The Solid State - Part 4

Objectives

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

- Electrical properties of solids
- Magnetic properties of solids
- Types of semiconductors

Contents Outline

- Introduction
- Electrical Properties of Solids
- Magnetic Properties of Solids
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Introduction

In the previous modules you have studied about the different types of solids, arrangement of constituent particles in crystalline solids and the defects in the arrangement of these particles. In this module, you will study about the electrical and magnetic properties of various solids which have widespread applications.

Electrical Properties of Solids

Solids exhibit an immense array of electrical conductivities, extending over 27 orders of magnitude ranging from 10^{-20} to 10^{7} ohm^{-1} m^{-1}. Solids can be classified into three types on the basis of their conductivities.

(i) **Conductors**:

- The solids with conductivities ranging between 10^{4} to 10^{7} S m^{-1} ($ohm^{-1}m^{-1}$) are called conductors.
- Metals which have conductivities in the order of 10^{7} S m^{-1} are good conductors.
- Conductivity of metals decreases with increase in temperature.

(ii) **Insulators:**

- These are the solids which do not allow electricity to pass through.

- They have very low conductivities ranging between 10^{-20} to 10^{-10} S m^{-1}.
- Rubber, plastics and glass are some insulators.

(iii) **Semiconductors:**

- Electrical conductivity of a semiconductor at normal temperatures lies between a good conductor and an insulator.
- These are the solids with conductivities in the range from 10^{-6} to 10^{4} S m^{-1}.
- Semiconductors are perfect insulators at absolute zero.
- At room temperature the conductivity of semiconductors is extremely low but at higher temperatures the bonds begin to break down ejecting the electrons and hence conductivity increases.
- Unlike metals, the conductivity of semiconductors increases with increase in temperature.
- Silicon and germanium are semiconductors.

Table 1: Comparison of conductors, insulators and semiconductors

Conductors	Insulators	Semiconductors
Substances which allow electricity to pass through them easily. For example, Metals	Substances which do not allow electricity to pass through them easily. For example, Rubber, wood, glass	Substances which allow electricity to pass through them partially. For example, Doped Silicon
The solids having no gap (there is no forbidden zone) between conduction band and filled band. Since the energy gap is not there therefore electrons can easily/freely move from one band to another band.	There is a large gap (large forbidden zone) between conduction band and filled band. Electrons cannot move easily/freely.	There is a small gap (Small forbidden zone) between conduction band and filled band. Electrons can move/jump when energy is supplied.
Conductivity decreases with the increase in temperature.		Conductivity increases with the increase in temperature.

Electrical Properties of Solids

Conduction of Electricity in Metals

- A substance may conduct electricity through movement of electrons or ions.
- Metallic conductors belong to the former category and electrolytes to the latter.
- Metals conduct electricity in solid as well as in molten state.
- The conductivity of metals depends upon the number of valence electrons available per atom.

The conduction of electricity can be explained on the basis of *band theory*. When a solid is formed, a large number of atomic orbitals form molecular orbitals which are so close in energy to each other as to form bands**.** The highest energy band filled with the electrons is known as the *valence band*. The next band of higher energy which is not occupied by the electrons is known as the *conduction band.* In metals, the valence band is partially or completely filled. It overlaps with an unoccupied higher energy conduction band, so the electrons can easily flow from valence band to conduction band under an applied electric field and the metal shows conductivity (Fig.1a).

If the gap between filled valence band and conduction band is large, then the electrons cannot jump across it to the conduction band. Therefore, such a substance has very small conductivity and it behaves as an insulator (Fig.1b).

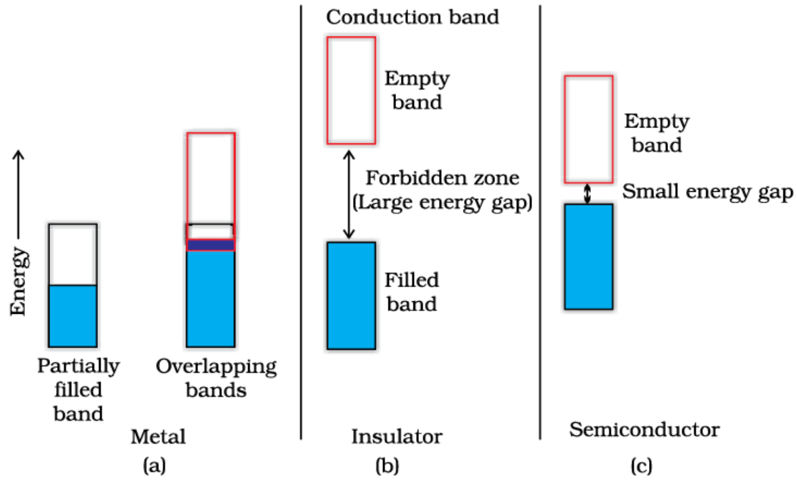

Fig. 1: Representation of energy gap between valence band and conduction band in (a) conductor (b) insulator (c) semiconductor

