

B.Sc. (Honours) Part-III

Paper-VA

**Topic: Solid State- Defects & Magnetic
Properties**

UG

Subject-Chemistry

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In general, the packing of atoms in covalent crystals is loose in comparison to ionic and metallic crystals. Thus, covalent crystals have open structure.

3. Metallic crystals: The metallic crystals have positive metal ions as lattice points surrounded by a sea of mobile electrons. Each electron belongs to a number of positive ions and each positive ion belongs to a number of electrons. The force that binds a metal ion to a number of electrons within its sphere of influence is known as **metallic bond**. Metallic crystals mostly belong to cubic face-centred (fcc), cubic body-centred (bcc) and hexagonal close-packed (hcp) systems. Metallic crystals exhibit the following properties:

(i) **Good conductors:** On account of the presence of mobile electrons, metals are good conductors of electricity. The electrical conductivity decreases with increase of temperature. This is due to the fact that positive ions also begin to oscillate with the increase of temperature. The oscillation of positive ions hinders the movement of mobile electrons. Metals are also good conductors of heat.

(ii) **Lustre:** When freshly cut or scratched, most of the metals have a shining surface. When light falls on freshly cut surface, the electrons get excited. The excited electrons give off energy in the form of light when they return to their original position and hence the metal looks bright. The metallic properties are explained on the basis that the metallic bond is non-directional and non-rigid. The result is that M^{n+} ions can be easily moved from one lattice site to another. The nearest neighbours can be thus changed easily and new metal bonds can be formed readily. This explains why metals are malleable and ductile.

(iii) **Physical characteristics:** Most of the metals are quite hard and tough. They are malleable and ductile. They have high tensile strength. Except alkali metals, they have high melting and boiling points. They also possess elasticity.

4. Molecular crystals: In molecular crystals, the lattice points are occupied by molecules which do not carry any charge. The forces responsible for binding these molecules are dipole-dipole attractions and van der Waals' forces. Dipole-dipole forces are present in solids when polar molecules occupy the lattice points as in the case of water. van der Waals' forces are more general and occur in all kinds of molecular crystals. The binding energy in molecular crystals is, therefore, weak. Molecular crystals show the following general properties:

- (i) They are generally soft and easily compressible.
- (ii) They have low melting or boiling points.
- (iii) They are bad conductors of electricity as the electrons are localised in the bonds.
- (iv) They have low density.

The following table provides a comparative summary of the properties of various types of crystals:

Property	Ionic crystals	Covalent crystals	Metallic crystals	Molecular crystals
1. Constituent particles occupying lattice points	Positive and negative ions	Neutral atoms	Positive ion in sea of electrons	Molecules polar or non-polar
2. Binding force	Electrostatic attraction	Shared pairs of electrons	Electrostatic attractions between positive ions and electrons	Weak polar forces or van der Waals' forces
3. Hardness	Hard and brittle	Very hard	Hard or soft	Very soft
4. Melting and boiling points	High	Very high	High or low	Low
5. Electrical conductivity	Bad conductors; Good conductors in fused state or in solution	Bad conductors with few exceptions	Good conductors	Bad conductors
6. Examples	NaCl, KNO ₃ , CaF ₂	Diamond, graphite, carborundum	Cu, Na, Fe metals	Ice, solid CO ₂

4.24 IMPERFECTION IN SOLIDS

An ideal crystal is one which has the same unit cell containing the same lattice points across the whole crystal. Any departure from perfectly ordered arrangement of constituent particles in the crystals is called imperfection or defect.

Perfect of ideal crystals can exist only at absolute zero or zero Kelvin. At absolute zero the crystalline substances have zero entropy, i.e., have no randomness. Above absolute zero, entropy or randomness increases, i.e., some deviations from perfectly ordered arrangement takes places.

The imperfection may be **intrinsic** or **extrinsic**. Crystalline defects can profoundly alter the properties of a solid material. Imperfections or defects not only alter the properties but also give rise to new characteristics. Extrinsic defects due to presence of certain impurities give rise to interesting changes in the properties. For example, gem stones are crystals containing impurities that give them beautiful colours. The presence of Fe^{3+} ions makes sapphire blue and Cr^{3+} ions presence makes ruby red. (Gems are actually crystals of Al_2O_3 which is colourless).

