BYJU'S Classes

Solid State

Crystal Defects and Electrical Properties of Solids

What you already know

- Anti-Fluorite (Na_2O) Structure: Radius ratio and coordination number calculation
- Caesium chloride (CsCl) Structure: Radius ratio and coordination number calculation
- Effect of temperature and pressure on crystal structure
- Truncated polyhedron
- Defects in crystals - (a) Point defect (b) Line defect (c) Surface defect (d) Volume defect
- Types of point defects - (a) Stoichiometric defects (b) Impurity defects (c) Non-Stoichiometric defects

Crystal Defects and Electrical Properties of Solids

What you will learn

- Defects in ionic solids
- Schottky effect
- Frenkel defect
- Effect of Schottky & Frenkel defect on properties of crystal
- Non-stoichiometric defects
- Metal excess defect
- Heating of NaCl
- Metal deficiency defect
- Substitutional impurity defects
- Interstitial impurity defect
- Point Defects in non-ionic solids
- Vacancy defect
- Interstitial defect
- Properties of solids
- Electrical properties of solids
- Band theory
- Band gap
- Practice questions

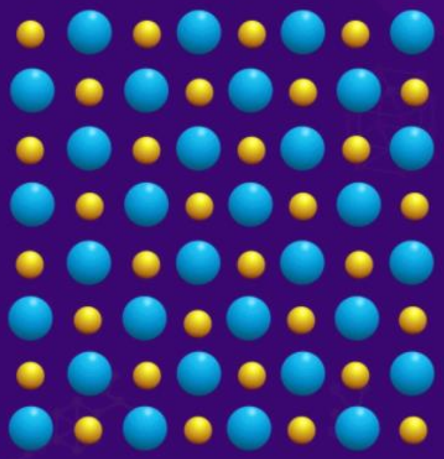
Defects in Ionic Solids

- Point defects in ionic solids
  - Stoichiometric defects
    - Schottky
    - Frenkel
  - Non-stoichiometric defects
  - Impurity defects

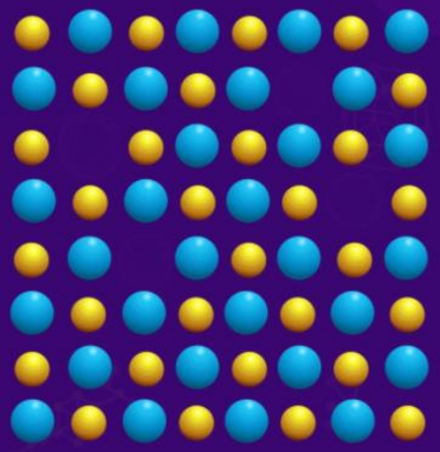
Schottky Defect

Schottky defect consists of **ion vacancy** in a crystal lattice, but the **stoichiometry** of a compound (and thus, electrical neutrality) is **retained**.

Pure ionic crystal is shown and yellow spheres are cations blue spheres are anions, pair of cation and anion is removed from the lattice.



Perfect crystal



Crystal with Schottky defect

Schottky Defect

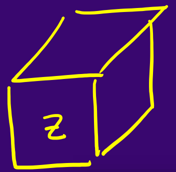
Characteristics

(i) Shown by **ionic substances** in which the cation and anion are of almost **similar sizes.**
E.g.: NaCl, KCl, AgBr, & CsCl

(ii) Schottky defect **decreases the density** of the crystal.

In **NaCl**, there is approximately **one schottky defect per 10^{16} ions** at room temperature.

Schottky Defect $\downarrow$ $\boxed{\rho} = m \downarrow$ ✓



$$\rho_{th} = \frac{Z_{th}\cdot M}{\cancel{N_A}\cdot \cancel{a^3}}$$

$$\rho_{exp} = \frac{Z_{exp}\cdot M}{\cancel{N_A}\cdot \cancel{a^3}}$$

$$= \frac{Z_{th}}{Z_{exp}} = \frac{Z_{th}}{Z_{th} - Z_{missing})}$$

% Missing units $= \left(\frac{d_{th} - d_{exp}}{d_{th}}\right) \times 100$

$$\therefore \frac{\rho_{exp}}{\rho_{th}} = \frac{Z_{th} - Z_{missing}}{Z_{th}} = 1 - \frac{Z_{missing}}{Z_{th}}$$

d_{th} = Theoretical density = density without defects

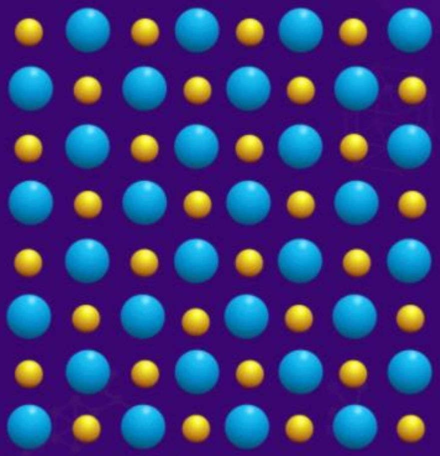
d_{exp} = Experimental density (ρ with defects)

$$\therefore \frac{Z_{missing}}{Z_{th}} = 1 - \frac{\rho_{exp}}{\rho_{th}} = \left(\frac{\rho_{th} - \rho_{exp}}{\rho_{th}}\right)$$

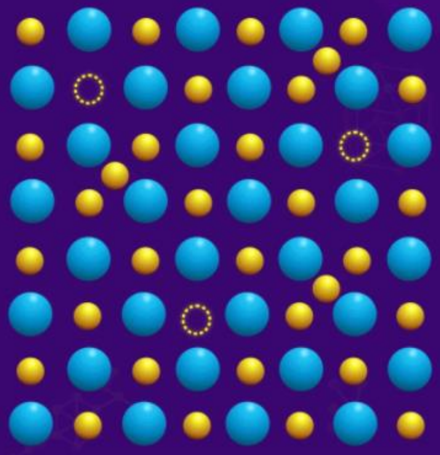
Frenkel Defect

When ions (usually cations) are **displaced from normal lattice positions** and are present in some interstitial voids.

Frenkel defect is also called **dislocation defect.**



Perfect crystal



Crystal with Frenkel defect

Pure ionic crystal is shown and yellow spheres are cations blue spheres are anions, usually cation is smaller and it is dislocated from its lattice point.

