

(c) Non-Stoichiometric Defects

The defects discussed so far do not disturb the stoichiometry of the crystalline substance. However, a large number of non-stoichiometric inorganic solids are known which contain the constituent elements in non-stoichiometric ratio due to defects in their crystal structures. These defects are of two types: (i) metal excess defect and (ii) metal deficiency defect.

(i) Metal Excess Defect

- *Metal excess defect due to anionic vacancies:* Alkali halides like NaCl and KCl show this type of defect. 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 to the surface of the crystal and combine with Na atoms to give NaCl. This happens by loss of electron by sodium atoms to form Na⁺ ions. The released electrons diffuse into the crystal and occupy anionic sites (Fig. 1.32). As a result the crystal now has an excess of sodium. The anionic sites occupied by unpaired electrons are called *F-centres* (from the German word *Farbenzenter* for colour centre). They impart yellow colour to the crystals of NaCl. The colour results by excitation of these electrons when they absorb energy from the visible light falling on the crystals. Similarly, excess of lithium makes LiCl crystals pink and excess of potassium makes KCl crystals violet (or lilac).

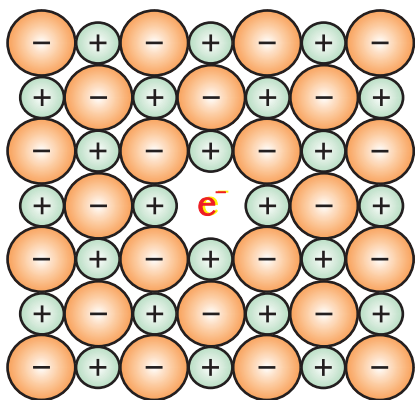
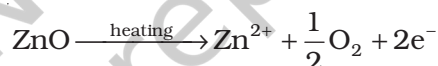


Fig. 1.32: An F-centre in a crystal

- *Metal excess defect due to the presence of extra cations at interstitial sites:* Zinc oxide is white in colour at room temperature. On heating it loses oxygen and turns yellow.



Now there is excess of zinc in the crystal and its formula becomes Zn_{1+x}O. The excess Zn²⁺ ions move to interstitial sites and the electrons to neighbouring interstitial sites.

(ii) Metal Deficiency Defect

There are many solids which are difficult to prepare in the stoichiometric composition and contain less amount of the metal as compared to the stoichiometric proportion. A typical example of this type is FeO which is mostly found with a composition of Fe_{0.95}O. It may actually range from Fe_{0.93}O to Fe_{0.96}O. In crystals of FeO some Fe²⁺ cations are missing and the loss of positive charge is made up by the presence of required number of Fe³⁺ ions.

1.10 Electrical Properties

Solids exhibit an amazing range of electrical conductivities, extending over 27 orders of magnitude ranging from 10⁻²⁰ to 10⁷ ohm⁻¹ m⁻¹. Solids can be classified into three types on the basis of their conductivities.

- *Conductors:* The solids with conductivities ranging between 10⁴ to 10⁷ ohm⁻¹ m⁻¹ are called conductors. Metals have conductivities in the order of 10⁷ ohm⁻¹ m⁻¹ are good conductors.

- (ii) *Insulators* : These are the solids with very low conductivities ranging between 10^{-20} to 10^{-10} ohm⁻¹m⁻¹.
- (iii) *Semiconductors* : These are the solids with conductivities in the intermediate range from 10^{-6} to 10^4 ohm⁻¹m⁻¹.

1.10.1 Conduction of Electricity in Metals

A conductor 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 molten state. The conductivity of metals depend upon the number of valence electrons available per atom. The atomic orbitals of metal atoms form molecular orbitals which are so close in energy to each other as to form a **band**. If this band is partially filled or it overlaps with a higher energy unoccupied conduction band, then electrons can flow easily under an applied electric field and the metal shows conductivity (Fig. 1.33 a).

If the gap between filled valence band and the next higher unoccupied band (conduction band) is large, electrons cannot jump to it and such a substance has very small conductivity and it behaves as an insulator (Fig. 1.33 b).