Conduction of Electricity in Semiconductors

- In case of semiconductors, the gap between the valence band and conduction band is small (Fig.1c). Therefore, some electrons jump to the conduction band and the substance shows some conductivity.

- Electrical conductivity of semiconductors increases with the rise in temperature, since more electrons can have sufficient energy to jump to the conduction band.
- Substances like silicon and germanium show this type of behaviour and are called *intrinsic semiconductors.*
- The conductivity of these intrinsic semiconductors is too low at room temperature to be of practical use.
- Their conductivity is increased by adding an appropriate amount of suitable impurity. This process is called *doping*. The added impurity is known as *dopant*.
- Doping can be done with an impurity which is electron rich or electron deficient as compared to the intrinsic semiconductor silicon or germanium.
- Such impurities introduce *electronic defects* in the semiconductors.

Doping enhances the conductivity and the products are called *extrinsic semiconductors*. They are two types :

(a) n- type semiconductor formed by adding electron rich impurities.

(b) **p**-type semiconductors formed by adding electron deficient impurities.

(a) Electron – rich impurities

Silicon and germanium belong to group 14 of the periodic table and have four valence electrons each. In their crystals each atom forms four covalent bonds with its neighbouring atoms (Fig. 2a). When doped with a group 15 element like P or As, which contains five valence electrons, the atoms of added impurity occupy some of the lattice sites in silicon or germanium crystal (Fig. 2b). Four out of five electrons of P or As are used in the formation of four covalent bonds with the four neighbouring silicon atoms. The fifth electron is extra and becomes delocalised. These delocalised electrons increase the conductivity of doped silicon (or germanium). Here the increase in conductivity is due to the *negatively* charged electron, hence silicon doped with electron-rich impurity is called *n*-type semiconductor.

(b) Electron – deficit impurities

Silicon or germanium can also be doped with a group 13 element like B, Al or Ga which contains only three valence electrons. Each atom in the crystal is surrounded by four neighbouring atoms. The atom of group 13 element forms covalent bonds with three out of four neighbouring silicon or germanium atoms. The place where the fourth valence electron is missing is called *electron hole* or *electron vacancy* (Fig. 2c). An electron from a neighbouring atom can come and fill the electron hole, but in doing so it will leave an electron hole at its original position. If it happens, it would appear as if the electron hole has moved in the direction opposite to that of the electron that filled it. Under the influence of electric field, electrons will move towards the positively charged plate through electronic holes, but it will appear as if the electron holes are positively charged and are moving towards negatively charged plate. This type of semiconductor is called *p-type semiconductor*.