There are mainly two types of imperfections.

1. Electronic imperfections
2. Atomic imperfections.

1. Electronic Imperfections

This type of imperfection arises due to irregular arrangement of electrons in the crystal structure. At 0 K (absolute zero), the electrons in both ionic and covalent solids are present in fully occupied lowest energy orbitals or states and these electrons do not move under the influence of applied electric field. However, when temperature is raised above 0 K, some electrons may occupy higher energy states. For example, in crystals of pure silicon or germanium, some electrons are released from the covalent bonds above 0 K. These free or mobile electrons become responsible for electrical conductance. The bonds from which the electrons have been removed on heating become electron deficient and these are referred to as **holes**. Like free electrons, holes also conduct electric current. Holes in an electric field move in a direction opposite to that in which electrons move. Both electrons and holes present in the solids give rise to electronic imperfection. Electrons and holes are denoted by the symbols 'e' and 'h' and their concentrations are represented by 'n' and 'p'. In pure covalent solids like silicon and germanium, the number of free electrons and holes will be equal. Electrons and holes can be obtained preferentially according to the requirement by adding appropriate impurities.

Silicon and germanium are the elements of group 14th; thus, they have maximum covalency of four. A number of solids can be obtained by the combination of the elements of groups 13 and 15 or groups 12 and 16 to get average valency of four as in silicon and germanium. Examples are : InSb; AlP; GaAs. In these materials, In, Al and Ga belong to group 13 and Sb, P and As belong to group 15 of the extended form of the periodic table. Other examples are : ZnS, CdS, CdSe, HgTe. In these materials, Zn, Cd and Hg belong to group 12 and S, Se and Te belong to group 16 of the periodic table. These combinations are not purely covalent but possess an ionic character due to difference in the electronegativities of the two elements. These combinations show interesting electrical, magnetic and optical properties which have been utilised in the electronic industries for photovoltaic cells, light emitting diodes, thermocouples and semiconductors, etc.

2. Atomic Imperfections or Point Defects

When the deviations exist in the regular or periodic arrangement of the constituent particles (atoms or ions) in the crystal, these defects are termed **atomic imperfections or point defects**.

These defects are caused by the following points.

(i) When some of the constituent particles are missing from their normal positions, these unoccupied positions are termed **holes or vacancies**.

(ii) When some of the constituent particles are missing from their positions and these particles have shifted either to interstitial vacant sites or to positions which are meant for other particles.

Types of point defects : Point defects are classified into the following three types:

- (A) Defects in stoichiometric crystals,
- (B) Defects in non-stoichiometric crystals,
- (C) Impurity defects

(A) Defects in stoichiometric crystals

The crystals in which cations and anions are exactly in the same ratio as indicated by their molecular formulae are termed **stoichiometric crystals**. Point defects do not alter the stoichiometry of the solid; these defects are called as **intrinsic or thermodynamic defect**. Two types of point defects are observed in these crystals :

(i) Schottky defect, (ii) Frenkel defect.

(i) **Schottky defect :** This defect was first observed by the German scientist Schottky in 1930. In this defect equal number of cations and anions (from AB type crystal) are missing from their normal lattice sites, i.e., equal number of cationic and anionic **vacancies or holes** will be developed. The crystal maintains electrical neutrality.

This defect is usually observed in strongly ionic compounds which have high coordination number and the sizes of two ions (cations and anions) are almost same.

Examples : NaCl, KCl, KBr, CsCl, AgBr etc.

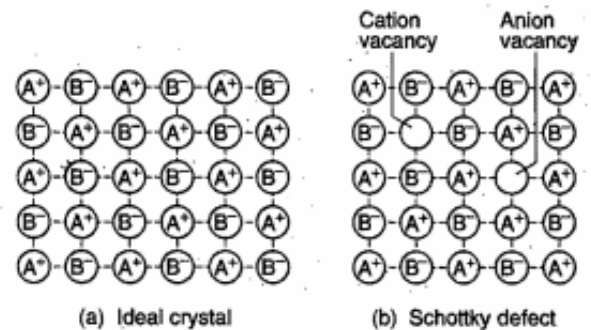


Fig. 4.54

In 1 cm^3 of NaCl there are 10^{22} ions and 10^6 Schottky pairs, thus there is one Schottky defect per 10^{16} ions.

