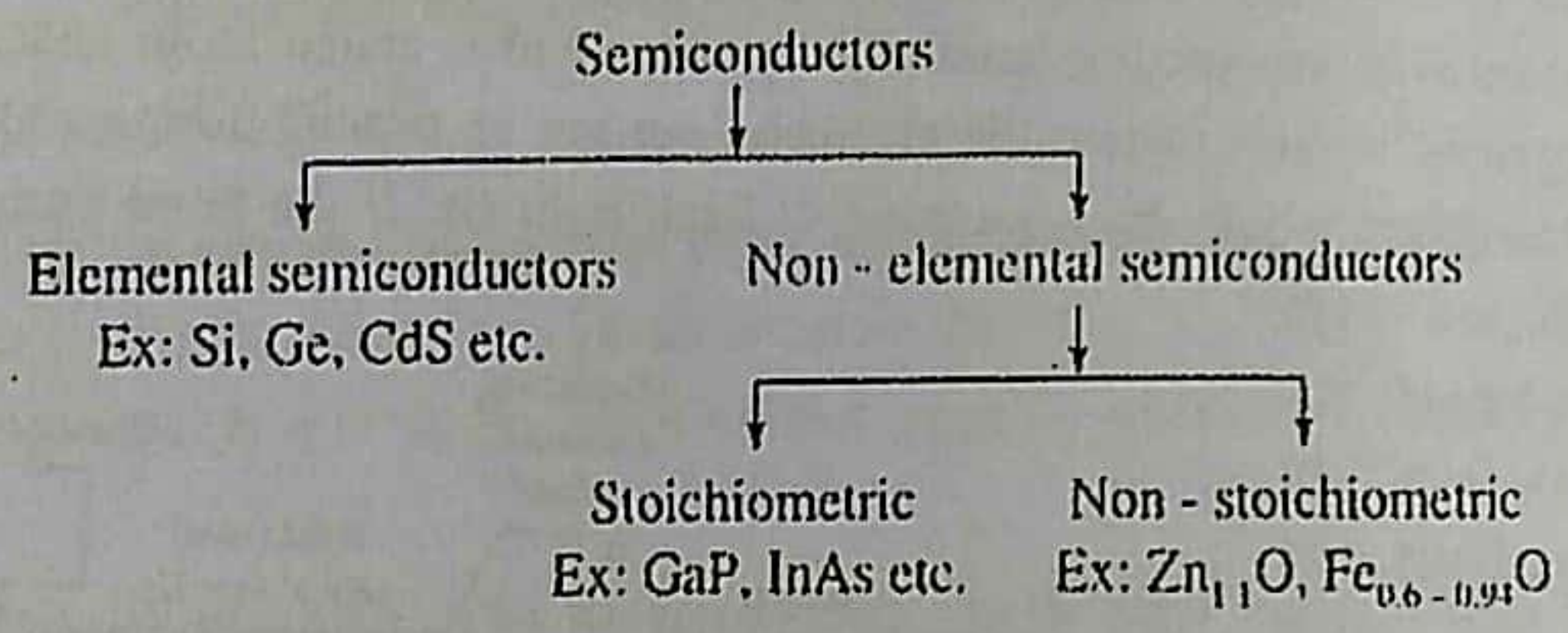


5.6 CLASSIFICATION OF SEMICONDUCTING MATERIALS

The semiconducting materials are classified into two types.

- 1. Elemental semiconductors
- 2. Non elemental semiconductors

1. Elemental semiconductors are the semiconductors that are elements and the examples are Si, Ge, Ga etc.
2. Non elemental semiconductors are two types stoichiometric and non-stoichiometric. Stoichiometric semiconductors are formed by the combination of elements of group III and group V or group II and VI and many intermetallic compounds like Ga, P, As etc. Non - stoichiometric (defect) semiconductors are certain compounds like $Fe_{0.6-0.94}O$ and $Zn_{1.1}O$, which have vacancies in their structures and non - stoichiometric compositions. They behave like n - type or p - type semiconductors.



5.7 NON - ELEMENTAL SEMICONDUCTORS

These semiconductors are formed by the combination of elements of group III - V or group II - VI and certain other compounds which have valencies in non - stoichiometric compositions.

