By- S. SHUKLA SIR

Imperfections in Solids

The irregularities or deviations observed in ideal arrangement of constituent particles in a solid crystal are called imperfections or defects in solids.

It may be of following two types-

(A) Point defects- Irregularities in the arrangement of constituent particles around a point or constituent particle in a crystalline substance is called point defect.

(B) Line defects- Irregularities in the arrangement of constituent particles in entire rows of lattice points is called line defect.

Types of Point Defects

Point defects may be of following three types:

(1) Stoichiometric defects
(2) Non-stoichiometric defects
(3) Impurity defect

(1) Stoichiometric Defects

In this type of point defect stoichiometry of the solid remains unchanged. It is also called intrinsic or thermodynamic defect and may be of following two types:

(i) Vacancy defect

It is specially shown by non-ionic solids. Here, some of the lattice sites left vacant during packing of constituent particles.

Such defects are produced on heating the solid crystals and results in the decrease of density of the crystal.

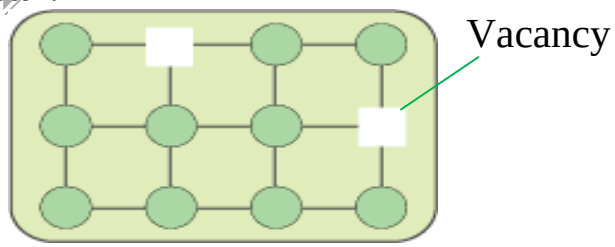


Fig.- Vacancy Defect

In ionic solids this defect is called **Schottky defect.**

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(ii) Interstitial defect

It is also shown by non-ionic solids, where some of the constituent particles (atoms or molecules) get dislocalised and occupy an interstitial site of the crystal.

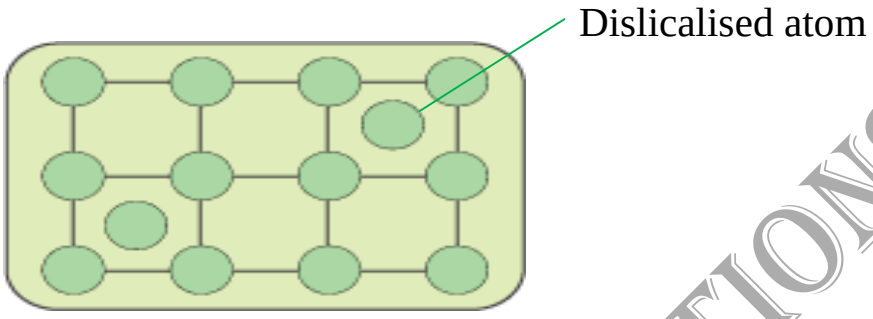


Fig.- Interstitial Defect

In ionic solids this defect is called Frenkel defect.

Schottky defect

It is basically a vacancy defect shown by ionic solids, where equal number of cations and anions are completelly missing from the crystal lattice. Thus,

"Such stoichiometric point defect in which equal number of cations and anions are completelly missing from the crystal lattice is called **Schottky** defect.**"**

In Schottky defect, due to formation of vacancies, the density of the crystal gets decreased and electrical conductance gets increased, but the electrical neutrality remains unchanged.

Significant number of Schottky defect is present in ionic solids such as NaCl, KCl CsCl, AgBr etc. For example, in NaCl, there are approximately 10^6 Schottky pairs per cm^3, at room temperature.

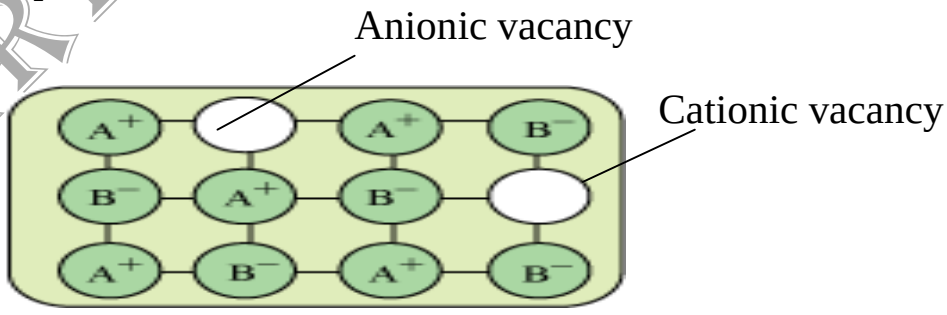


Fig.- Schottky defect

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Conditions for showing Schottky Defect

(1)The ionic size of cation and anion should be comparable.