Frenkel Defect

Characteristics

(i) Shown by **ionic solids** having **large difference** in size between the positive & negative ions.
E.g: ZnS, AgCl, AgBr, & AgI

(ii) **Density** of a solid **does not change.**

AgBr shows both, **Frenkel** as well as **Schottky** defect.

Effect of Schottky & Frenkel Defect on Properties of Crystal

(i) **Stability** of crystal

Defects $\uparrow$

Repulsions between Like - charged ions $\uparrow$

Stability $\downarrow$

(ii) Electrical conductivity

Defects $\uparrow$

Mobility of ions in the crystal $\uparrow$

Electrical conductivity $\uparrow$

Effect of Schottky & Frenkel Defects on Properties of Crystal

(iii) **Dielectric constant** of the substance

Due to the accumulation of similar charge (locally)

↓

Polarity is induced in the crystal

↓

Dielectric constant ↑

The theoretical density of ZnS is d g/cm³. If the crystal has **4% Frenkel defect**, then the **actual density** of ZnS should be:

BOARDS MAIN

Solution

No change in density is observed in Frenkel defect.

Hence, option (a) is the correct answer.

a. d g/cm^3

b. 0.04d g/cm^3

c. 0.96d g/cm^3

d. 1.04d g/cm^3

In an antifluorite structure, cations occupy:

BOARDS MAIN

a. Octahedral voids

b. Centre of the cube

c. Tetrahedral voids

d. Corners of the cube

Solution

Antifluorite structure is A_2B like structure where cations occupy all the tetrahedral voids and anions occupy FCC lattice points.

Hence, option (c) is the correct answer.

Antifluorite structure is derived from fluorite structure by:

BOARDS

a. Heating fluorite crystal lattice

b. Subjecting fluorite structure to high pressure

c. Inter changing the positions of positive and negative ions in the lattice

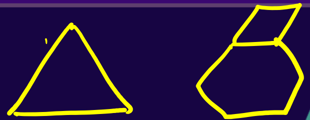
d. None of these

Solution

Inter changing the positions of positive and negative ions in the fluorite lattice gives antifluorite structure.

Hence, option (c) is the correct answer.

Select the **correct** statement(s):



8 faces

a. The ionic crystal of AgBr may have Schottky defect.

b. Truncated octahedron has 36 edges.

$6 \times 4 = 24$ edges

$3 \times 8 \times \frac{1}{2} = 12$ edges

36

c. In ionic compounds having Frenkel defect the ratio r_+/r_- is high.

low

d. The coordination number of Na^+ ion in NaCl is 6.

Hence, option (a), (b) and (d) is the correct answer.

Which of the following may have Frenkel defect?

BOARDS MAIN

a. ZnS

b. $AgCl$

c. $AgBr$

d. AgI

Solution

All silver halides can show Frenkel defect and ZnS also shows Frenkel defect.

Hence, all options are the correct answer.

The number of square faces in a truncated octahedron is ‘x’ and the effective number of carbon atoms per unit cell in diamond is ‘y’, then the value of 'y – x' is:

BOARDS MAIN

Solution

The number of square faces in a truncated octahedron is ‘x’ = 6.

Effective number of carbon atoms per unit cell in diamond is ‘y’ = 8.

Hence, $y - x = 8 - 6 = 2$.

Defects in Ionic Solids

Point defects in ionic solids

- Stoichiometric defects
- Non-stoichiometric defects
- Impurity defects

Non-Stoichiometric Defects

The formula of compound will get **modified** because of the presence of these defects.

Non-stoichiometric defects → Metal excess

Non-stoichiometric defects → Metal deficiency

Metal Excess Defect

Instead of anion, electron **occupies** the lattice site of **anion**.

E.g: **NaCl** and **KCl** show such defects

Heating of NaCl

When crystals of NaCl are **heated** in an atmosphere of sodium vapour

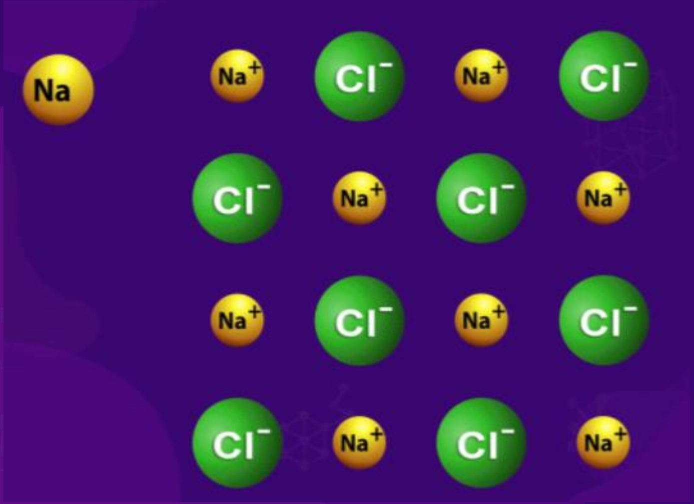
Cl^- ions diffuse to the **surface** of the crystal and combine with Na atoms to give NaCl

This happens due to **loss of electron** by sodium atoms to form Na^+ ions.

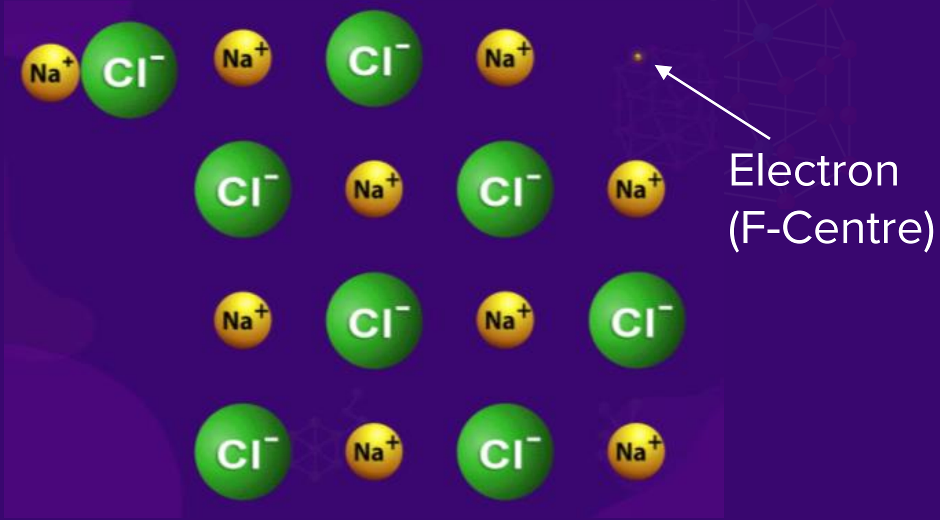
The **released electrons** diffuse into the crystal and **occupy anionic sites.**