Consequences of Schottky defect

(a) Due to Schottky defect, the density of crystalline solid decreases.

(b) Lattice energy and thereby stability of the crystalline solid decreases.

(c) Entropy increases.

(ii) **Frenkel defect :** This defect was discovered and studied by a Russian scientist, Frenkel, in 1926. This defect is caused if some of the ions (usually the cations) of the lattice occupy interstitial sites leaving a corresponding number of normal lattice sites vacant. This defect creates **vacancy defect** at original site and **interstitial defect** at new site. Frenkel defect is also called **dislocation defect**.

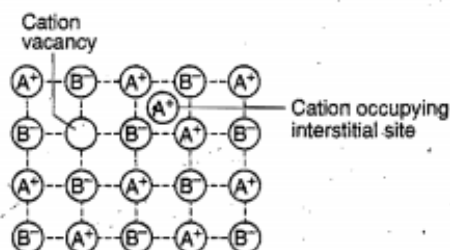


Fig. 4.55 Frenkel defect in the crystal

Main conditions for Frenkel defect are:

- Coordination number should be low.
- Size of anion should be bigger than cation.

Examples : This defect is not found in alkali metal halides because cations and anions have almost equal sizes and cations cannot be accommodated in interstitial sites. This defect is mainly found in transition metal halides like AgCl, AgBr, AgI, ZnS, etc. Silver ion (Ag^+) being smaller in size can be accommodated in interstitial site. AgBr shows both Frenkel and Schottky defect.

Consequences of Frenkel defect

- (a) There is no change in the density of the solid.
- (b) There is increase in the dielectric constant as the like charge ions come closer.
- (c) The solids having Frenkel defect show conductivity and diffusion in solid state due to presence of vacant lattice sites.
- (d) Lattice energy and thereby stability of crystalline solids decreases.
- (e) This defect influences the chemical properties of ionic compound.
- (f) Entropy of the solid increases.

Thermodynamic facts about point defects in stoichiometric solids : Frenkel and Schottky defects are also called as intrinsic or thermodynamic defects.

Number of point defects increases with temperature. The number of defects formed per unit volume (cm^3) n' is given by,

$$n = Ne^{-W/2RT}$$

where, N = number of sites per unit volume (cm^3) which could be left vacant

W = Work necessary to create a defect

T = Absolute temperature

Electrical conductance of crystals increases due to point defects. When potential difference is applied to the solid then ions may move from the lattice sites to occupy the holes or vacancies. Such movement is responsible for electrical conductance.

Difference between Schottky and Frenkel defect

Schottky defect	Frenkel defect
1. Equal number of cationic and anionic vacancies are present in this defect.	Some ions are displaced from normal lattice sites to the interstitial sites.

2. Density is lowered in this defect.	Density is unaffected in it.
3. Dielectric constant remains same.	Dielectric constant increases.
4. It is shown by those ionic compounds which have high coordination number, sizes of cations and anions are almost equal.	It is shown by those ionic compounds which have low coordination number and size of cations is smaller than size of anions.

(B) Defects in non-stoichiometric solids

The compounds in which the number of positive and negative ions are not exactly in the ratio as indicated by their chemical formulae are called non-stoichiometric compounds. Non-stoichiometric solids are also known as **Berthollide compounds**.

Examples :

- (i) Ferrous oxide FeO exists in non-stoichiometric form as $\text{Fe}_{0.95}\text{O}$ called wüstite.
- (ii) Vanadium oxide has non-stoichiometric formula VO_x , where x lies between 0.6 and 1.3.
- (iii) ZnO exists as a non-stoichiometric compound having excess zinc.
- (iv) Stoichiometric compounds like NaCl, KCl, etc., can be non-stoichiometric under suitable conditions.

The defects which bring change in overall chemical composition are termed as **non-stoichiometric defects**. In such crystals, there is excess of either positive particles (cations) or negative particles (anions). However, the crystal as a whole is neutral in nature. If positive particles are in excess, the charge is balanced by the presence of extra electrons. In case the negative particles are in excess, the charge is balanced by acquiring higher oxidation state by metal atoms.