(2) The coordination number of cation should be high.

Frenkel defect

It is shown by ionic solids containing very larged sized anions as compared to cations. Here, small sized cations get dislocalised from their normal site to the interstitial sites. Hence, it is also called dislocation defect. Thus,

"Such stoichiometric point defect in which one or more cations get dislocalised from their normal site and occupy the interstitial sites is called **Frenkel** defect.**"**

It creates both vacancy as well as interstitial defects and is most common in ionic solids such as AgCl, AgBr, AgI, ZnS etc.

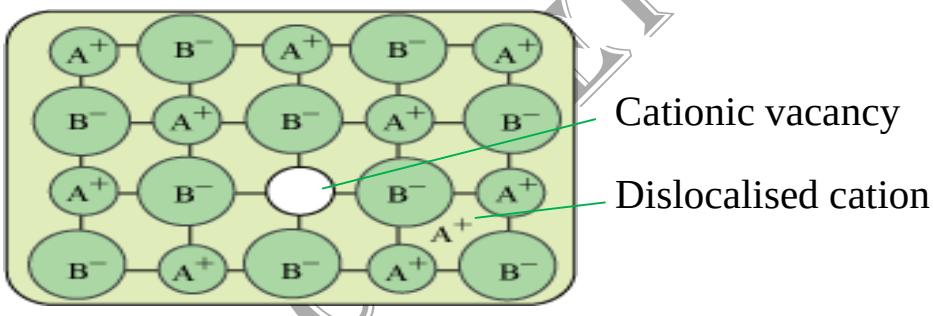


Fig.-Frenkel Defect

In Frenkel defect, the density and electrical neutrality of the crystal remains unchanged but electrical conductance gets increased.

Conditions for showing Frenkel Defect

(3)The ionic size of anion should be much more larger than that of cation.

(4) The coordination number of cation should be low.

(2) Non-Stoichiometric Defects

In this type of point defect, the stoichiometry of the solid gets changed. It may be of following two types:

(i) Metal excess defect

(ii) Metal deficiency defect

(i) Metal excess defect

(a) Metal excess defect due to anionic vacancies

Alkali metals like NaCl and KCl show this type of defect.

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When crystals of NaCl are heated in an atmosphere of sodium vapour, the sodium atoms are deposited on the surface of the crystal. The Cl^- ions diffuse from the crystal to its surface and combine with Na atoms, forming NaCl. During this process, the Na atoms on the surface of the crystal lose electrons. These released electrons diffuse into the crystal and occupy the vacant anionic sites, creating F-centres.

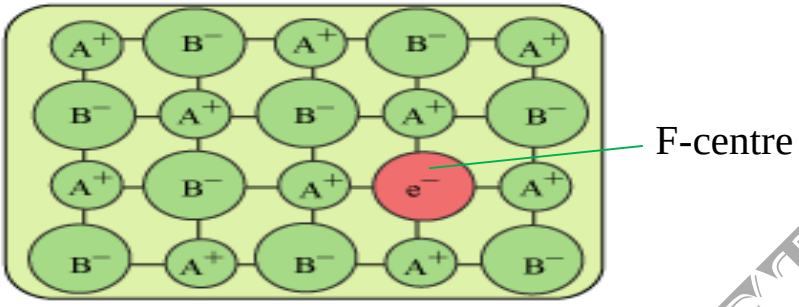


Fig.- Metal excess defect due to anionic vacancies

F- centres provide a definite colour to the crystals, For example, due to presence of F-centres NaCl is yellow, KCl is violet and LiCl is Pink in colour.

(b) Metal excess defect due to the presence of extra cations at interstitial sites-

When white coloured zinc oxide is heated, it loses oxygen and turns yellow.

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

Thus, zinc becomes excess in the crystal, leading the formula of the oxide to $Zn_{1+x}O$. The excess Zn^{2+} ions move to the interstitial sites, and the electrons occupy the neighbouring interstitial sites.