5.7.1 Stoichiometric Semiconductors

The crystal structures and band structures similar to that of Silicon (Si) and Germanium (Ge) are developed by the combination of group III and group V elements and group II and group VI elements named as stoichiometric semiconductors. For example Ga - As semiconductor. The $4s^2, 4p^1$ level of Ga and $4s^2, 4p^3$ level of As overlap to give rise to hybrid band containing $4N$ electrons per N atom of Ga and As with fermi energy gap (E_g) 2.24 (eV). The following is the list of some stoichiometric semiconductors and their fermi energy gaps.

Group III & V combination		Group II & VI combination	
Semiconductor	Fermi energy gap (E_g) (eV)	Semiconductor	Fermi energy gap (E_g) (eV)
GaP	2.24	CdS	2.42
GaAs	1.35	CdSe	1.74
GaSb	0.67	PbS	0.37
In As	0.36		

Characteristics of stoichiometric semiconductors:

1. Stoichiometric semiconductors have wide energy gap, which leads to broad exhaustion zone with high conductivities. Hence they can be used at wider range of temperatures.
2. It is possible to alter the energy gap (E_g) of these semiconductors by substituting one of the elements in its composition by an element of lower atomic number belonging to the same group. For Ex: In GaP, if P is replaced by As the energy gap reduces from 2.24 to 1.35 (eV).
3. They can be doped to n or p - type semiconductors.

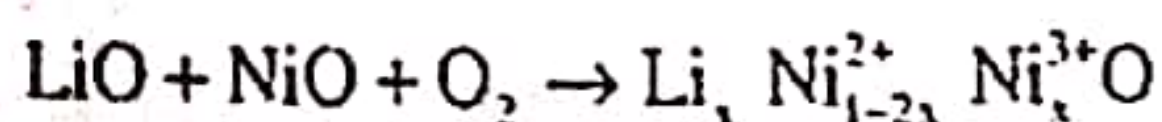
5.7.2 Non - Stoichiometric (defect) Semiconducting Compounds

This type of semiconductors possess vacancies in their structure and non - stoichiometric compositions. They also behave like n - type or p - type semiconductors. For Eg: $Zn_{1-x}O$ is formed by exposing ZnO to reduce atmosphere where some Zn^{2+} are reduced to Zn^+ ions, which is richer by one electron can donate an electron to promote to conduction band there Zn^+ creates a donor level band between valence band and conduction band.

When FeO is heated under oxidizing conditions, Fe^{2+} ions are oxidized to Fe^{3+} ions to produced $Fe_{1-x}O$. As Fe^{3+} has one less electron than Fe^{2+} , it produces a positive hole where electrons can hop from Fe^{2+} to Fe^{3+} under the influence of electric field producing conductivity. Such semiconductors are called hopping semiconductors. These semiconductors behave as p - type semiconductors.

5.7.3 Controlled Valency Semiconductors

$Ni_{1-x}^{2+} Ni_x^{3+} O$ is a hopping semiconductor producing hopping semiconductivity by hopping of electrons from Ni^{2+} to Ni^{3+} ions. The concentration and conductivity of Ni^{3+} is controlled by the addition of small amount of Li^+ ions.



The semiconductor (I) shows conductivities depending on temperatures and find applications as thermistors. (thermally sensitive resistors). These semiconductors can be used over a wide range of temperature upto 200 °C. The compound containing the composition $\text{Li}_{0.05}^+ \text{Ni}_{0.9}^{2+} \text{Ni}_{0.05}^{3+} \text{O}$ is electroneutral semiconductor which is shown as below

Positive charge	Negative charge
$\text{Li}_{0.05}^+ = 0.05 \times 1 = 0.05$	$\text{O}^{2-} = 2$
$\text{Ni}_{0.9}^{2+} = 0.9 \times 2 = 1.8$	
$\text{Ni}_{0.05}^{3+} = 0.05 \times 3 = \underline{0.15}$	—
<u>2.0</u>	<u>2</u>

Thus $\text{Li}_{0.05}^+ \text{Ni}_{0.9}^{2+} \text{Ni}_{0.05}^{3+} \text{O}$ is neutral semiconductor

5.7.4 Chalcogen Photo Semiconductors

Oxygen (O), Sulphur (S), Selenium (Se) and Tellurium (Te) are collectively called **chalcogens** or **ore forming elements** because a large number of metal ores are oxides or sulphides.