1.10.2 Conduction of Electricity in Semiconductors

In case of semiconductors, the gap between the valence band and conduction band is small (Fig. 1.33 c). Therefore, some electrons may jump to conduction band and show some conductivity. Electrical conductivity of semiconductors increases with rise in temperature, since more electrons can 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 to be of practical use. Their conductivity is increased by adding an appropriate amount of suitable impurity. This process is called

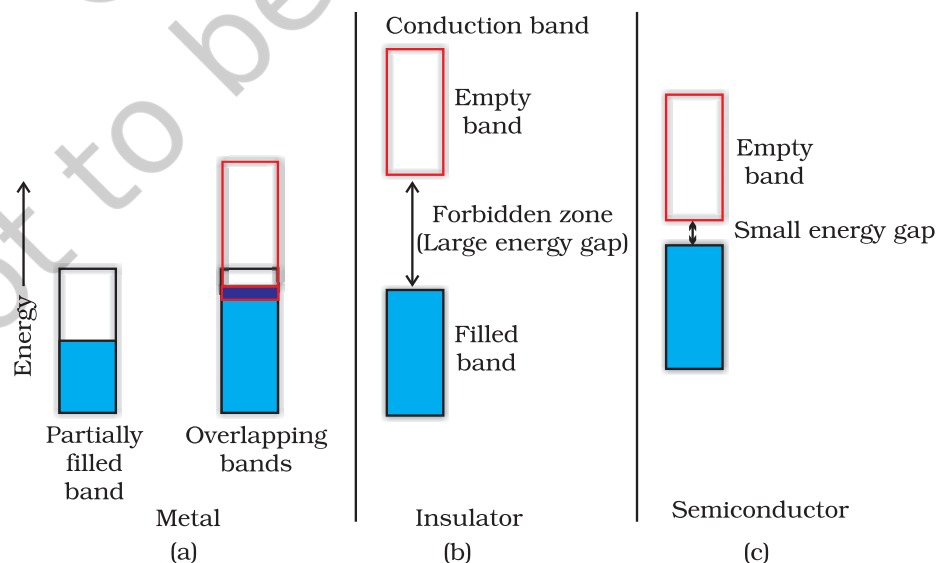


Fig. 1.33
Distinction among
(a) metals
(b) insulators and
(c) semiconductors.
In each case, an
unshaded area
represents a
conduction band.

doping. 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 them.

(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 neighbours (Fig. 1.34 a). When doped with a group 15 element like P or As, which contains five valence electrons, they occupy some of the lattice sites in silicon or germanium crystal (Fig. 1.34 b). Four out of five electrons 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. The place where the fourth valence electron is missing is called *electron hole* or **electron vacancy** (Fig. 1.34 c). An electron from a neighbouring atom can come and fill the electron hole, but in doing so it would 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 would move towards the positively charged plate through electronic holes, but it would appear as if electron holes are positively charged and are moving towards negatively charged plate. This type of semi conductors are called *p-type* semiconductors.

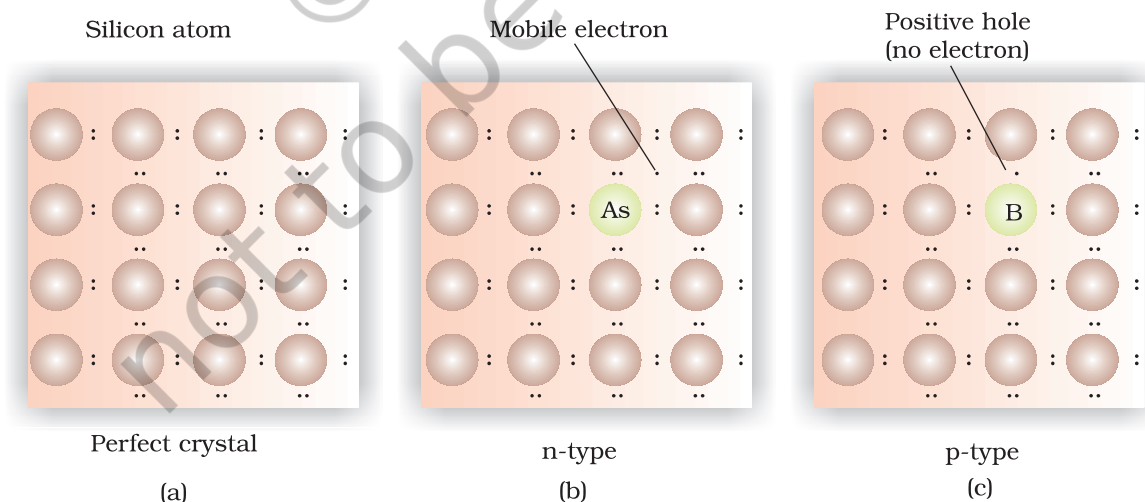


Fig. 1.34: Creation of *n-type* and *p-type* semiconductors by doping groups 13 and 15 elements.