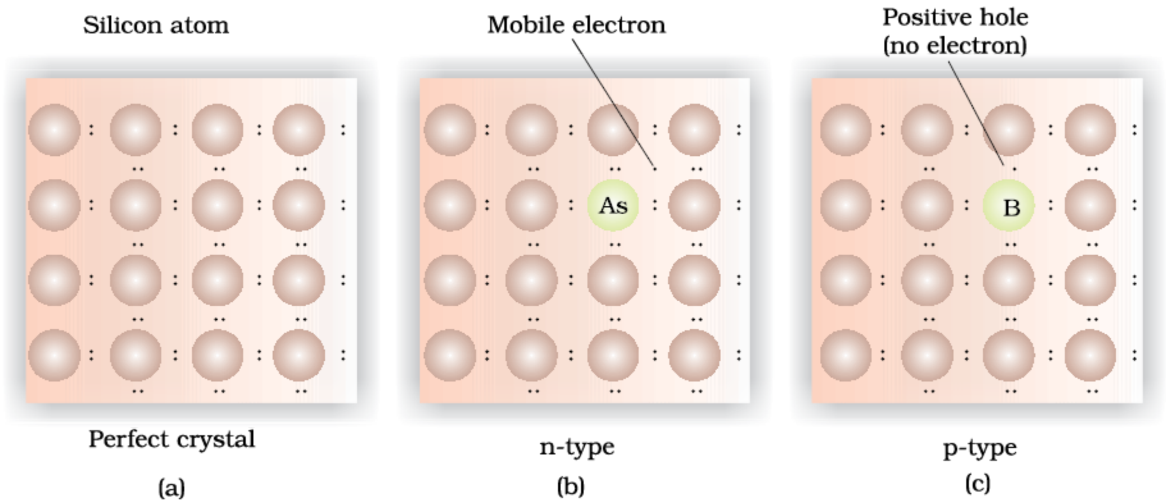

Fig. 2: Creation of n-type and p-type semiconductors by doping groups 13 and 15 elements

The conduction in extrinsic semiconductors can also be explained on the basis of band theory. When impurity is introduced in the intrinsic semiconductor, a new energy band is created between the valence band and the conduction band. Depending upon the type of impurity it can be an unoccupied energy band nearer to valence band or an occupied band nearer to conduction band. When the current is passed, the electron can either jump from the valence band to the unoccupied energy band or move from the new energy band to the conduction band creating an electron hole in the valence band, which can be occupied by another electron.

Applications of n-type and p-type semiconductors

Various combinations of *n*-type and *p*-type semiconductors are used for making electronic components.

- *Diode* is a combination of *n*-type and *p*-type semiconductors and is used as a rectifier.
- *Transistors* are made by sandwiching a layer of one type of semiconductor between two layers of the other type of semiconductor.
- *npn* and *pnp* type of transistors are used to detect or amplify radio or audio signals.

- The solar cell is an efficient photo-diode used for conversion of light energy into electrical energy.

Germanium and silicon are group 14 elements and therefore, have a characteristic valence of four and form four bonds as in diamond. A large variety of solid state materials have been prepared by combination of groups 13 and 15 or 12 and 16 to simulate average valence of four as in Ge or Si. Typical compounds of groups 13 – 15 are In-Sb, Al-P and Ga-As. Gallium arsenide (GaAs) semiconductors have very fast response and have revolutionised the design of semiconductor devices. ZnS, CdS, CdSe and HgTe are some examples of groups 12 – 16 compounds. In these compounds, the bonds are not perfectly covalent and the ionic character depends on the electronegativities of the two elements.

It is interesting to learn that transition metal oxides show marked differences in electrical properties. TiO, CrO_2 and ReO_3 behave like metals. Rhenium oxide, ReO_3 is like metallic copper in its conductivity and appearance. Certain other oxides like VO, VO_2, VO_3 and TiO_3 show metallic or insulating properties depending on temperature.

Magnetic Properties of Solids

Every substance has some magnetic properties associated with it. The origin of these properties lies in the electrons. Each electron in an atom behaves like a tiny magnet. Its magnetic moment originates from two types of motions:

(i) its orbital motion around the nucleus and

(ii) its spin around its own axis (Fig. 3).

Electron being a charged particle and undergoing these motions can be considered as a small loop of current which possesses a magnetic moment. Thus, each electron has a permanent spin and an orbital magnetic moment associated with it. Magnitude of this magnetic moment is very small and is measured in the unit called *Bohr magneton,* μ. It is equal to 9.27×10^{-24} A m^2.

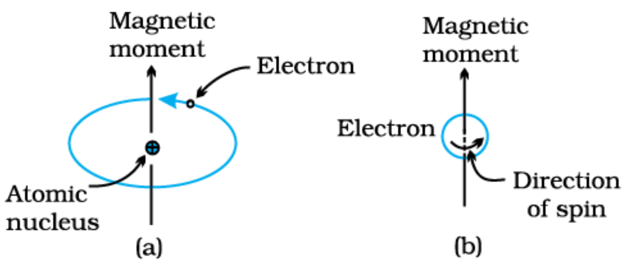

Fig.3: Demonstration of the magnetic moment associated with (a) an orbiting electron and (b) a spinning electron.

On the basis of their magnetic properties, substances can be classified into five categories, namely, (i) Paramagnetic (ii) Diamagnetic (iii) Ferromagnetic (iv) Antiferromagnetic and (v) Ferrimagnetic.