The characteristics of chalcogens are:

1. They behave as semiconductors or photo conductors either alone or by combining with other elements.
2. They rapidly form glass on cooling and viscous liquids on melting.
3. Chalcogen based glasses have conductivities in the range of $10^{-3} - 10^{-11}$ mho/cm
4. The conductivities of pure chalcogens increase with increase in atomic mass.
5. Selenium is an excellent photo conductor. Its conductivity increases enormously on exposing to light, hence it is used in photo copying process (xerox).

5.8 PREPARATION OF SEMICONDUCTORS

The semiconducting elements used for the application of semiconductor devices must be 99.9999% pure. i.e., one atom of impurity for every 10^6 atoms of Si or Ge. To prepare such ultra pure materials the following steps were involved.

1. Preparation of ultra pure Si or Ge
2. Preparation of single crystal of Si or Ge
3. Doping

5.8.1 Preparation of Ultra Pure Ge

(GeCl_4) Germanium tetra chloride is used as a starting material, which contains arsenic (As) impurity which is removed as AsCl_3 and separated by distillation.

- a) **Distillation:** It is a process where separation is carried out by taking the difference in boiling points as advantage. Germanium is taken in a series of stills with a layer of HCl over it and heated it, while passing chlorine through it. The vapours produced were collected and passed into a fractionality column. The distilled vapours are collected into a receiver placed in ice bath. Pure GeCl_4 thus obtained is treated with water to get GeO which is reduced in an atmosphere of N_2 to elemental germanium, which is further subjected purification by zone refining.
- b) **Zone refining:** Zone refining is a metallurgical process which is based on the principle that the impurities present in a metal are more soluble in molten metal than in solid metal. For the purification of Ge vertical zone refiner (Fig. 5.25) is used. A rod of Ge to be purified is clamped and heated by RF coil to about 1000°C in a reducing atmosphere. The heater moves from top to bottom very slowly. As the RF coil is moved down, the impurities move with the molten part of the material. Pure Ge rod solidifies at the upper portion. The process is repeated several times to reduce the impurity level and the lower end of the rod is removed after getting the desired purity because it is concentrated with impurities. By zone refining process the impurity level 1 atom in 10^{12} atoms of Ge is obtained.

