an atmosphere of sodium vapour, the excess of sodium atoms are deposited on the surface of the crystal. The Cl^- ions diffuse to the surface of the crystal and combine with Na atoms to give NaCl. In the process, there is loss of electrons by sodium atoms to form Na^+ ions. The electrons, thus produced by the ionization of the sodium atoms diffuse into the crystal and get trapped at the anion vacancies. The electrons trapped in anion vacancies are referred to as **F-centers** (from **German word farbenzenter meaning colour center**). This impart yellow colour to the crystal of NaCl. The colour results from the excitation of these electrons when they absorb energy from the visible light falling on the crystal. Similarly, Potassium in KCl makes the crystal appear violet (or lilac), while the excess of lithium ion in LiCl makes the crystal appear pink.

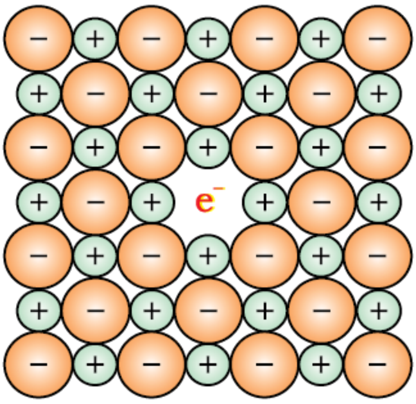


Fig. 9: Metal excess defect and the formation of F-centre

- *Excess cations occupying interstitial sites*: In this case, there are extra positive ions occupying 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 Frenkel defect. The common example is zinc oxide (ZnO) which is white in color at room temperature. On heating it loses oxygen reversibly at high temperature and turns yellow in colour.

$$ZnO \xrightarrow{Heat} Zn^{2+} + \frac{1}{2}O_2 + 2e^-$$

The excess Zn^{2+} ions are trapped in interstitial sites and equal numbers of electrons are trapped in the neighbouring interstitial sites to balance the electrical charge. This electron gives rise to enhanced electrical conductivity.

Consequences of metal excess defects:

The crystals with metal excess defect conduct electricity due to presence of free electrons. However, the conductivity is very low because the number of free electrons is very small. Because of low conductivity as compared to conductivity of metals, these are called semiconductors. These compounds are also called **n-type semiconductors.** You will study the semiconductors in the next module. The crystals with metal excess defects are generally coloured, e.g. non-stoichiometric sodium chloride is yellow, non-stoichiometric potassium chloride is violet.

Solved Example 2

Sometimes, common salt is yellow instead of being pure white. Why?

Solution:

Sometimes, common salt is yellow instead of being pure white due to the presence of electrons in some lattice sites in place of anions. These sites act as F-centers and impart colour to common salt by the excitation of these electrons when they absorb energy from the visible light falling on the crystal.

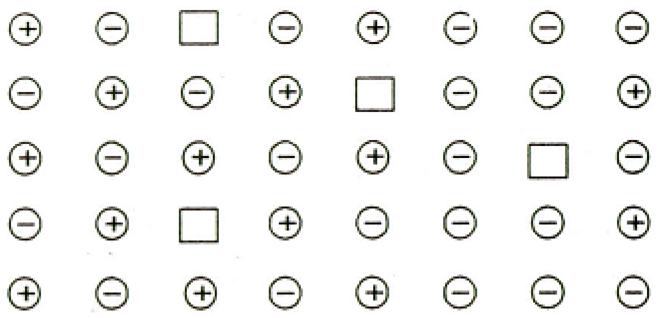
Metal deficiency defects: These defects occur when the crystal contains less number of positive ions than negative ions. These defects can arise due to the following two reasons:

- Cation vacancies
- 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 state. The common examples of compounds having this defect are ferrous oxide, ferrous sulphide and nickel oxide.

  In case of iron pyrites (FeS), 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 result, the crystal has a metallic luster. Because of the natural colour of iron pyrites and metallic lustre 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+} are missing and the loss of positive charge is made up by the presence of the required number of Fe^{3+} ions. Moreover, since there is exchange of electrons, the substances become conductors.

Solved Example 3

Answer the following questions based on a portion of the defective crystal given below. :



1. What are these types of vacancy defects called?
2. How is the density of a crystal affected by these defects?
3. Name one ionic compound which can show this type of defect in the crystalline state.
4. How is the stoichiometry of the compound affected?

Solution:

In the illustration it is observed that equal numbers of cations and anions are missing from their respective lattice sites. Based on this fact:

i) It is a Schottky defect.

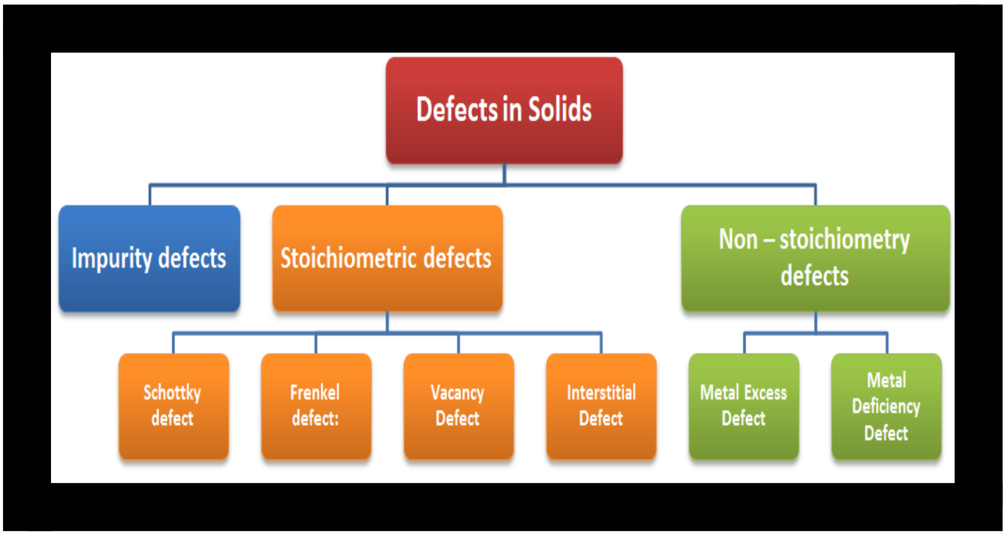
ii) The density of the crystal decreases since there are less number of constituent particles in the given volume of crystal.

iii) KCl shows this type of defect

iv) Stoichiometry of the compound remains the same as an equal number of cations and anions are missing.