Paramagnetism

- Paramagnetic substances are weakly attracted by a magnetic field.
- They are magnetised in a magnetic field in the same direction as the direction of the magnetic field.
- They lose their magnetism in the absence of a magnetic field.
- Paramagnetism is due to the presence of one or more unpaired electrons which are attracted by the magnetic field.
- The common examples are Cu^{2+}, Fe^{3+}, Cr^{3+}, O_2, TiO, Ti_2O_3, VO_2, CuO, etc.
- Solids like TiO_2 which are expected to be diamagnetic often show paramagnetism due to the presence of slight non-stoichiometry.

Diamagnetism

- Diamagnetic substances are weakly repelled by a magnetic field.
- H2O, NaCl and C6H6 are some examples of such substances.
- They are weakly magnetised in a magnetic field in the opposite direction of the field.
- Diamagnetism is shown by those substances in which all the electrons are paired and there are no unpaired electrons. Pairing of electrons cancels their magnetic moments and they lose their magnetic character.

Ferromagnetism

- The substances which are strongly attracted by the magnetic field and show magnetism even when the magnetic field is removed are known as ferromagnetic substances.
- Once such material is magnetized, it remains magnetized permanently. Iron is the most common example. Other examples are cobalt , nickel, gadolinium (Gd), CrO_2, etc.
- At room temperature these substances are very important in technology. For example, CrO_2 is the oxide used to make magnetic tapes for use in cassette recorders.

- In solid state the metal ions of ferromagnetic substances are grouped together in small regions called domains. Thus, each domain acts as a tiny magnet.
- In an unmagnetized piece of ferromagnetic substance, the domains are randomly oriented and their magnetic moments get cancelled. When the substance is placed in a magnetic field all the domains get oriented in the direction of the magnetic field and a strong magnetic effect is produced. This ordering of domains persists even when the magnetic field is removed and the ferromagnetic substance becomes a permanent magnet.
- Each ferromagnetic substance has a characteristic temperature above which no ferromagnetism is observed. This temperature is known as Curie Temperature.

Anti-ferromagnetism

- A substance is said to show anti-ferromagnetism if it is unaffected in the magnetic field.
- The alignment of magnetic moments of domains is in a compensatory way so there is zero net magnetic moment because of cancellation of the individual magnetic moments.
- In antiferromagnetic solids, when the substance is placed in a magnetic field all the domains get oriented in the antiparallel (↑↓↑↓↑↓↑↓) direction of the magnetic field, which leads to a decrease in magnetic moment.
- Some examples of anti-ferromagnetic substances are MnO, MnO_2, Mn_2O_3.

Ferrimagnetism

- They are weakly attracted by magnetic fields as compared to ferromagnetic substances.
- When the magnetic moment of domains are aligned in parallel and anti-parallel directions in unequal numbers resulting in net magnetic moment we get ferrimagnetism (↑↑↓↑↑↓).
- When a ferrimagnetic solid is placed in a magnetic field all the domains get oriented randomly which leads to the presence of uncompensated spins in the opposite direction resulting in some magnetic moment.
- Some examples of ferromagnetic substances are Magnetite (Fe_3O_4), ferrites like $MgFe_2O_4$ and $ZnFe_2O_4$. These substances also lose ferrimagnetism on heating and become paramagnetic.

All the magnetically ordered solids (ferromagnetic, anti-ferromagnetic and ferrimagnetic) transform to paramagnetic state at a higher temperature due to the randomization of their spins for example, V_2O_3 transforms from anti-ferromagnetic state to paramagnetic state at 150 K while Fe_3O_4 becomes paramagnetic from ferrimagnetic at 850 K. Fig. 4 shows the arrangement of domains in (a) ferromagnetic solid (b) anti-ferromagnetic solid and (c) ferrimagnetic solid.