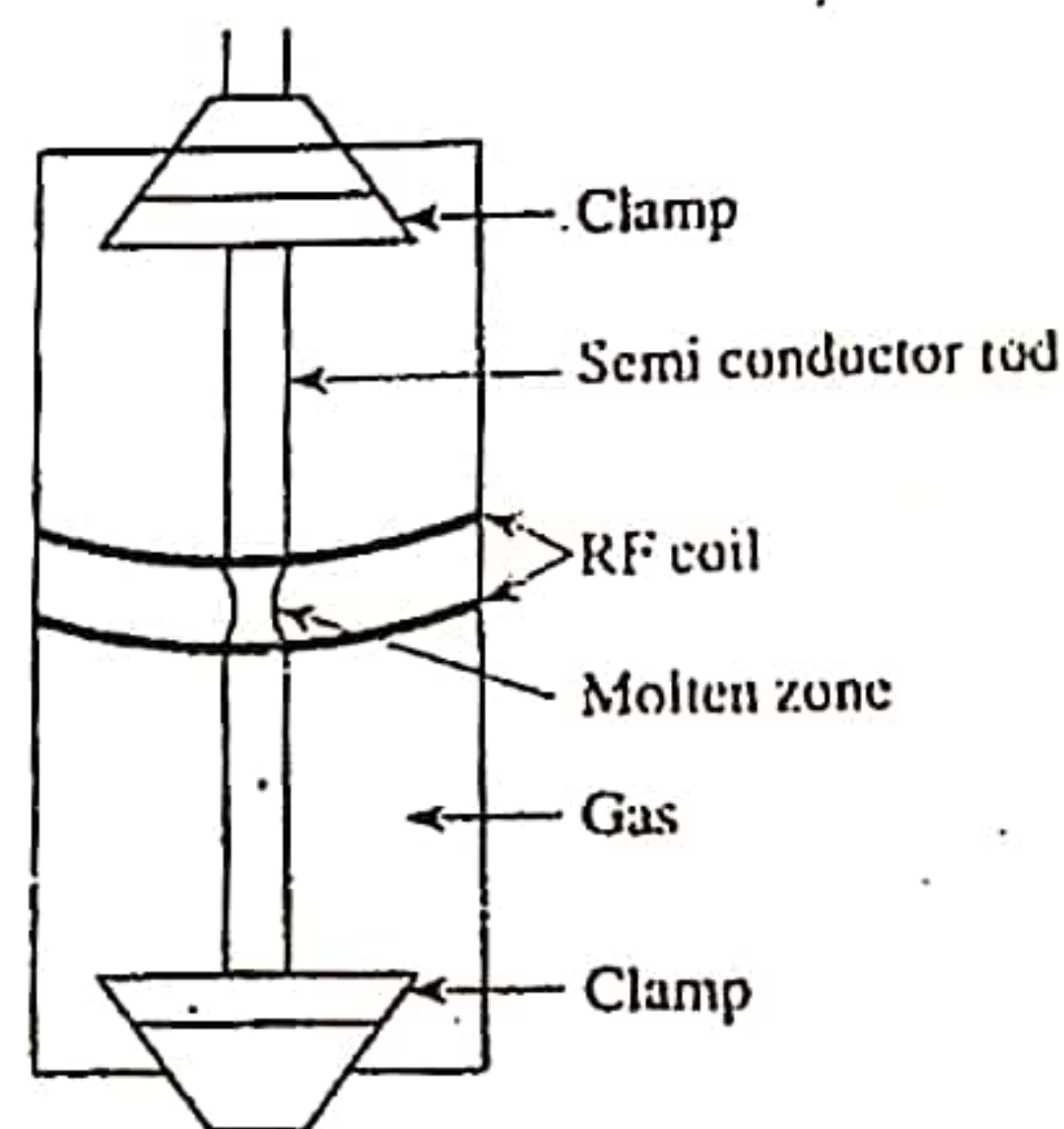


Fig. 7.25 Vertical zone refiner

- c) **Preparation of ultrapure silicon:** Ultrapure silicon is prepared by the following method.
Chemical method: Trichlorosilane is first distilled to get pure trichlorosilane. Then it is reduced to elemental silicon by heating in an atmosphere of hydrogen by bubbling hydrogen through trichlorosilane which vaporizes.

The vapours are fed into a tubular furnace fitted with a highly pure silicon rod and heated to 950°C . At this temperature, the vapours of trichlorosilane decompose leaving behind pure silicon on the surface of the highly pure silicon rod. The thickness of the silicon rod increases from 2.5 to 10 cm.

HCl vapours produced in the reaction are removed through a vent. Zone purification cannot be adopted for the preparation of ultrapure silicon, because boron impurity has same solubility in molten and solid silicon and a high temperature (1420 °C) is required to melt silicon.

5.8.2 Preparation of single crystals of Si or Ge

The basic requirement for the fabrication of a semiconductor device is that the semiconductor used must be a single crystal. The preparation of Si and Ge produces polycrystalline products i.e., crystals of various sizes. Hence single crystal of Si and Ge are produced by czochralski crystal pulling technique.

Czochralski crystal pulling technique: This process was named after the polist scientist Jan czochralski who invented the method in 1916 by accident while studying crystallization methods.

In this method single crystals are grown in such a way that during crystal growth atoms reproduce the same atomic arrangement as that of the seed crystal. The process begins when the chamber which contains a crucible with silicon is heated to approximately 1500 °C. When silicon is fully melt, a small seed crystal mounted on the end of the rotating shaft is slowly lowered until it just dips below the surface of the molten silicon. The shaft rotates in anti clockwise and the crucible rotates in clockwise direction. The rotating rod is then drawn upwards very slowly about 25 mm per hour when making a crystal of silicon allowing in the form of boule to be formed. The boule can be from one to two metres, depending on the amount of silicon in the crucible.