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 InSb, AlP and GaAs. Gallium arsenide (GaAs) semiconductors have very fast response and have revolutionised the design of semiconductor devices. ZnS, CdS, CdSe and HgTe are 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, CrO₂ and ReO₃ behave like metals. Rhenium oxide, ReO₃ is like metallic copper in its conductivity and appearance. Certain other oxides like VO, VO₂, VO₃ and TiO₃ show metallic or insulating properties depending on temperature.

1.11 Magnetic Properties

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. 1.35).

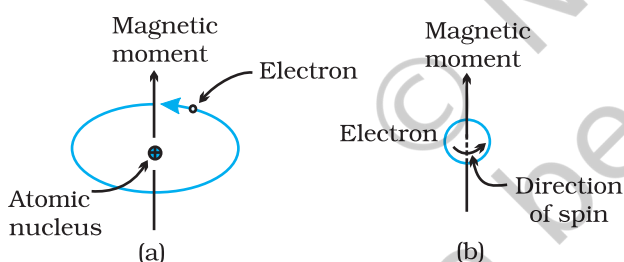


Fig.1.35: Demonstration of the magnetic moment associated with (a) an orbiting electron and (b) a spinning electron.

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_B . It is equal to $9.27 \times 10^{-24} \text{ A m}^2$.

On the basis of their magnetic properties, substances can be classified into five categories: (i) paramagnetic (ii) diamagnetic (iii) ferromagnetic (iv) antiferromagnetic and (v) ferrimagnetic.

- (i) **Paramagnetism:** Paramagnetic substances are weakly attracted by a magnetic field. They are magnetised in a magnetic field in the same direction. They lose their magnetism in the absence of magnetic field. Paramagnetism is due to presence of one or more unpaired electrons which are attracted by the magnetic field. O₂, Cu²⁺, Fe³⁺, Cr³⁺ are some examples of such substances.

- (ii) *Diamagnetism*: Diamagnetic substances are weakly repelled by a magnetic field. H_2O , NaCl and C_6H_6 are some examples of such substances. They are weakly magnetised in a magnetic field in opposite direction. 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.
- (iii) *Ferromagnetism*: A few substances like iron, cobalt, nickel, gadolinium and CrO_2 are attracted very strongly by a magnetic field. Such substances are called ferromagnetic substances. Besides strong attractions, these substances can be permanently magnetised. In solid state, the metal ions of ferromagnetic substances are grouped together into small regions called *domains*. Thus, each domain acts as a tiny magnet. In an unmagnetised piece of a 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 (Fig. 1.36 a) 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.
- (iv) *Antiferromagnetism*: Substances like MnO showing antiferromagnetism have domain structure similar to ferromagnetic substance, but their domains are oppositely oriented and cancel out each other's magnetic moment (Fig. 1.36 b).
- (v) *Ferrimagnetism*: Ferrimagnetism is observed when the magnetic moments of the domains in the substance are aligned in parallel and anti-parallel directions in unequal numbers (Fig. 1.36c). They are weakly attracted by magnetic field as compared to ferromagnetic substances. Fe_3O_4 (magnetite) and ferrites like MgFe_2O_4 and ZnFe_2O_4 are examples of such substances. These substances also lose ferrimagnetism on heating and become paramagnetic.

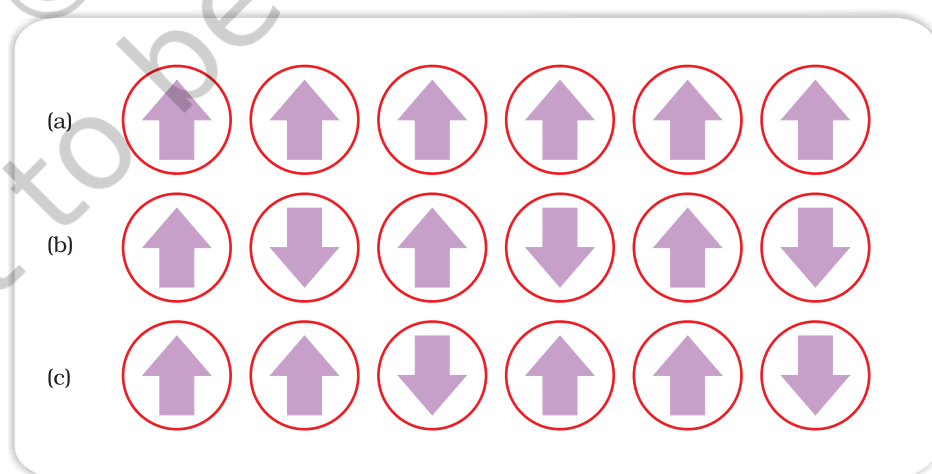


Fig 1.36: Schematic alignment of magnetic moments in (a) ferromagnetic (b) antiferromagnetic and (c) ferrimagnetic.