These anionic sites occupied by unpaired electrons are called **F-centres.**

Heating of NaCl



Na vapour approaching perfect crystal



Defect due to anionic vacancy

Metal Excess Defect

Zinc oxide is **white** in colour at room temperature.

On heating, it **loses some** $\mathbf{O^{2-}}$ ions in the form of $\mathbf{O_2}$ and turns yellow.

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

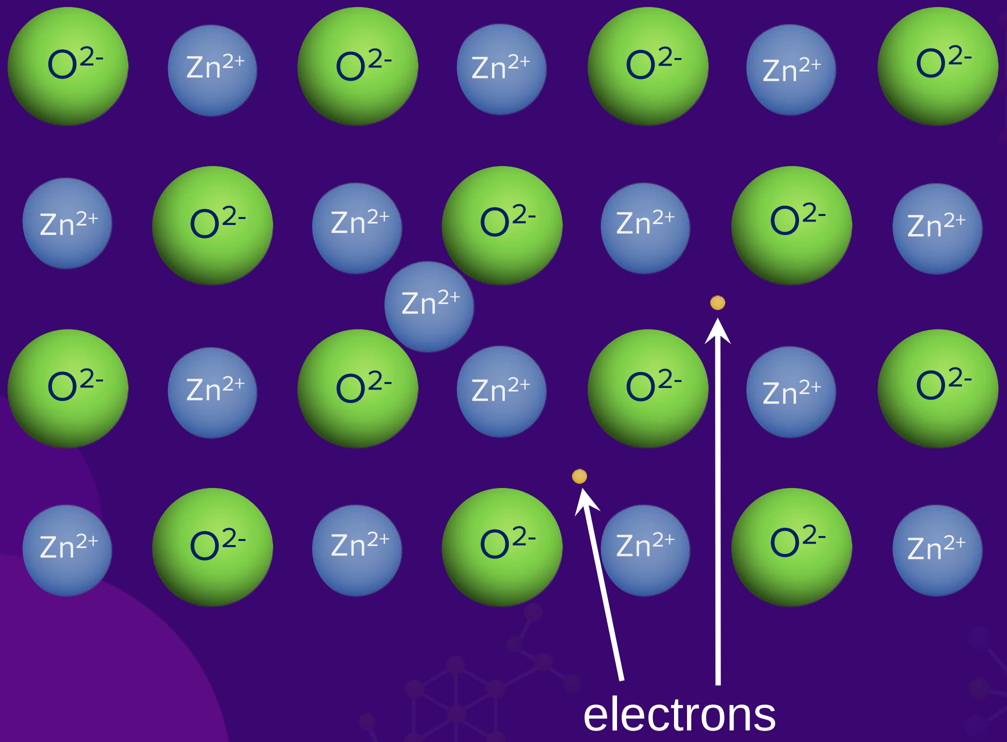
Electrical property and **colour** of solid gets modified

Substance becomes **paramagnetic**

E.g.: Crystal of NaCl is **yellow**, KCl is **violet** or **lilac** and LiCl is **pink.**

Metal Excess Defect

$Zn_{1+x}O$



Metal Deficiency Defect

$3\,Fe^{2+}$: $+6$

$2\,Fe^{3+}$: $+6$

1 Fe atom missing

If a **positive charge is absent** from its lattice site, the charge can be balanced by an **adjacent metal ion** having an extra positive charge.

Fe^{3+} O^{2-} Fe^{2+} O^{2-} Fe^{2+} O^{2-}

O^{2-} Fe^{2+} O^{2-} O^{2-} Fe^{3+}

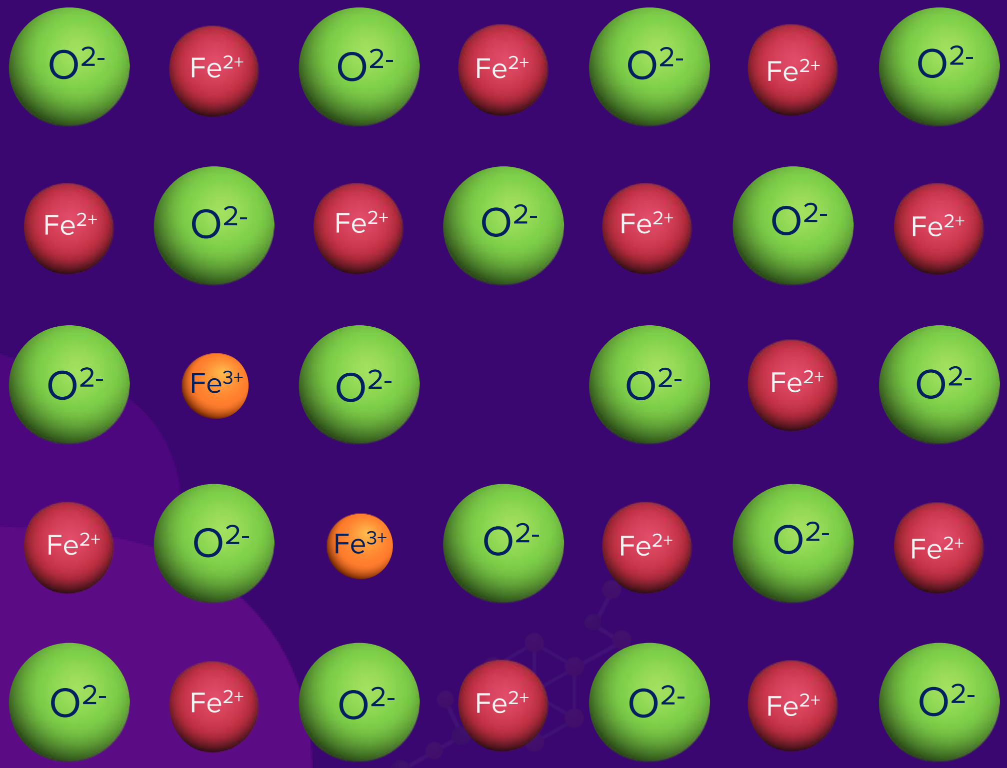
Example,

FeO is mostly found with a composition of **$Fe_{0.93}O$ to $Fe_{0.96}O$**

Loss of some Fe^{2+} ions is compensated by the presence of required number of Fe^{3+} ions.