Non-stoichiometric defects are of two types:

1. Metal excess defect, 2. Non-metal excess defect

1. Metal excess defect : In this defect, metal ions or cations are in excess. This defect may develop on account of the following two ways :

(a) **Anion vacancies :** A negative ion may be missing from its lattice site leaving behind a vacancy or hole. This vacancy or hole is occupied by an extra electron to maintain electrical neutrality. This defect is somewhat similar to Schottky defect but differs in having only one hole and not a pair as in the latter case.

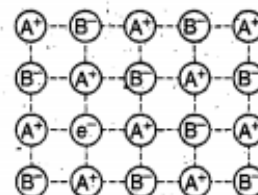


Fig. 4.56 Metal excess defect due to anion vacancy

Anion vacancies in alkali metal halides are produced by heating the metal halides in the atmosphere of alkali metal

vapours. Metal atoms get adsorbed on the surface of the metal halides. Halide ions move towards the surface and combine with metal ions formed by the adsorbed atoms on account of their ionisation. The electrons released in the process diffuse into the crystal and occupy anion vacancies. The electrons trapped in anion vacancies are referred to as **F-centres**. 'F' stands for **Farben**, a German word, meaning colour. Greater is the number F-centres, more is the intensity of colour. For example, non-stoichiometric sodium chloride with excess sodium is yellow, non-stoichiometric; potassium chloride with excess of potassium is violet and non-stoichiometric; lithium chloride with excess of lithium is pink.

(b) **Excess cations occupying interstitial positions** : Metal excess defect may also be developed by the presence of extra cation in the interstitial site. Electrical neutrality is achieved by an electron presence in another interstitial site. This defect is similar to Frenkel defect. For example, when ZnO is heated, it loses oxygen and turns yellow.

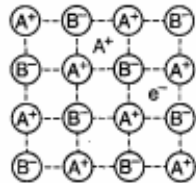
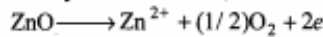


Fig. 4.57 Metal excess defect due to the presence of extra cation in the interstitial position

The Zn^{2+} ions thus formed occupy interstitial sites and the electrons occupy the neighbouring interstitial sites. The crystals having metal excess defects contain few free electrons and, thus, such solids act as semi-conductors.

2. **Non-metal excess or metal deficiency defect** : These contain lesser number of positive particles than negative particles. These defects arise due to cation vacancies or anions occupying interstitial sites. The extra negative charge is balanced by oxidation of some of the nearby metal ions. Thus, this defect occurs when metal shows variable valency, i.e., especially in the case of transition metals. Examples are : FeO, FeS, NiO, etc. Crystals with metal deficient defects are semiconductors of *p*-type.

(C) Impurity defects in ionic crystalline solids

A defect in an ionic solid can be introduced by adding foreign ions. If the impurity ions have a different oxidation state than that

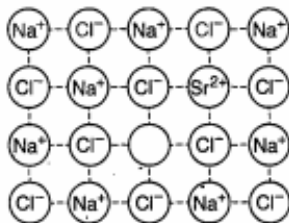


Fig. 4.58 Impurity defect

of the host ions, vacancies are created. For example, if molten NaCl containing a little SrCl_2 or CaCl_2 as impurity is allowed to cool, some lattice sites will be occupied either by Ca^{2+} ions or Sr^{2+} ions in place of Na^+ ions. For every Ca^{2+} ion or Sr^{2+} ion, two Na^+ ions are removed in the crystal lattice in order to maintain electrical neutrality. Thus, one of these lattice sites is occupied by Ca^{2+} or Sr^{2+} ion and the other site remains vacant.

Cationic vacancies developed due to introduction of impurity cause higher electrical conductivity of ionic solids. Addition of about 0.1% SrCl_2 to NaCl increases the electrical conductivity by 10000 times. Solid solution of CdCl_2 and AgCl is another example of this type of impurity defect.

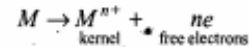
Electric Properties of Solids

On the basis of electrical conductivity, solids are divided into three categories:

(i) Metals (ii) Insulators (iii) Semiconductors

Metals have conductivity $10^8 \text{ ohm}^{-1} \text{ cm}^{-1}$ and insulators have $10^{-12} \text{ ohm}^{-1} \text{ cm}^{-1}$.