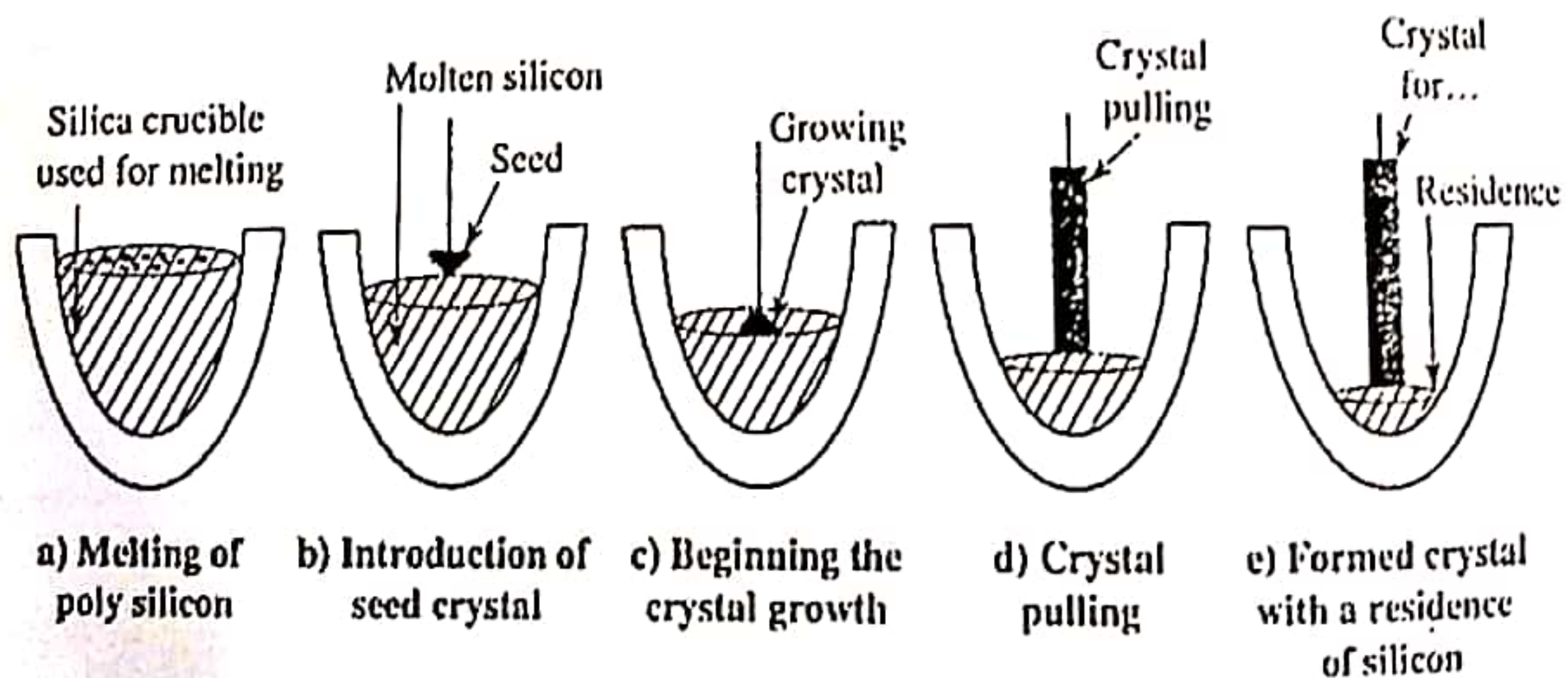


Fig. 5.26 Czochralski process

When silicon is grown in silica crucible O₂ from crucible is introduced as an impurity at a concentration of 10¹⁸ cm³. Careful an annealing process condition were adopted to remove oxygen. The above process is adopted even for the crystal pulling of germanium.

5.8.3 Doping

Introducing an impurity into the semiconducting crystal is called doping. Doping is carried out by a epitaxy diffusion implantation techniques. Doping is carried out in the crystal pulling state. Calculated amounts of dopants (about 1 atom of B or P in 100 million atoms of Si or Ge) are added to the melt before crystal pulling.