Metal Deficiency Defect

FeO



Experimentally, it was found that a metal oxide has formula $M_{0.98}O$. Metal M, present as M^{2+} and M^{3+} in its oxide. Fraction of the metal which exists as M^{3+} would be:

BOARDS MAIN

a) 7.01%

b) 4.08%

c) 6.05%

d) 5.08%

Solution

Let us suppose that the formula of metal oxide is $M_{98}O_{100}$.

We know that the total charge should be zero. Out of 98 metal atoms, let x atoms of metal be of +3 charge. So (98 – x) atoms would be of +2 charge.

Now, Total charge = $[3x + 2(98 - x) - 2 \times 100] = 0 \Rightarrow x = 4$.

Therefore, percentage of fraction of metal atoms with +3 charge will be

$(4/98) \times 100 = (2/49) \times 100 = 4.08$ %.

Hence, option (b) is the correct answer.

The correct statement(s) regarding defects in solids is(are):

BOARDS MAIN

(a) Frenkel defect is usually favored by a very small difference in the sizes of cation and anion.

(b) Frenkel defect is a dislocation defect.

(c) Trapping of an electron in the lattice leads to the formation of F-Centre.

(d) Schottky defects have no effect on the physical properties of solids

Solution

Frenkel defect is a dislocation defect, usually favored by a very high difference in the sizes of cation and anion.
Trapping of an electron in the lattice leads to the formation of F-Centre.
Schottky defects have effect on the physical properties (density) of solids.
Hence, option (b) and (c) are the correct statements.

NaCl shows Schottky defects and AgCl show Frenkel defects. Their electrical conductivity is due to:

BOARDS MAIN

a. Motion of ions & not the motion of electrons

b. Motion of electrons & not the motion of ions

c. Lower coordination number of NaCl

d. Higher coordination number of AgCl

Solution

The motion of ions is responsible for the electrical conductivity and not the electrons in Frenkel and Schottky defects.

Hence, option (a) is the correct answer.

If an element (At. wt. = 50) crystallises in **FCC** lattice, with **a = 0.50 nm**. Calculate the **density** of unit cell if it contains **0.25 %** Schottky defects. (Use $N_A = 6 \times 10^{23}$)

BOARDS MAIN

% defects

$$\rho_{th} = \frac{4 \times 50}{6 \times 10^{23} (5 \times 10^{-8}\,cm)^3}$$

$$= \frac{2\cancel{4} \times \cancel{50}\,10}{3\,\cancel{6} \times 5^{\cancel{3}\,2} \times 10^{-1}}$$