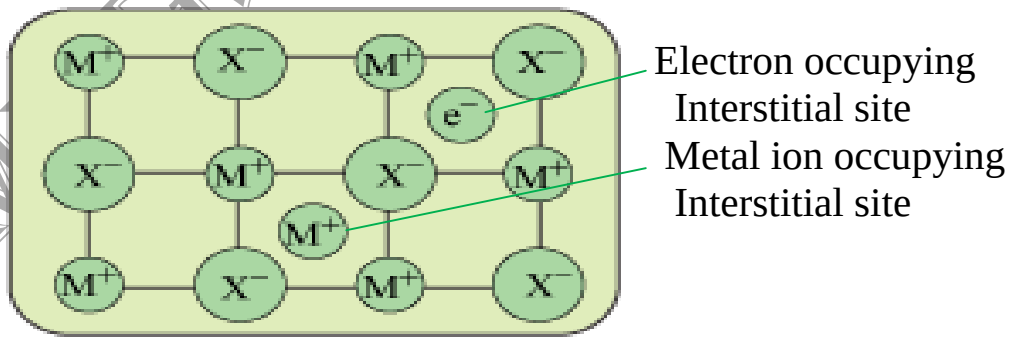


Fig.- Metal excess defect due to the presence of extra cations

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(ii) Metal deficiency defect

It arises due to presence of lesser number of cations as compared to the stoichiometric proportion in the solid. For example, FeO is mostly found with a composition of $Fe_{0.95}O$. In fact in crystals of FeO, some of the Fe^{2+} ions are missing, and this loss of positive charge is compensated by the presence of the required number of Fe^{3+} ions.

(1) Impurities Defects- It is specially found in ionic crystals where, some of the cations of crystals are replaced by same sized some other ions. For example, when molten NaCl is allowed to crystallize in presence of traces of $SrCl_2$ or $CaCl_2$, some lattice sites of the Na^+ ions of the crystal lattice are replaced by Sr^{2+} or Ca^{2+} ions. Here, in order to maintain electrical neutrality of the crystal, for each Sr^{2+} or Ca^{2+} ions to be introduced, two Na^+ ions are removed from the crystal lattice. One of these two vacant sites is occupied by Sr^{2+} or Ca^{2+} ion, while other remains vacant. Formation of these vacancies increases the electrical conductance of the crystal.