Metals: Metals have free electrons and fixed **kernel**s at their lattice sites:



Free electrons make the metal good conductor of electricity and heat. Conductivity of metals is nearly independent of impurity of metals. Resistance ratio may be taken to check the impurity level of metals, i.e., $\rho_{300\text{K}} / \rho_{4.2\text{K}}$. Conductivity of metals depends on number of valence electrons, i.e., number of free electrons produced by the metal.

Nature of Metallic Bond

A metal is regarded as group of positively charged metal ions packed as closely as possible in a regular geometrical fashion and immersed in a sea or pool of mobile electrons. The attraction force that binds the metal ions and mobile electrons is called metallic bonding.

1. **Conductivity:** When potential difference is applied electrons (mobile) conduct electric current. It has been observed that the conductivity of most of the metals decreases with increase in temperature. At high temperature, positive metal ions start vibration and create resistance to the flow of electrons; thus resistance of metal increases.

Good thermal conductivity of metals can also be explained on the basis of mobile electrons.

2. **Opacity and lustre:** Mobile electrons absorb quantum energy of visible light and become excited; when excited electrons return to normal state, visible light is evolved. Since, the light is fully absorbed by metal hence it is opaque.

3. **Elasticity:** On applying mechanical stress, temporary deformation of the metal crystal takes place and the kernels with their electron cloud return to their original position as soon as mechanical stress is removed.

4. **Microproperties of metals:** Some other properties of metals are summarised ahead:

- (a) Metals possess high tensile stress.
- (b) Metals are usually hard and solid.
- (c) Some metals like alkali and alkaline earth metals show photoelectric effect, *i.e.*, ejection of electron from metal surface when exposed to light of appropriate energy.
- (d) Metals have low ionization energy.
- (e) Strength of metallic bond depends on the following factors:

Strength increases with:

- (i) increase in number of valence electrons,
- (ii) increase in charge on the nucleus,
- (iii) decrease in size of positive metal ion.

Valence band: Group of electrons containing valence electrons.

Conduction band: The free electrons for conduction constitute conduction band.

Band structure of metals may be given as shown in Fig. 4.59.

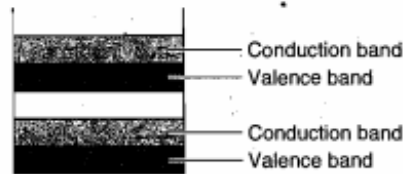


Fig. 4.59

There is no energy gap between valence and conduction band, *i.e.*, width of forbidden zone is zero. Thus, as soon as potential difference is applied electrons jump to conduction band from valence band and conduct electric current. All valence electrons are free to conduct electric current. **When temperature is raised conductance of metals decreases because at high temperature kernels vibrate and create obstruction in the flow of electron.**

Semiconductors: Conductivity of semiconductors is intermediate between metals and insulators. These are of two types:

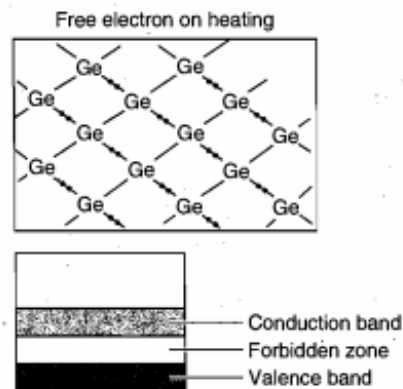


Fig. 4.60

(i) **Intrinsic semiconductors:** These are insulators at room temperature and become semiconductors when temperature is raised.

On heating, some covalent bonds are broken to give free electrons. These free electrons make it semiconductor.

Width of forbidden zone in semiconductors is very low; thus on heating, electrons are easily tossed to conduction band from valence band and conduct electric current.

(ii) **Extrinsic semiconductors or Impurity semiconductors:** These are formed by doping impurity of lower or higher group.

n-type Semiconductor

Doping of higher group impurity forms *n*-type semiconductor, *e.g.*, when 'As' is doped to 'Ge', an extra valence electron of arsenic makes the mixture *n*-type semiconductor. Current carriers are negatively charged, hence called *n*-type.