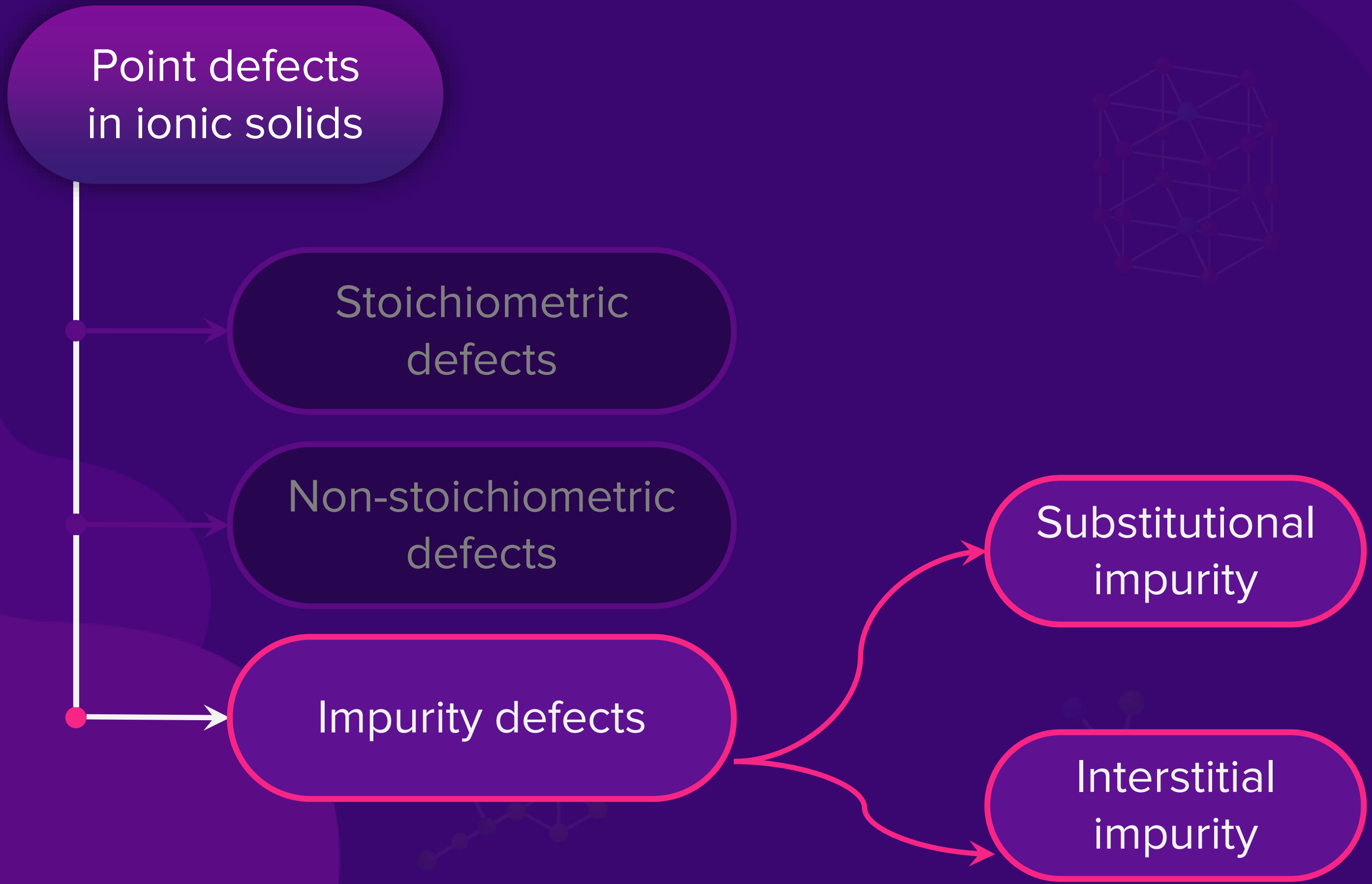
$= \frac{8}{3}$ g cm^{-3}

$$\rho_{ex} = \frac{8}{3} \times \cancel{0.9975}\ .3325 =$$

$= 2.66$

≈ 2.66 g cm^{-3}

Defects in Ionic Solids



Substitutional Impurity Defects

Defects in ionic crystals, can be introduced by **adding impurities**.

Similar sized cation **substitute** the existing cation of ionic crystal.

Example:
solid solution of
$CdCl_2$ and AgCl.

For example:

When molten **NaCl** is crystallised having a small amount of **$SrCl_2$**

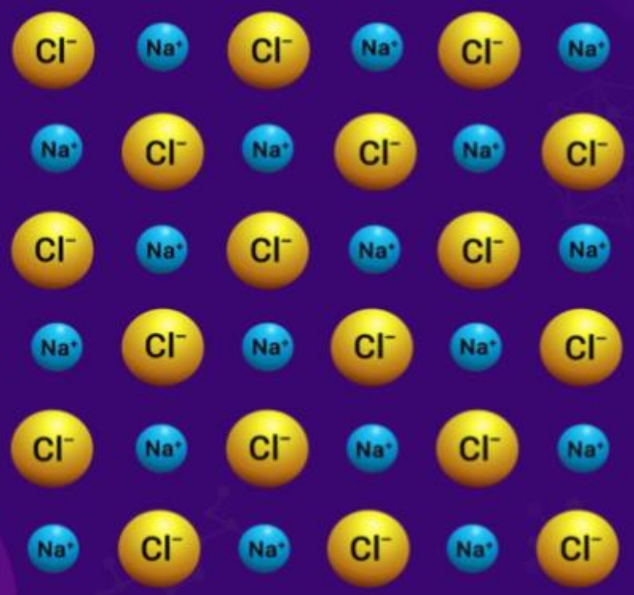
↓

Some **Na^+** ions' lattice points are occupied by **Sr^{2+}** ions

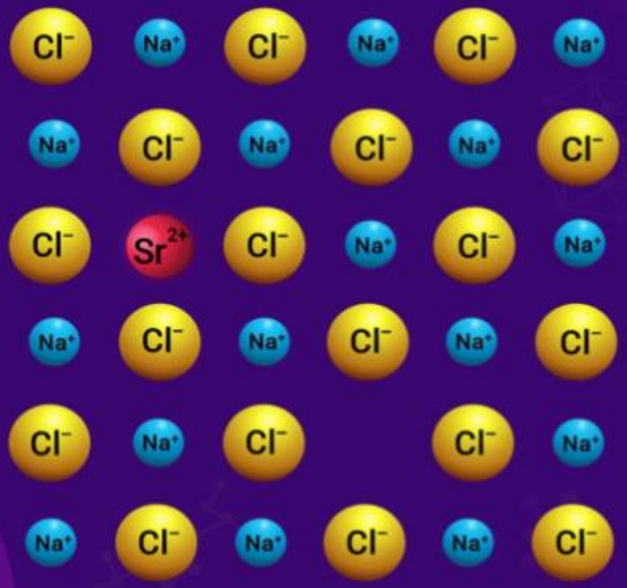
↓

Each **Sr^{2+}** replaces **two Na^+** sites by occupying a site of one Na^+ and other site remains vacant.

Substitutional Impurity Defects



Perfect crystal



Impure crystal

Number of cationic vacancies generated = Number of Sr^{2+} in the crystal

Interstitial Impurity Defect

When some **small foreign atoms** (like B, C, N, H) are **trapped** in interstitial voids of the lattice without any chemical reaction.

Formula remains the **same**.

d_{exp} > $d_{theoretical}$

Point Defects in Non-Ionic Solids

Point defects in non-ionic compounds

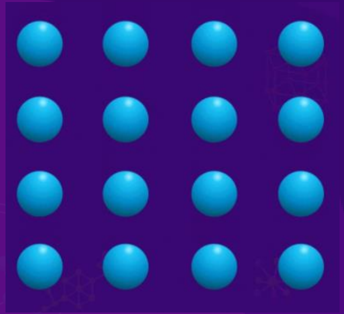
- Vacancy defect
- Impurity defects

Vacancy Defect

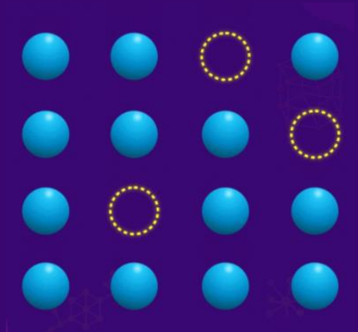
Such defect arises when some of the **lattice sites** in the crystal are **vacant**.

Density of crystal **decreases**.