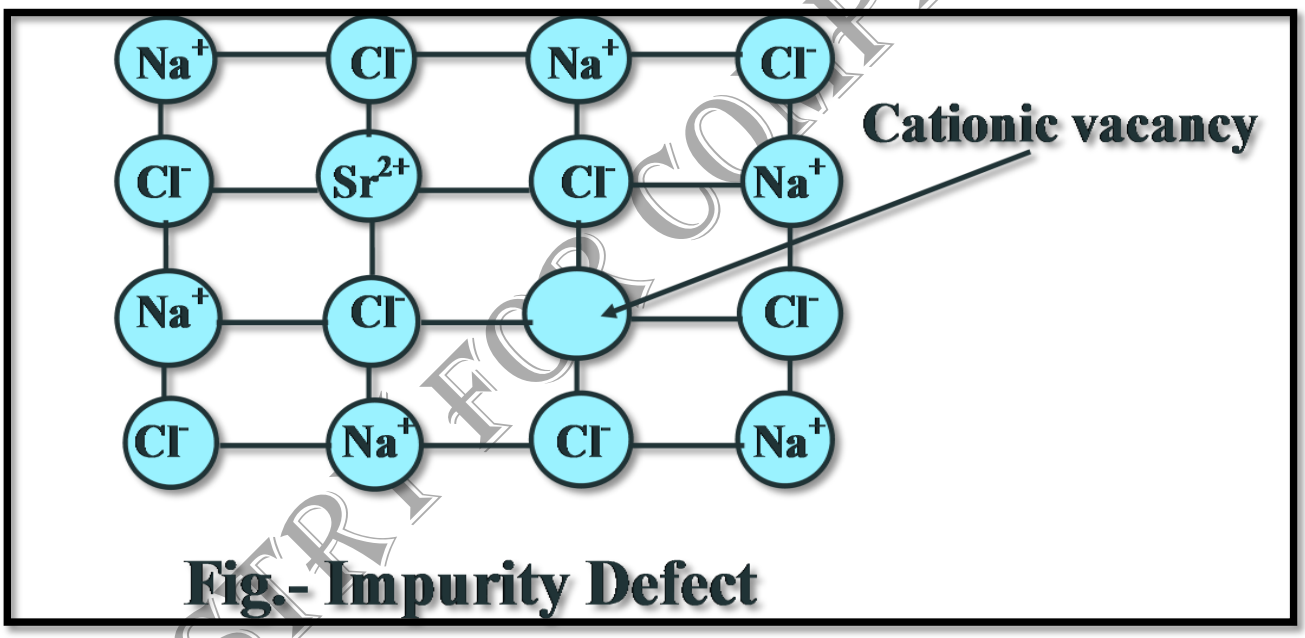
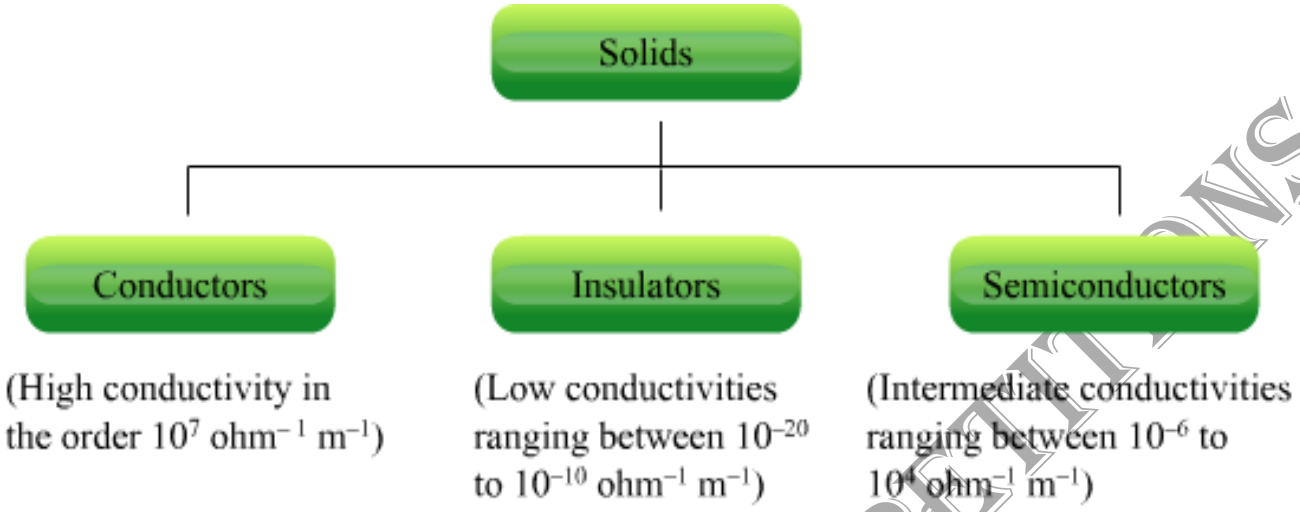


Fig.- Impurity Defect

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Electrical Properties of Solids



Conduction of Electricity in Metals-

Metals conduct electricity due to flow of electrons. Hence, the conductivity of metals depends upon the number of their valence electrons. The larger the number of valence electrons, more is electrical conductance of respective metal.

In fact in metals, the valence shell is partially filled and remains overlaped with a higher energy unoccupied conduction band. Hence, the electrons can flow easily through the conduction band under an applied electric field.

In insulators, the gap between filled valence band and the next higher unoccupied conduction band is very large. Hence, the electrons cannot jump from the valence band to the conduction band.

Conduction of Electricity in Semiconductors-

In semiconductors, the gap between the valence band and conduction band is relatively small. Hence, some electrons get jumped to the conduction band and flow under an applied electric field.