Summary

- Any departure from a perfectly ordered arrangement of constituent particles (atoms, molecules or ions) in a crystal is called imperfection or defect.
- Imperfections/defects occur due to the fast rate of crystallization because constituent particles (atoms, molecules, ions) do not get sufficient time to arrange themselves in a perfect order.
- Even during the preparation of a single crystal, by carrying out the crystallization at an extremely slow rate, the crystal may not have a perfect arrangement.
- There are two types of defects, namely Point defects and Line defects.
- When the deviations or irregularities exist from the ideal arrangement around a point or an atom in a crystalline substance the defects are called Point defects.
- When the deviation from the ideal arrangement exists in the entire row of lattice points , the defect is called line defect.



- If defects in the crystals are such that the ratio between the cations and anions remains the same as represented by the molecular formula, i.e., the stoichiometry of the solid is not disturbed, the defects are called stoichiometric defects.
- These are also called intrinsic defects (deviation within the crystal) or thermodynamic defects (due to absorption of heat from the surrounding).
- When in crystalline substance, some of the lattice sites are vacant, the crystal is said to have vacancy defects. It results in the decrease in the density of the substance. This defect is shown by non- ionic solids.

- When some constituent particles (atoms, molecules) are present in the interstitial sites, the crystals are said to have interstitial defects. This defect increases the density of the substance (because mass increases but volume remains same). This defect is shown in non-ionic solids.
- In the Frenkel defect the smaller ion, usually cation, is missing from its lattice site causing a vacancy or a hole there and occupies the interstitial site. In this defect electrical neutrality as well as the stoichiometry of the compound is maintained. This defect is a combination of vacancy defect and interstitial defect.
- In Schottky defect equal number of cations and anions are missing from the lattice site.
- Impurity defects arise when foreign atoms are present at the lattice site in place of host atoms (substitutional solid solutions) or at the vacant interstitial site (interstitial solid solution).
- In non-stoichiometric defects the ratio of the number of cations to the number of anions is different from that indicated by the ideal chemical formula. That is, the stoichiometry of the compound is disturbed.
- In metal excess defect by anion, a negative ion may be missing from its lattice site, leaving a hole which is occupied by an electron thereby maintaining the electrical neutrality. These sites containing the electron are called F- centres (F-Farbenzenter a *German* word for colour).
- In another type of metal excess defect an extra cation may occupy an interstitial site and an extra electron may be present in an interstitial site.
- Metal deficiency defect occurs in those solids which contain less amount of metals compared to stoichiometric composition. This occurs in metals which show variable valency like transition metals. This defect generally occurs due to the missing cation from its lattice site and the presence of the cation having higher charge (e.g. +2 instead of +1) in the adjacent site.

Questions

Fill in the blanks:

1. Point defect that occurs in a crystal of zinc sulphide is ____________

   Frenkel defect
2. Anionic vacancies occupied by electrons are known as ____________

   F centre

3. The crystal defect which lowers the density of an ionic crystal is ________

   Schottky defect

4. The crystal of ________ shows both Frenkel and Schottky defects.

   AgBr

5. LiCl is pink in colour due to the presence of _________

   F centre

6. Crystal defect produced when NaCl is doped with $MgCl_2$ is __________

   Cation vacancy

7. KCl appears violet in colour due to the presence of _________

   F centre

8. In Frenkel defect the density of the crystal _____________

   Remain unchanged

9. In Schottky defect the density of the crystal _________

   Decreases

10. Addition of _______ to AgCl causes cation vacancy in its crystal.

    $CdCl_2$ or $SrCl_2$

MCQ

1. Stoichiometric defect shown by AgBr crystal

A. Schottky defect

B. Frenkel defect

C. Schottky and Frenkel defect

D. Vacancy defect

2. Which one of the following statements is incorrect about vacancy defects?

A. Some constituent particles are missing from the lattice site.

B. Some constituent particles occupy the interstitial sites.

C. The density of the crystal decreases due to the presence of vacancy defects.

D. It arises when the crystal is heated.

3. In 1 cm^3 of NaCl crystal there are 10^6 Schottky pairs and 10^{16} ions in at room temperature. The number of NaCl present in 1 cm^3 of the crystal is

A. 10^{22}

B. 10^{23}

C. 10^{16}

D. 10^{6}

4. Which of the following statements are correct about the crystals showing Frenkel defect?

A. Some ions leave their lattice sites and occupy the interstitial.

B. It is shown by the ionic solids when the cation is much smaller in size than the anion.

C. The density of the crystal is unaffected.

D. All of above

Answer

Fill in the blanks:

1. Frenkel defect
2. F centre
3. Schottky defect
4. AgBr
5. F centre
6. Cation vacancy
7. F centre
8. Remain unchanged
9. Decreases
10. $CdCl_2$ or $SrCl_2$

MCQs

1. C
2. B
3. A
4. D