Intext Questions

- 1.19** What type of defect can arise when a solid is heated? Which physical property is affected by it and in what way?
- 1.20** What type of stoichiometric defect is shown by:
(i) ZnS (ii) AgBr
- 1.21** Explain how vacancies are introduced in an ionic solid when a cation of higher valence is added as an impurity in it.
- 1.22** Ionic solids, which have anionic vacancies due to metal excess defect, develop colour. Explain with the help of a suitable example.
- 1.23** A group 14 element is to be converted into n-type semiconductor by doping it with a suitable impurity. To which group should this impurity belong?
- 1.24** What type of substances would make better permanent magnets, ferromagnetic or ferrimagnetic. Justify your answer.

Summary

Solids have definite mass, volume and shape. This is due to the fixed position of their constituent particles, short distances and strong interactions between them. In **amorphous** solids, the arrangement of constituent particles has only **short range order** and consequently they behave like **super cooled liquids**, do not have sharp melting points and are isotropic in nature. In crystalline solids there is long range order in the arrangement of their constituent particles. They have sharp melting points, are anisotropic in nature and their particles have characteristic shapes. Properties of **crystalline** solids depend upon the nature of interactions between their constituent particles. On this basis, they can be divided into four categories, namely: **molecular**, **ionic**, **metallic** and **covalent** solids. They differ widely in their properties.

The constituent particles in crystalline solids are arranged in a regular pattern which extends throughout the crystal. This arrangement is often depicted in the form of a three dimensional array of points which is called crystal lattice. Each **lattice point** gives the location of one particle in space. In all, fourteen different types of lattices are possible which are called **Bravais lattices**. Each lattice can be generated by repeating its small characteristic portion called **unit cell**. A unit cell is characterised by its edge lengths and three angles between these edges. Unit cells can be either **primitive** which have particles only at their corner positions or **centred**. The centred unit cells have additional particles at their body centre (**body-centred**), at the centre of each face (**face-centred**) or at the centre of two opposite faces (**end-centred**). There are seven types of **primitive unit cells**. Taking centred unit cells also into account, there are fourteen types of unit cells in all, which result in fourteen **Bravais lattices**.

Close-packing of particles result in two highly efficient lattices, **hexagonal close-packed (hcp)** and **cubic close-packed (ccp)**. The latter is also called face-centred cubic (**fcc**) lattice. In both of these packings 74% space is filled. The remaining space is present in the form of two types of voids-octahedral voids and tetrahedral voids. Other types of packing are not close-packings and have less

efficient packing of particles. While in **body-centred cubic lattice (bcc)** 68% space is filled, in simple cubic lattice only 52.4 % space is filled.

Solids are not perfect in structure. There are different types of **imperfections** or **defects** in them. Point defects and line defects are common types of defects. Point defects are of three types - **stoichiometric defects**, **impurity defects** and **non-stoichiometric defects**. **Vacancy defects** and **interstitial defects** are the two basic types of stoichiometric point defects. In ionic solids, these defects are present as **Frenkel** and **Schottky defects**. Impurity defects are caused by the presence of an impurity in the crystal. In ionic solids, when the ionic impurity has a different valence than the main compound, some vacancies are created. Non-stoichiometric defects are of **metal excess type** and **metal deficient type**. Sometimes calculated amounts of impurities are introduced by **doping in semiconductors** that change their electrical properties. Such materials are widely used in electronics industry. 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.