- a) **Epitaxy:** It is a process of deposition of a crystalline over layer on a crystalline substrate. The over layer can be called as an epitaxial film or layer. The term epitaxy comes from Greek - epi means 'over' and taxis meaning an 'ordered manner'. Epitaxy refers to the deposition of a crystalline over layer on a crystalline substrate which acts as seed crystal. The following are some of the technique molecular beam epitaxy (MBE). A source of material is heated to produce an evaporated beam of particles, which travel through high vacuum (10^{-8} practically free space) to the substrate, where they condense. MBE has lower throughput than other forms of epitaxy. This is widely used for growing group III, IV and V semiconductor crystals.
- b) **Diffusion:** An epitaxial layer can be doped during deposition by adding impurities to source gas such as arsine, phosphine or diborane. The concentration of impurity in the gas phase determines its concentration in the deposited film. The impurities change the deposition rate. At high temperatures the chemical vapour deposition may allow dopants to diffuse into the growing layer from layer to the other layer in the water. p - type Ge water is heated just below the melting point in an atmosphere of n - type dopant such as P or Sb causing diffusion of impurity into the material and produces pn - type semiconducting material.
- c) **Ion implantation technique:** In this technique a semiconductor material is bombarded with an electrically controlled beam having higher energy of 10 keV containing impurity ions like boron or phosphorous. This results in the implantation of some dopants into the semiconducting crystal. Ion implantation method is extensively used in the fabrication of high frequency devices.

5.9 p - n JUNCTION

When a single crystal of Si or Ge is doped with Indium at one end arsenic at the other end which constitutes one part p - type semiconductor and the other n - type semiconductor with middle boundary region where the two sides meet. This is known as p - n junction. The

group III elements B, Al, Ga or In and group V element like P or As are mostly used because of their low melting point, which is useful for high temperature diffusion of the appropriate dopant element.

5.9.1 p - n Junction as a Rectifier

Current from an outside source is allowed to flow through a rectifier only in one direction and this is very useful because it helps in converting alternate current (AC) to direct current (DC). The function of p - n - junction as rectifier is discussed below. A transistor with two zones, one p - type and the other n - type with p, n - junction in between is known diode. If p - type semiconductor region is connected to the positive terminal of battery and n - type region is connected to the negative terminal of the same battery [Fig. 5.27 (a)]. From n - type region electrons will migrate towards the p, n - junction, where as holes will migrate towards the p - n junction. At the p - n junction of diode, the migrating electrons from the n - type region move into the vacant holes in the valence band of the p - type region. This migration of electrons and holes can continue and a current flows as long as the external voltage than a battery is supplied.