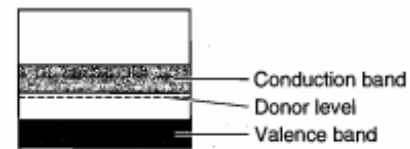
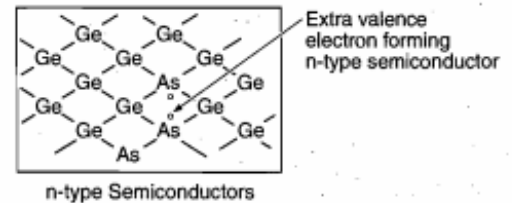


Fig. 4.61 n-type Semiconductor

Impurity doping creates donor level just below the conduction band.

On applying potential difference, electrons jump from donor level to the conduction band and conduct electric current.

p-type Semiconductor

Impurity of lower group creates acceptor level just above the valence band. When electrons jump from valence band to acceptor level, a *p*-hole (positively charged hole) is created in valence band. On applying potential difference, these *p*-holes conduct electric current.

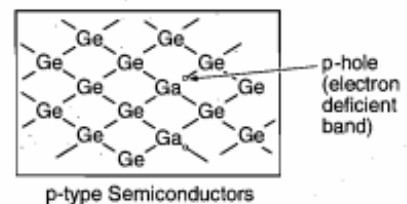


Fig. 4.62 p-type Semiconductor

Insulators: Such substances do not conduct electric current; their conductivity is very low. Width of forbidden zone between valence and conduction band is very big; hence electrons are not tossed from valence band to conduction band. On heating they decompose but do not give free conducting electrons.



Fig. 4.63

Examples: Classification of transition metal oxides

Metallic	Semiconductors	Insulators
VO	FeO, V ₂ O ₅	MnO
TiO	Fe ₂ O ₃ , Mn ₂ O ₃ Co ₃ O ₄ , Mn ₃ O ₄	
CrO ₂	CuO Cu ₂ O	

TiO and NbO become superconductors at low temperature, about 2 K.

4.25 MAGNETIC PROPERTIES

(i) Paramagnetic Solids

The presence of one or more unpaired electrons in an atom, molecule or ion gives rise to paramagnetism. Such materials are weakly attracted in the field. When they are placed in a magnetic field they become parallel to the field. Domain significance of unpaired electrons are given below:

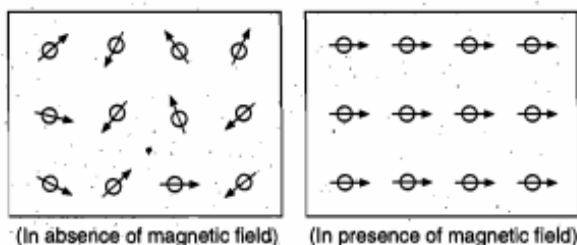


Fig. 4.64

Resultant magnetic field for n -unpaired electrons may be calculated as:

$$\mu_M = \sqrt{n(n+2)}$$

The magnetic field produced by unpaired electrons is due to—
(a) their spin and (b) their orbital motion.

Magnetic moment is measured in Bohr Magnetron (BM)

$$BM = \frac{eh}{4\pi mc}$$

$\mu_S = 1.73$ BM (one unpaired electron)

$\mu_S = 2.83$ BM (two unpaired electrons)

$\mu_S = 3.87$ BM (three unpaired electrons)

$\mu_S = 4.90$ BM (four unpaired electrons)

5.92, 6.93, 7.94 values for five, six and seven unpaired electrons respectively.

(ii) Diamagnetic Solids

The solids, which are weakly repelled by external magnetic field, are called diamagnetic solids and the property thus exhibited is called diamagnetism.

In diamagnetic solids, all electrons have paired spins, i.e., only fully filled orbitals are present. Examples are: NaCl, TiO₂, ZrO₂, KCl etc. Some diamagnetic solids like TiO₂ show paramagnetism due to presence of slight non-stoichiometry.

(iii) Ferromagnetic Solids

The solids which are strongly attracted by external magnetic field and do not lose their magnetism when the external field is removed, are called ferromagnetic solids. The property thus exhibited is termed ferromagnetism.

Ferromagnetic substances can be permanently magnetised. Only three elements, iron (Fe), cobalt (Co) and nickel (Ni) show ferromagnetism at room temperature. Some other examples are: EuO, CrO₂, etc. CrO₂ is the oxide used to make magnetic tapes for use in cassette recorders.

Ferromagnetism arises due to spontaneous alignment of magnetic moments due to unpaired electrons in the same direction as shown below (Fig. 4.65).