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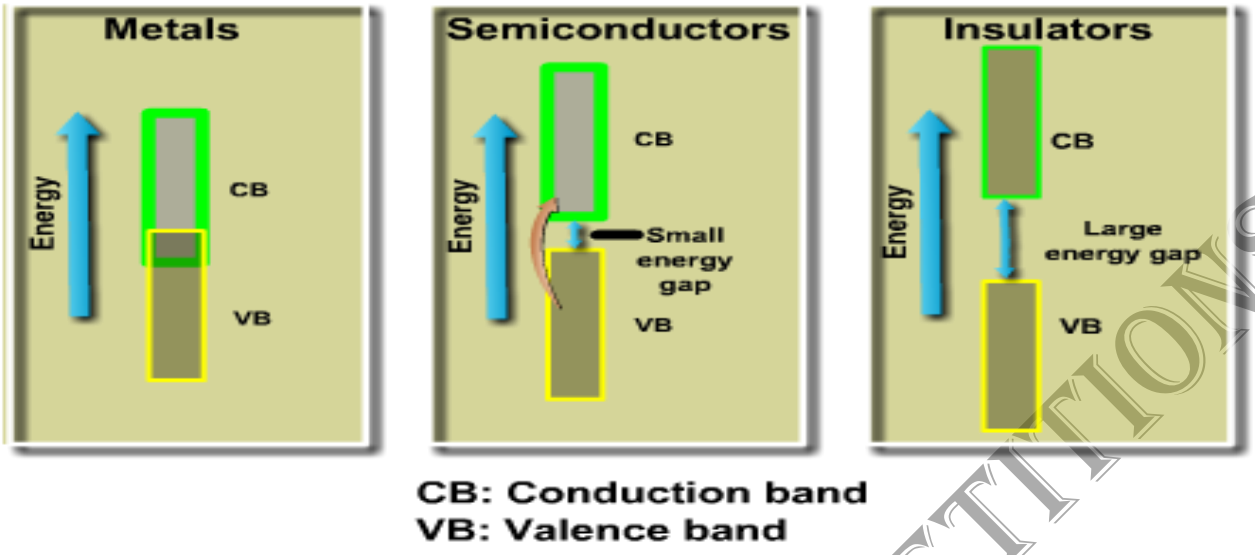


Fig.- Energy difference of valence and conduction bands in metals, semiconductors and insulators

Doping –

The conductance of semiconductors is too low and therefore it has no practical use. However, for practical use their conductance is increased by adding some suitable impurities. This process of adding an appropriate amount of suitable impurity to increase conductivity of intrinsic semiconductors is called Doping.

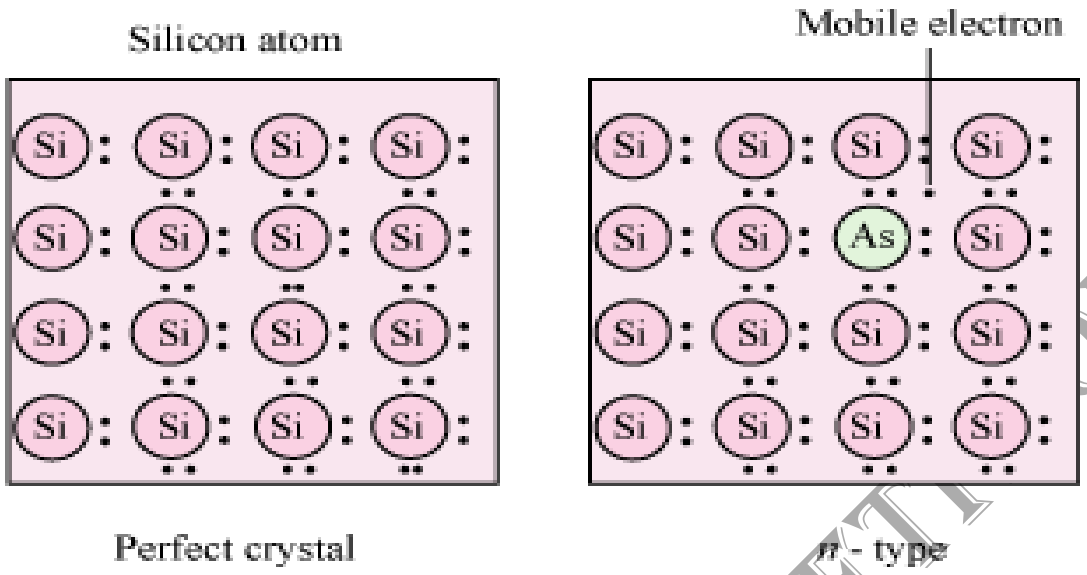
Doping is done with either electron-rich or electron-deficient impurity as compared to the intrinsic semiconductor s i.e. Si or Ge. On this basis there are two types of semiconductors-

(a) n-type semiconductors

This type of semiconductors are produced by doping of the crystals of Si or Ge, with a group 15 element such as P or As. Here out of the five valence electrons of doped atoms four get involved in bonding with Si or Ge, while the rest one occupies interstitial site and is free to move. Thus, the conductance of the crystal gets increased.