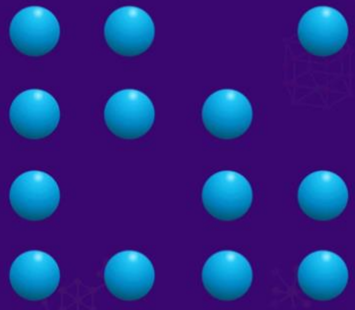
Vacancy Defect



Perfect crystal



Vacancies

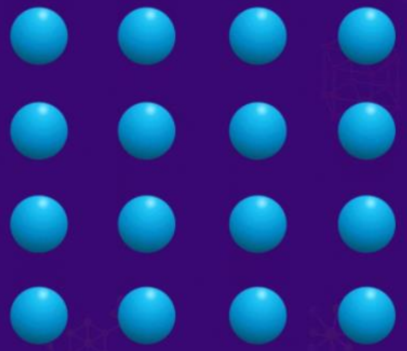


Crystal with
Vacancy defect

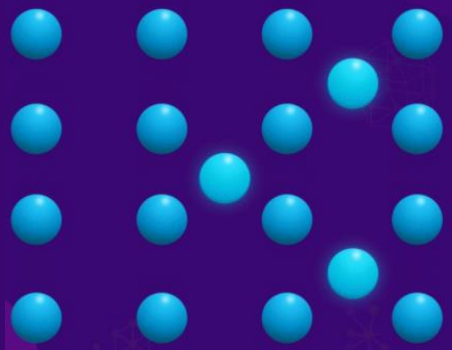
Interstitial Defect

Arises when some small **foreign atoms** (like B, C, N, H) are trapped in interstitial voids of the lattice without any chemical reaction.

Density of crystal **increases**.



Perfect crystal



Crystal with interstitial defect

Calcium crystallises in a ~~face-centred~~ cubic unit cell with a = 0.556 nm. Calculate the density, if it contained 0.1% vacancy defects.

99.9 %

MAIN

Solution

$\rho_{th} = \frac{4 \times 40}{(N_A)\, a^3} = \frac{4 \times 40}{6 \times 10^{23}\,(5.56 \times 10^{-8}\,cm)^3}$

$= \frac{2\cancel{4} \times 40}{\cancel{6}_3 \times 5.56^3 \times 10^{-1}}$

$\rho_{actual} = \rho_{th} \times 0.999$

$8\cancel{00} \times \frac{1}{3} \times \cancel{0.18} \times \cancel{1.8} \times .18$

$= 8 \times 3.24 \times 0.06$

$= 1.551\ g\ cm^{-3}$

5.5555

$= \frac{1}{0.18}$

$\rho_{th} = \frac{800}{3 \times 5.56^3} \times .999$

$= \frac{800 \times .333}{5.56^3}$

Which type of 'defect' has the presence of cations in the interstitial sites?

BOARDS MAIN

a Frenkel defect

b Metal deficiency defect

c Schottky defect

d Vacancy defect

Solution

Presence of cations in interstitial sites is observed in Frenkel defect.

Hence, option (a) is the correct answer.

Select the correct statement/s:

BOARDS MAIN

a When Li_2O is doped in NiO crystals, then one Li^+ replaces (or displaces) one Ni^{2+} but to maintain electrical neutrality one Ni^{2+} is oxidised to Ni^{3+}.

b Frenkel defect is usually shown by ionic compounds having low coordination number.

Select the correct statement/s:

BOARDS MAIN

c F-centres generation is a responsible factor for imparting the colour to the crystal.

d Density of crystal always increases due to substitutional impurity defect.

Hence, option (a, b, c) are the correct options.

Properties of Solids

Properties of Solids

Properties of solids

- Electrical properties
- Magnetic properties

Electrical Properties of Solids

Solids exhibit an amazing range of **electrical conductivities**.

The range of electrical conductivities varies from **10^{-20} to 10^{7} ohm^{-1} m^{-1}**.

On the basis of electrical conductivity

- Conductors
- Semiconductors
- Insulators

Electrical Properties of Solids

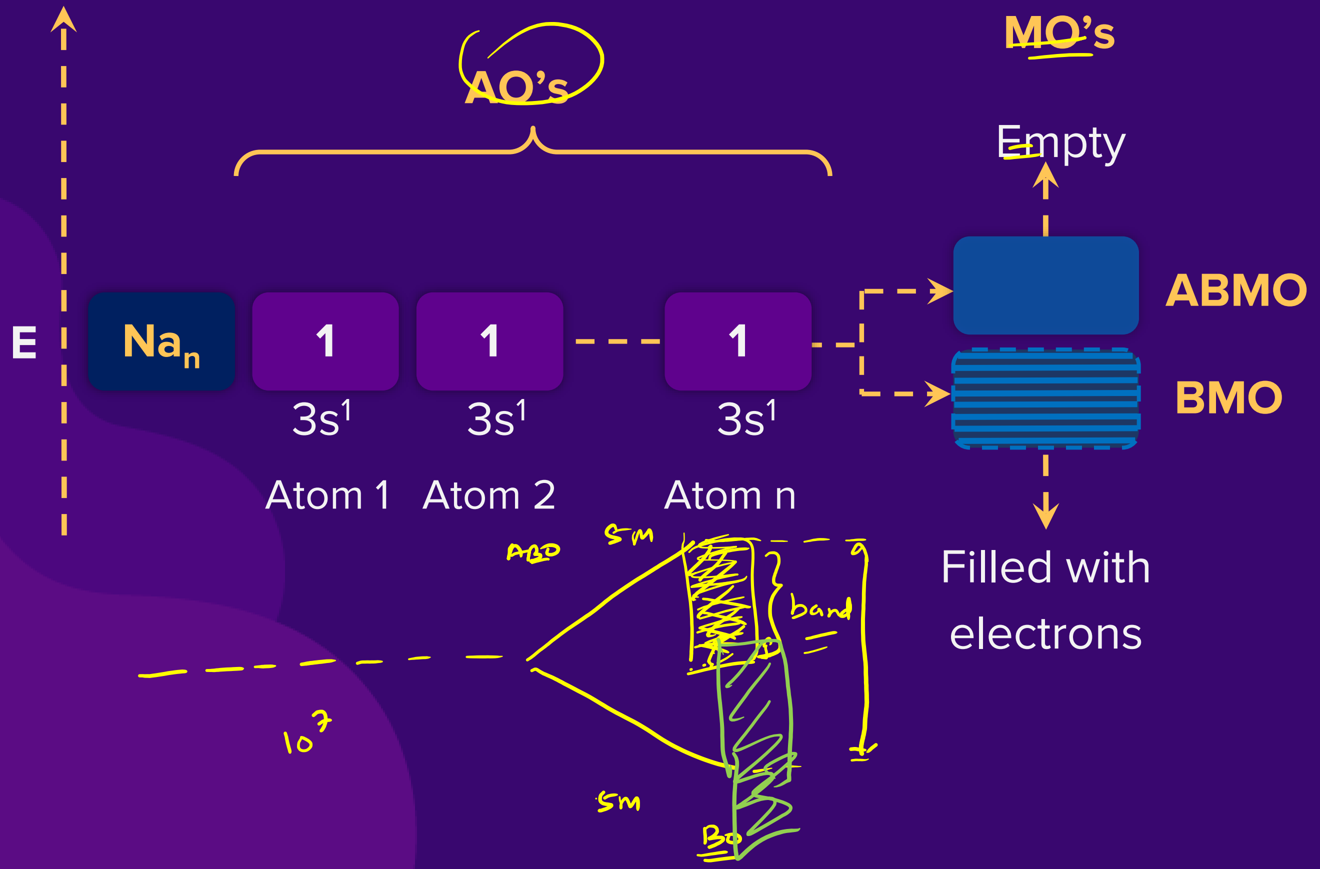
Type of solid	Conductivity range ($ohm^{-1}\ m^{-1}$)	Examples
Conductor	10^4 to 10^7	Metal
Semiconductor	10^{-6} to 10^4	Germanium (Ge), Silicon (Si) etc.
Insulator	10^{-20} to 10^{-10}	MnO, CoO; NiO, CuO