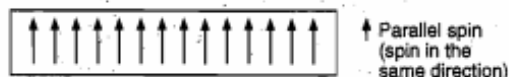


Fig. 4.65 Ferromagnetism

Mechanism of magnetisation of ferromagnetic substances: Unpaired electron in one atom interacts strongly with unpaired electron of neighbourhood atom, thus they align themselves spontaneously in a common direction in a small volume of solid called domains. Magnetic moments of all atoms in a domain are parallel to each other hence the domain possesses a net magnetic dipole moment. In absence of external magnetic field, the direction of magnetic moments in different domains are randomly oriented in different direction. When external magnetic field is applied then the domains in which the magnetic moments are parallel to external field, expand at the expense of remaining domains and ultimately all the magnetic moments align themselves in the direction of external magnetic field.

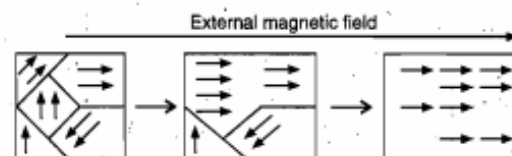


Fig. 4.66 Magnetisation of ferromagnetic substance

(iv) Antiferromagnetic Solids

The solids which are expected to show paramagnetism or ferromagnetism on the basis of unpaired electrons but actually

have zero net magnetic moment are called antiferromagnetic solids.



Fig. 4.67 Antiferromagnetism

Magnetic moments are aligned in a compensatory way so as to give zero net magnetic moment. Antiferromagnetism is due to the presence of equal number of magnetic moments in opposite directions as shown above (Fig. 4.67). The important examples are : MnO, MnO₂, Mn₂O₃, NiO, CoO, etc.

(v) Ferrimagnetic Solids

The solids which are expected to show large magnetism due to the presence of unpaired electrons but in fact have small net magnetic moment are called ferrimagnetic solids.

Ferrimagnetism arises due to alignment of magnetic moments in parallel and antiparallel directions in unequal numbers resulting in some net magnetic moment. This alignment has been shown ahead (Fig. 4.68).



Fig. 4.68 Ferrimagnetism

Examples are : Fe₃O₄ and ferrites of the formula $M^{2+}Fe_2O_4$ where $M = Zn, Cu, Mg$, etc.

Influence of temperature on magnetic character of solids : All magnetically ordered solids (ferromagnetic, antiferromagnetic and ferrimagnetic) change into paramagnetic state on increasing temperature. This is due to randomisation of their spins. The following examples explain this point :

(i) Ferrimagnetic solid, Fe₃O₄, becomes paramagnetic when heated to 850 K.

(ii) Antiferromagnetic solid, V₂O₃, becomes paramagnetic when heated to 750 K.

It should be noted that each ferromagnetic solid has a characteristic temperature above which it becomes paramagnetic. The characteristic temperature is called **Curie point** for **Curie temperature**.

Table 4.1 Magnetic Properties of Solid at a Glance

Properties	Information	Magnetic alignment	Example	Application
1. Diamagnetic	Repelled weakly in magnetic field. Such 'solids' have only paired electrons.	↑↓ ↑↓ ↑↓ ↑↓	Benzene, NaCl, TiO ₂ , V ₂ O ₅ , etc.	Insulators
2. Paramagnetic	Have unpaired electrons; weakly attracted in magnetic field. They cannot be permanently magnetised.	↑ ↓ ↗ ↘	O ₂ , VO, CuO, TiO	Electronic devices
3. Ferromagnetic	Also, have unpaired electrons. Strongly attracted in magnetic field. Such solids can be permanently magnetised. On heating to a temperature called Curie Point , these solids change to paramagnetic solid.	↑↑↑↑↑↑↑↑	Fe, Ni, Co, CrO ₂	CrO ₂ is used in audio, video tapes.
4. Antiferromagnetic	In these solids, unpaired electrons align themselves in such a way that resultant magnetic moment is zero.	↑↓↑↓↑↓↑↓	Cr ₂ O ₃ , CoO, Co ₃ O ₄ , Fe ₂ O ₃ , MnO, MnO ₂	Used in the instruments of magnetic susceptibility measurement
5. Ferrimagnetic	Unpaired electrons align themselves in such a way that there is a net magnetic moment.	↑↓↑↓↑↓↑↓ OR ↑↑↓↓↑↑↓↓↑↑ and so on	Fe ₃ O ₄ , ferrites	—