Since, these crystals contain extra electrons, they are known as *n*-type semiconductors.

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(b) p-type semiconductor

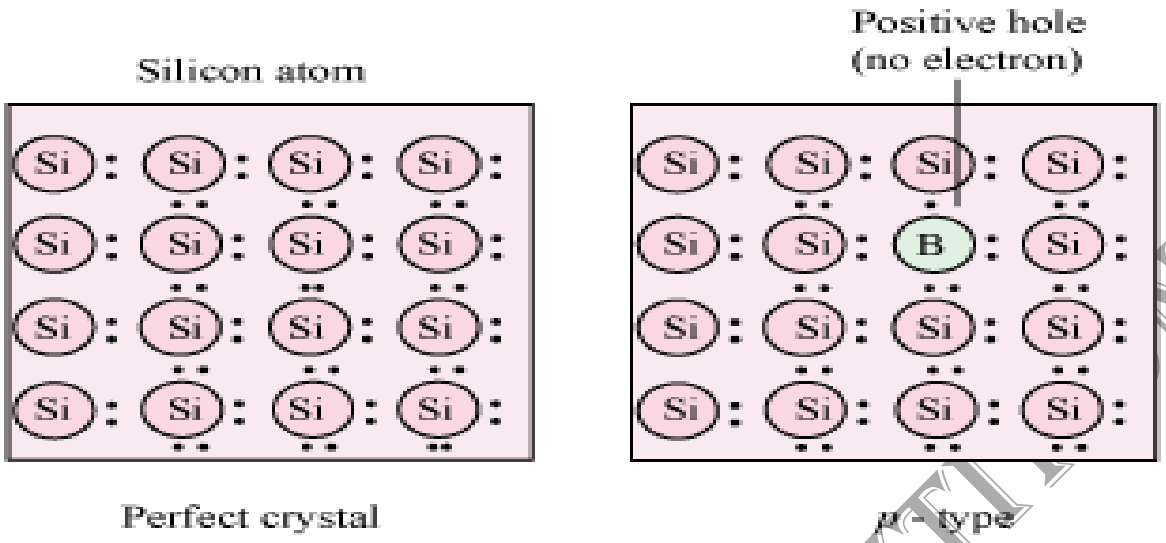
This type of semiconductors are produced by doping of the crystals of Si or Ge, with a group 13 element such as B, Al or Ga.

Here, three valence electrons of Si or Ge get involved in bonding with three valence electrons of doped atoms, while rest one electron of these atoms remains unpaired and an electron hole is produced at the place where the electron is absent. The neighbouring electrons can move into these holes, thereby creating newer holes.

Thus, due to formation of electron hole the conductance of the crystal gets increased.

Since, these crystals contain lesser electrons than un-doped crystals, they are known as *p*-type semiconductors.

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Applications of *n* − type and *p* − type semiconductors

(1) In making a diode, which is used as a rectifier.

(2) In making transistors, which are used for detecting or amplifying radio or audio signals.

(3) In making a solar cell, which is a photo diode used for converting light energy into electrical energy.

A large number of compounds (solid) have been prepared by the combination of groups 13 and 15 or 12 and 16 elements to stimulate average valence of four as in Si or Ge. For example,

(1) Compounds prepared by the combination of groups 13 and 15 elements- InSb, AlP, GaAs etc.

(2) Compounds prepared by the combination of groups 14 and 16 elements- ZnS, CdS, CdSe, HgTe etc.

- Some oxides like VO, VO_2, VO_3, TiO_3 etc. show both metallic and insulating properties depending upon temperature.
- Polyacetylene, an organic compound shows conductivity when exposed to iodine vapours.