Band Theory

Band Theory

Overlap of atomic orbitals in solids gives rise to **bands of energy levels.**

Band Theory

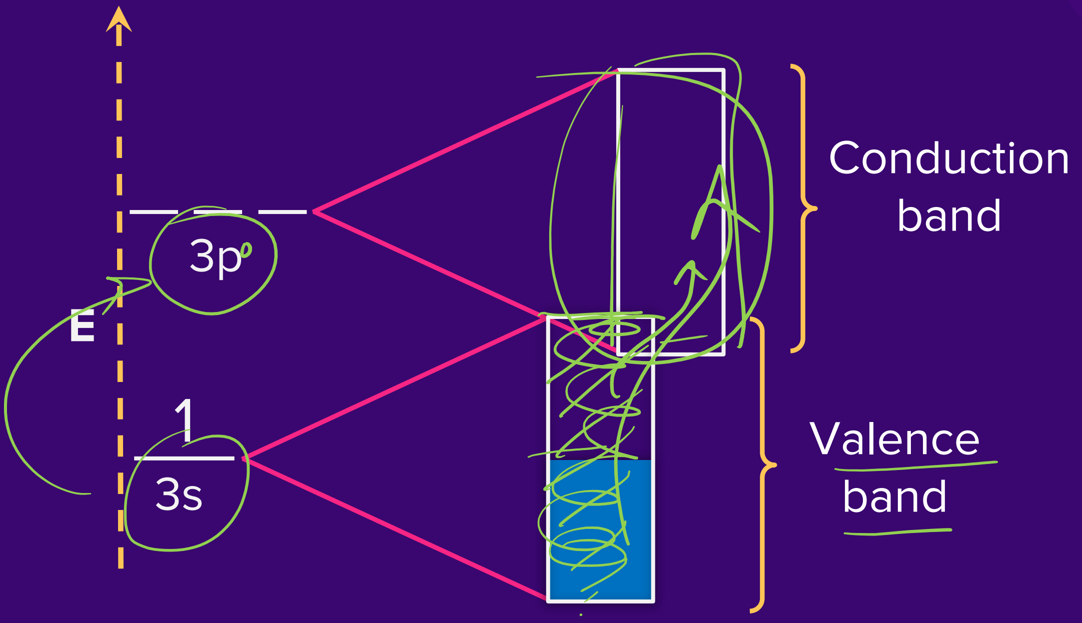


AO's
MO's
E
Na_n
1
1
1
$3s^1$
$3s^1$
$3s^1$
Atom 1
Atom 2
Atom n
Empty
ABMO
BMO
Filled with electrons
SM
ABO
band
10^7
SM
BO

Band of Orbital in Crystal of Sodium

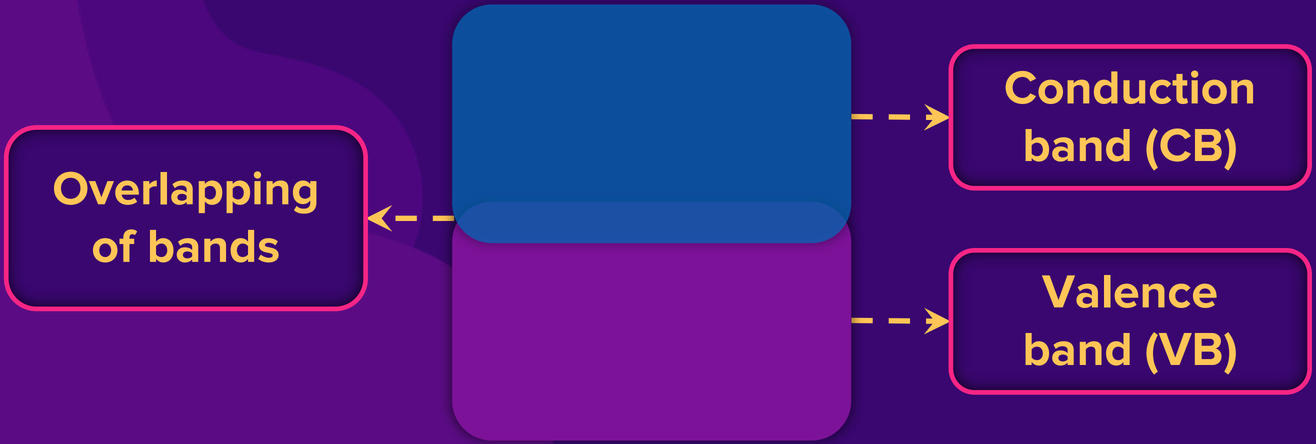
Valence band: In case of sodium it has its valence electron in 3s orbital, so 3s orbital makes a band with the valence electron and it is called as Valence band.

Conduction band : Incase of sodium the 1st empty orbital is 3p orbital and also 3p orbital acts as an empty band. if electron jumps from valence band to empty band then electron can easily move; this band is known as conduction band.