Table 4.2 Dielectric Properties of Solid at a Glance

Properties	Information	Dipolar property	Example	Application
1. Piezoelectricity	When a crystal of dielectrics is subjected to mechanical stress, then small magnitude current is produced. It is called direct Piezoelectric effect.	Development of charge in some part of crystal.	Quartz and Rochelle salt	Used in mechanical electric transducer, e.g., in record player, transmission of direct signals, sounding of sea depths.
2. Anti piezoelectricity	In some solids, electric field develops mechanical effect.	Crystal suffers elastic deformation in an electric field	—	
3. Ferroelectricity	Piezoelectric crystals having permanent dipoles are said to possess ferroelectricity.	↑↑↑↑↑↑	Ba TiO ₃ , KH ₂ PO ₄ Rochelle salt	Electromagnetic appliances.
4. Anti ferroelectricity	Piezoelectric crystals with zero dipole are said to possess anti ferroelectricity.	↑↓↑↓↑↓	PbZrO ₃ Lead zirconate	
5. Pyroelectricity	Some polar crystals produce electric impulse on heating.	—	Crystals of tartaric acid	Used in fire alarms, and thermostat

Superconductors

Copper and most other metals are good conductors of electricity. But even the best conductors present some resistance to the flow of electricity and a part of electrical energy is converted into heat energy. Thus, generators, turbines, motors of all kinds, transmission lines and other electrical equipment always operate at less than 100% efficiency.

A superconductor is a material that loses all electrical resistance below a characteristic temperature called the superconducting transition temperature, i.e., a superconductor presents no resistance to the flow of electricity.

Electrons move freely through a superconductor without any resistance or friction.

This phenomenon was discovered, in 1911, by the Dutch scientist **Heike Kamerlingh Onnes**, who found that mercury abruptly loses its electrical resistance when it is cooled with liquid helium to 4.2 K. Below its critical temperature (T_c), a superconductor becomes a perfect conductor and an electric current, once started, flows indefinitely without loss of energy. Most metals become superconductors at very low temperatures (generally around 2–5 K), but this temperature is far too cold for any commercial applications.

Since, 1911, scientists have been searching for materials that superconduct or at higher temperatures and more than 6000 superconductors are now known. Niobium alloys are particularly good superconductors and in 1973, a niobium alloy, Nb₃Ge, was found to show superconductivity at 23.2K. The situation changed dramatically in 1986 when **Müller** and **Bednorz** reported a T_c of 35K for the non-stoichiometric barium lanthanum copper oxide, Ba_xLa_{2-x}CuO₄, where x has a value of about 0.1. Soon

thereafter even higher values of T_c for other copper containing oxides : 90 K for YBa₂Cu₃O₇, 125K for Tl₂Ca₂Ba₂Cu₃O₁₀ and 133 K for HgCa₂Ba₂Cu₃O_{8+x}. [YBa₂Cu₃O₇ is also called 1-2-3 compound, i.e., 1 yttrium, 2 bariums and 3 coppers].

Room temperature ' T_c ' superconductors are yet to be discovered. The great advantage of these materials that offer no electrical resistance is the elimination of heating effects as electricity passes through. The energy saving and efficiencies that would be realised are substantial. Superconducting coils of wire could store electricity (in principle) forever, since no energy is lost. Thus, the energy can be tapped as needed. One of the most dramatic properties of a superconductor is its ability to levitate a magnet. When a superconductor is cooled below its T_c and a magnet is lowered towards it, the superconductor and magnet repel each other and the magnet hovers above the superconductor as though suspended in midair. The potential application of this effect will be in the high speed magnetically levitated trains. Some applications of superconductors already exist. For example, powerful superconducting magnets are essential components in the magnetic resonance imaging (MRI) instruments used in medical diagnosis. Superconductors are also used to make the magnets that bend the path of the charged particles in high energy particle accelerators. All the present applications, however, use conventional superconductors ($T_c \leq 20$ K). Of course, the search goes on for materials with higher values of T_c . For applications such as long distance electric power transmission, the goal is a material that superconducts at room temperature.