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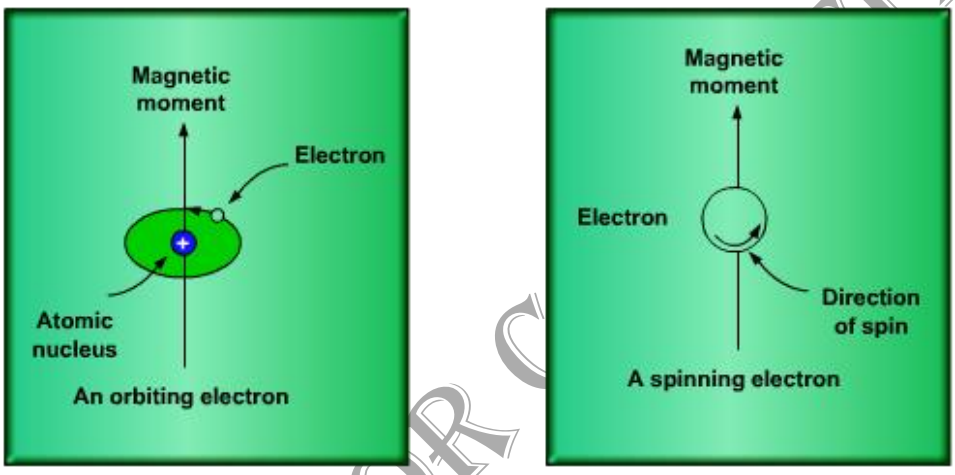
Magnetic Properties of Substances-

Each electron in an atom has a definite magnetic moment and behaves like a tiny magnet. The magnetic moment of an electron originates from its two types of motion-

(1) Orbital motion around the nucleus

(2) Spin around its own axis

Thus, an electron has a permanent orbital and spin magnetic moment associated with it.



An orbiting electron A spinning electron

Fig.- Different types of motion of electrons

Based on magnetic properties, substances are classified into following five categories −

(1) Paramagnetic substances-

Those substances which contain one or more unpaired electrons, are attracted in the magnetic field and are called paramagnetic substances and this phenomenon is called paramagnetism.

Some examples of paramagnetic substances are O_2, Cu^{2+}, Fe^{3+} and Cr^{3+} etc.

In magnetic field, Paramagnetic substances get magnetized in the direction of the magnetic field but lose their magnetism when the magnetic field is removed.

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(4) Ferrimagnetic Substances-

The substances in which the magnetic moments of the domains are aligned in parallel and anti-parallel directions, in unequal numbers, are said to have ferrimagnetism.

Examples include Fe_3O_4 (magnetite), ferrites such as $MgFe_2O_4$ and $ZnFe_2O_4$.

Ferrimagnetic substances are weakly attracted by a magnetic field as compared to ferromagnetic substances.

On heating, these substances become paramagnetic.

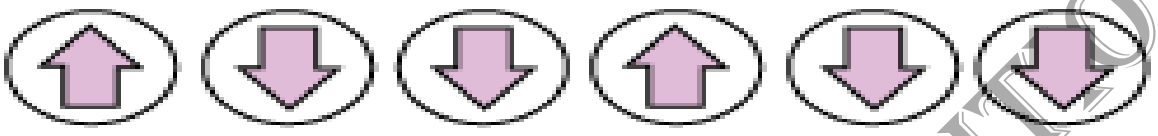


Fig.-Schematic alignment of magnetic moments of domains in ferrimagnetic substances

(5) Anti-ferromagnetic Substances-

The substances in which the magnetic moments of the domains are aligned in parallel and anti-parallel directions, in equal numbers, are said to have anti-ferrimagnetism.

Here, since the domains are oppositely oriented they cancel out the magnetic moments of one another.



Fig.- Schematic alignment of magnetic moments of domains in anti-ferromagnetic substances

Piezoelectric effect-

The production of electricity due to the displacement of ions, on the application of mechanical stress, or the production of mechanical stress and/or strain due to atomic displacement, on the application of an electric field is known as piezoelectric effect.

Piezoelectric materials are used in transducers − devices that convert electrical energy into mechanical stress/strain or vice-versa. Some piezoelectric materials are lead-zirconate ($PbZrO_3$), ammonium dihydrogen phosphate ($NH_4H_2PO_4$), quartz, etc.

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