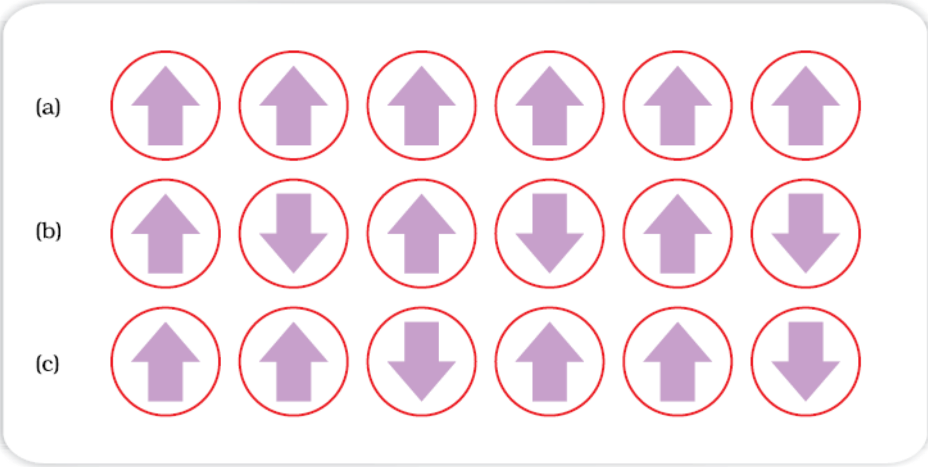

Fig. 4: Schematic alignment of magnetic moments in (a) ferromagnetic (b) antiferromagnetic and (c) ferromagnetic solid.

Example 1:

Discuss the nature of bonding in group 13 and 15 or group 12 and 16 compounds.

Solution:

In these compounds, the bonds are not perfectly covalent. The ionic character depends on the electronegativities of the two elements.

Example 2:

How is a metallic conductor different from an electrolyte?

Solution:

A metallic conductor conducts electricity through movement of electrons and An electrolyte conducts electricity through movement of ions.

Example 3:

On the basis of their conductance, what is the expected size of forbidden zone or energy gap in sodium, graphite, germanium and rubber ?

Solution:

Sodium and graphite are conductors, the gap between the valence band and conduction band is very small or the bands overlap.

In case of Germanium a semiconductors, the gap between the valence band and conduction band is small.

Rubber is an insulator, which implies that the gap between the valence band and conduction band is large.

Example 4:

Why does an electron in an atom behave as a tiny magnet?

Solution:

Each electron in an atom behaves like a tiny magnet. Its magnetic moment originates from two types of motions (i) its orbital motion around the nucleus and (ii) its spin around its own axis. Electron being a charged particle and undergoing these motions can be considered as a small loop of current which possesses a magnetic moment.

Example 5:

What happens when Fe_3O_4 and $MgFe_2O_4$ are heated?

Solution:

Fe_3O_4 (magnetite) and ferrites like $MgFe_2O_4$ are ferrimagnetic substances.. These substances lose ferrimagnetism on heating and become paramagnetic.

Example 6:

Why does the conductivity of semiconductors increase with the increase in temperature?

Solution:

Electrical conductivity of semiconductors increases with rise in temperature, since more electrons can jump to the conduction band**.**

Summary

- Solids exhibit an amazing range of electrical conductivities, extending over 27 orders of magnitude ranging from 10^{-20} to 10^{7} ohm^{-1} m^{-1}.
- Solids can be classified into conductors, insulators and semiconductors on the basis of their conductivities.
- Conductivities of conductors, insulators and semiconductors can be explained on the basis of the energy gap between the valence band and conduction band.
- Sometimes calculated amounts of impurities are introduced by doping in semiconductors that change their electrical properties. Such materials are widely used in the electronics industry.

- Addition of electron rich impurity like group 15 elements to silicon or germanium crystal give n-type semiconductor.
- Addition of electron deficient impurity like group 13 elements to silicon or germanium crystal give p-type semiconductor
- Solids show many types of magnetic properties like paramagnetism, diamagnetism, ferromagnetism, antiferromagnetism and ferrimagnetism. These properties are used in audio, video and other recording devices. All these properties can be correlated with their electronic configurations or structures.
- Paramagnetic substances are weakly attracted by a magnetic field, for example, Cu^{2+}, Fe^{3+}, Cr^{3+}, O_2, TiO.
- Diamagnetic substances are weakly repelled by a magnetic field for example, H_2O, NaCl and C_6H_6.
- Ferromagnetic substances are strongly attracted by the magnetic field and show magnetism even when the magnetic field is removed. For example, iron, cobalt, nickel.
- Anti-ferromagnetic substances are unaffected in the magnetic field. For example, MnO, MnO_2, Mn_2O_3.
- Ferrimagnetic substances are weakly attracted by magnetic fields as compared to ferromagnetic substances. For example, Magnetite (Fe_3O_4), ferrites like $MgFe_2O_4$ and $ZnFe_2O_4$.
- All ferromagnetic, anti-ferromagnetic and ferrimagnetic substances transform to paramagnetic state at a higher temperature due to the randomization of their spins.