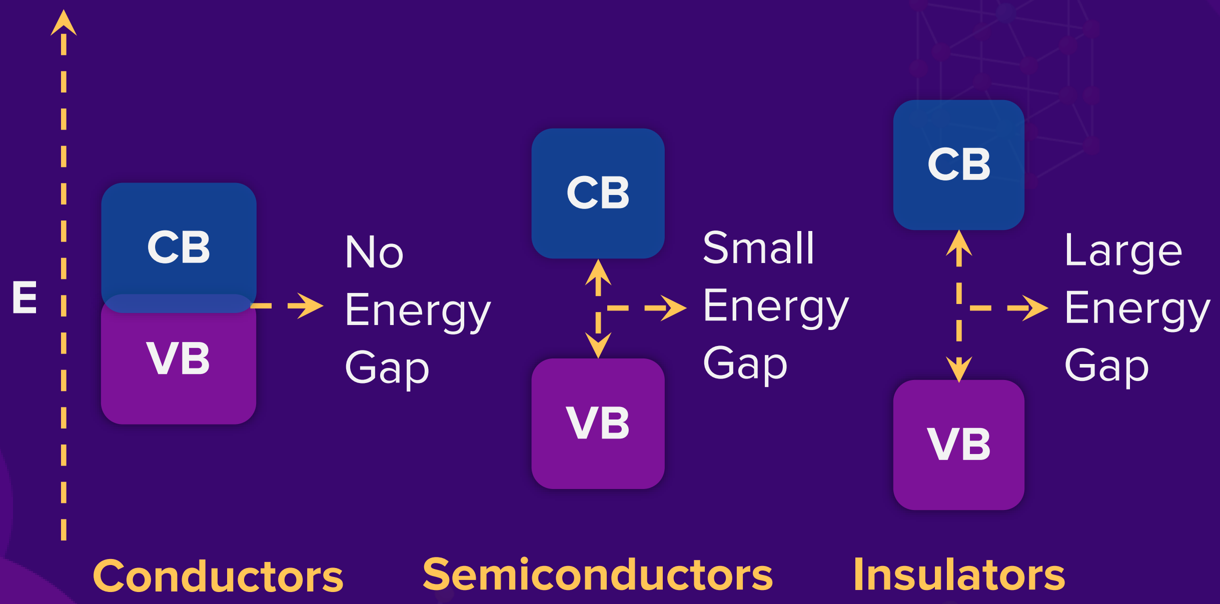
Band Theory

In metals the energy gap between valence band and conduction band is very low and it may overlap with each other. So electron can easily move to conductor band and conduct electricity hence known as electrical conductor.



Band Gap

Energy difference between the valence band and the conduction band



Band Theory

Metals

Temperature ↑

↓

Thermal vibrations of the nuclei produce electrical **resistance**

↓

Electrical conductivity ↓

Band Theory

Semiconductors

Temperature ↑ → Electrical conductivity ↑

On heating → **Electron easily jumps** from VB to CB

Band Theory

(1) **TiO, CrO_2, & ReO_3** behave like **metals** with respect to **electrical conductivity**.

(2) **VO, VO_2, VO_3, & TiO_3** show **metallic or insulating** properties depending on **temperature**.

How does the conductivity of a semiconductor change if its temperature is raised?

BOARDS MAIN

a. Conductivity increases with increase in temperature

b. Conductivity decreases with increase in temperature

c. No effect

d. Conductivity may increase or decrease

Solution

As we know that With increasing temperature electrical conductivity increases because on heating electron easily jumps from valence band to conduction band.

Hence, option (a) is the correct answer.

Statement-1: Electrical conductivity of semi-conductors increases with increasing temperature.

Statement-2: With increase in temperature, number of electrons from the valence bond can jump to the conduction band in semi-conductors.

BOARDS MAIN

a. If both statements are true and statement-2 is the correct explanation of statement-1

b. If both statements are true but statement-2 is not the correct explanation of statement-1

c. If statement-1 is true and statement-2 is false.

d. If statement-1 is false and statement-2 is true.

Solution

Statement-1: Electrical conductivity of semiconductors increases with increasing temperature. This statement is the true statement.
Statement-2: With increase in temperature, number of electrons from the valence bond can jump to the conduction band in semiconductors is also the true statement and correct explanation of statement – 1.

Hence, option (a) is the correct answer.

Which of the following is/are correct?

BOARDS MAIN

a. TiO, behaves like metals with respect to electrical conductivity

b. The range of electrical conductivities of solid varies from 10^{-20} to 10^{7} ohm^{-1} m^{-1}

Which of the following is/are correct?

BOARDS MAIN

c) TiO_3 show metalic or insulating properties depending on temperature

d) All of these

Ferrous oxide (FeO) is experimentally found to have the formula $Fe_{0.93}O$. Find the % of Fe ions in +3 oxidation state.

MAIN BOARDS

Solution

$Fe_{93}O_{100}$

$x \quad +3$

$(93-x) \quad +2$

Fe : +2

Fe : +3

$+3x + 2(93-x) - 2 \times 100 = 0$

$x = 14$

% of Fe in +3 $= \frac{x}{93} \times 100$

$= \frac{14}{93} \times 100$

$= \frac{2}{12.3} \times 100$

$\approx 16.4\ \%$

Therefore , the percentage of the Fe^{3+} is 15.5 %.

Ferrous oxide (FeO) is experimentally found to have the formula $Fe_{0.93}O$. Find the % of Fe ions in +3 oxidation state.

BOARDS MAIN

Solution

$Fe_{93}O_{100}$

x $+3$

$(93-x)$ $+2$

Fe : +2

Fe : +3

$+3x + 2(93-x) - 2\times100 = 0$

$x = 14$

$\% \text{ of Fe in } +3 = \frac{x}{93}\times100$

$= \frac{14}{93}\times100$

Therefore , the percentage of the Fe^{3+} is 15.05 %.

The appearance of color in solid **alkali metal halides** is generally due to:

BOARDS MAIN

a. Schottky defect

b. Frenkel defect

c. Interstitial position

d. F-centres

Solution

The appearance of color in solid alkali metal halides is generally due to F-centres.

Hence, option (d) is the correct answer.