Exercises

- 1.1 Define the term 'amorphous'. Give a few examples of amorphous solids.
- 1.2 What makes a glass different from a solid such as quartz? Under what conditions could quartz be converted into glass?
- 1.3 Classify each of the following solids as ionic, metallic, molecular, network (covalent) or amorphous.
 - (i) Tetra phosphorus decoxide (P_4O_{10})
 - (ii) Ammonium phosphate $(NH_4)_3PO_4$
 - (iii) SiC
 - (iv) I_2
 - (v) P_4
 - (vi) Plastic
 - (vii) Graphite
 - (viii) Brass
 - (ix) Rb
 - (x) LiBr
 - (xi) Si
- 1.4
 - (i) What is meant by the term 'coordination number'?
 - (ii) What is the coordination number of atoms:
 - (a) in a cubic close-packed structure?
 - (b) in a body-centred cubic structure?
- 1.5 How can you determine the atomic mass of an unknown metal if you know its density and the dimension of its unit cell? Explain.
- 1.6 'Stability of a crystal is reflected in the magnitude of its melting points'. Comment. Collect melting points of solid water, ethyl alcohol, diethyl ether and methane from a data book. What can you say about the intermolecular forces between these molecules?

- 1.7 How will you distinguish between the following pairs of terms:
(i) Hexagonal close-packing and cubic close-packing?
(ii) Crystal lattice and unit cell?
(iii) Tetrahedral void and octahedral void?
- 1.8 How many lattice points are there in one unit cell of each of the following lattice?
(i) Face-centred cubic
(ii) Face-centred tetragonal
(iii) Body-centred
- 1.9 Explain
(i) The basis of similarities and differences between metallic and ionic crystals.
(ii) Ionic solids are hard and brittle.
- 1.10 Calculate the efficiency of packing in case of a metal crystal for
(i) simple cubic
(ii) body-centred cubic
(iii) face-centred cubic (with the assumptions that atoms are touching each other).
- 1.11 Silver crystallises in fcc lattice. If edge length of the cell is 4.07×10^{-8} cm and density is 10.5 g cm^{-3} , calculate the atomic mass of silver.
- 1.12 A cubic solid is made of two elements P and Q. Atoms of Q are at the corners of the cube and P at the body-centre. What is the formula of the compound? What are the coordination numbers of P and Q?
- 1.13 Niobium crystallises in body-centred cubic structure. If density is 8.55 g cm^{-3} , calculate atomic radius of niobium using its atomic mass 93 u.
- 1.14 If the radius of the octahedral void is r and radius of the atoms in close-packing is R , derive relation between r and R .
- 1.15 Copper crystallises into a fcc lattice with edge length 3.61×10^{-8} cm. Show that the calculated density is in agreement with its measured value of 8.92 g cm^{-3} .
- 1.16 Analysis shows that nickel oxide has the formula $\text{Ni}_{0.98}\text{O}_{1.00}$. What fractions of nickel exist as Ni^{2+} and Ni^{3+} ions?
- 1.17 What is a semiconductor? Describe the two main types of semiconductors and contrast their conduction mechanism.
- 1.18 Non-stoichiometric cuprous oxide, Cu_2O can be prepared in laboratory. In this oxide, copper to oxygen ratio is slightly less than 2:1. Can you account for the fact that this substance is a p-type semiconductor?
- 1.19 Ferric oxide crystallises in a hexagonal close-packed array of oxide ions with two out of every three octahedral holes occupied by ferric ions. Derive the formula of the ferric oxide.
- 1.20 Classify each of the following as being either a p-type or a n-type semiconductor:
(i) Ge doped with In
(ii) Si doped with B.

- 1.21** Gold (atomic radius = 0.144 nm) crystallises in a face-centred unit cell. What is the length of a side of the cell?
- 1.22** In terms of band theory, what is the difference
(i) between a conductor and an insulator
(ii) between a conductor and a semiconductor?
- 1.23** Explain the following terms with suitable examples:
(i) Schottky defect (ii) Frenkel defect (iii) Interstitials and (iv) F-centres.
- 1.24** Aluminium crystallises in a cubic close-packed structure. Its metallic radius is 125 pm.
(i) What is the length of the side of the unit cell?
(ii) How many unit cells are there in 1.00 cm³ of aluminium?
- 1.25** If NaCl is doped with 10⁻³ mol % of SrCl₂, what is the concentration of cation vacancies?
- 1.26** Explain the following with suitable examples:
(i) Ferromagnetism
(ii) Paramagnetism
(iii) Ferrimagnetism
(iv) Antiferromagnetism
(v) 12-16 and 13-15 group compounds.

Answers to Some Intext Questions

- 1.14** 4
- 1.15** Total number of voids = 9.033×10^{23}
Number of tetrahedral voids = 6.022×10^{23}
- 1.16** M₂N₃
- 1.18** ccp