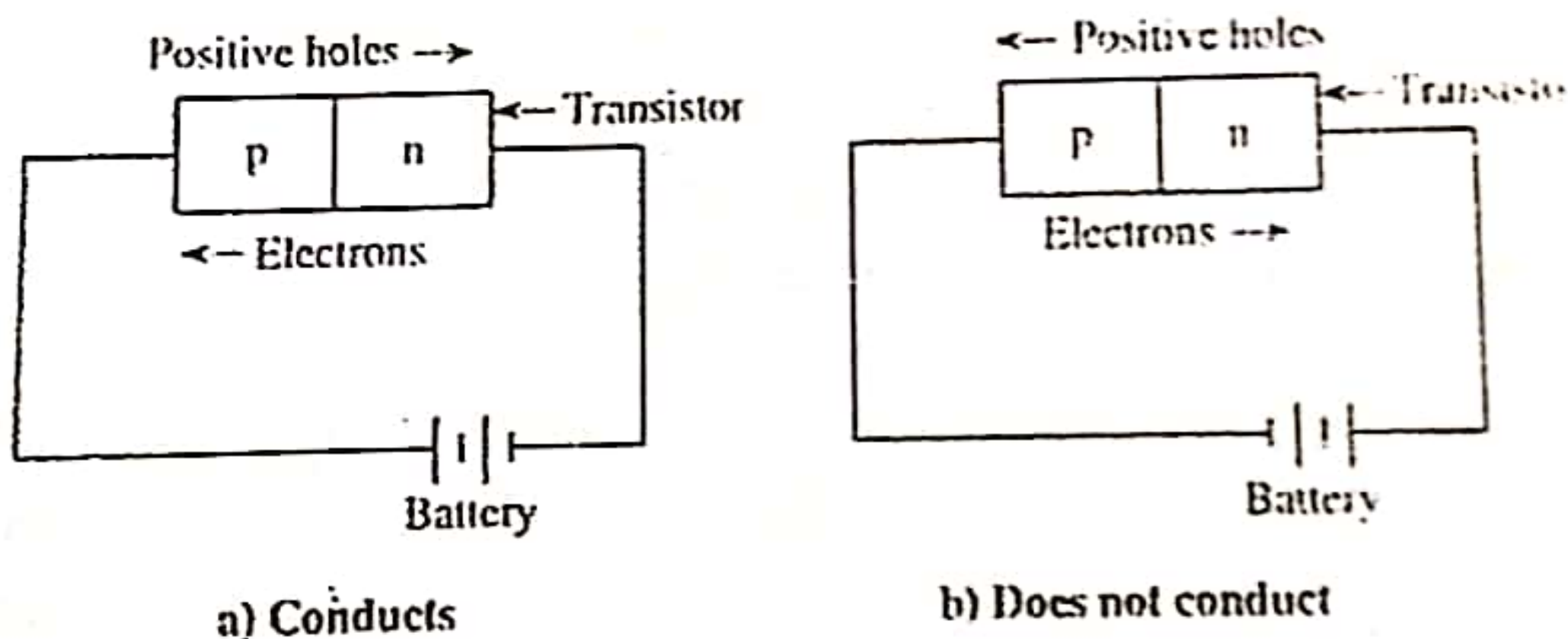


Fig. 5.27 A p - n junction as a rectifier

When the connection is reversed i.e., p - type region is connecting to the negative terminal of the battery and n -type region is connecting to the positive terminal of the battery (Fig. 5.27 (b)) the positive holes move away from p - n junction in p - type region and the electrons migrate away from p - n junction in the n - type region. The current does not flow at the junction as there are no electrons or positive holes.

5.9.2 Junction Transistors

Transistors are single crystals of silicon which have been doped to give three zones, either p - n - p or n - p - n as shown below. [Fig. 5.28 (a) & (b)]

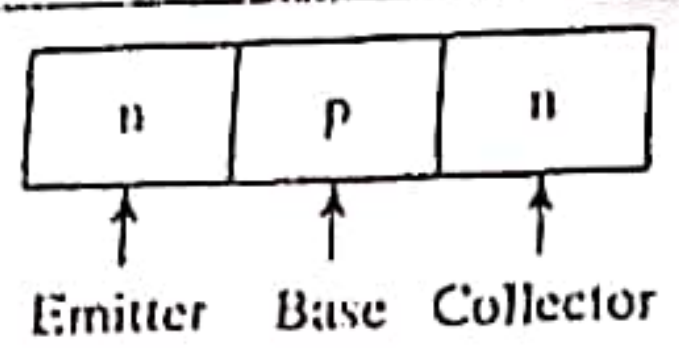


Fig. (a)

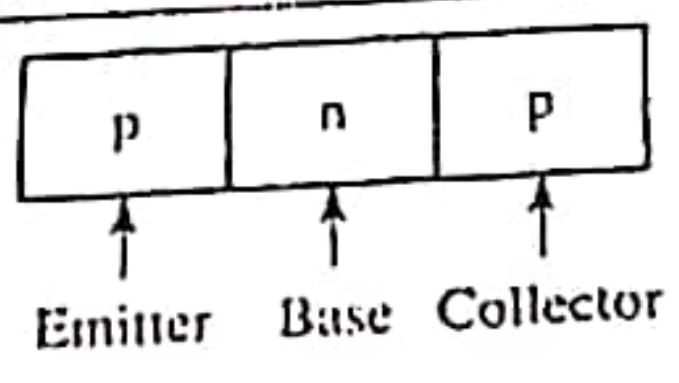


Fig. (b)

Fig. 5.28 p - n - p and n - p - n transistors

Different voltages must be applied to the three regions of the transistor to make it work with respect to the emitter, the base is typically -0.2 V and the collector is typically -2 volts . [Fig. 5.29 (a) & (b)]

In the p - n - p transistor, the charge carriers in the emitter are positive holes, which migrate from the emitter at 0 volts to the base at -0.2 volts . The positive holes cross the emitter / base p - n junction. In the n - type base region some holes combine with electrons and are destroyed. Electrons flow in the reverse direction from the base to the emitter. There is thus a small base current. Since the collector has much greater negative voltage and the base is very thin, most of the positive holes pass through the base to the collector, where they combine with electrons from the circuit. At the emitter, electrons leave the p - type semiconductor and enter the circuit by producing more positive holes. Typically if the emitter current is 1 mA , the base current is 0.02 mA and the collector current is 0.98 mA . The n - p - n transistor work in a similar way, except the polarity of the base voltage is reversed. Thus the collector and base are positive w.r.t the emitter.

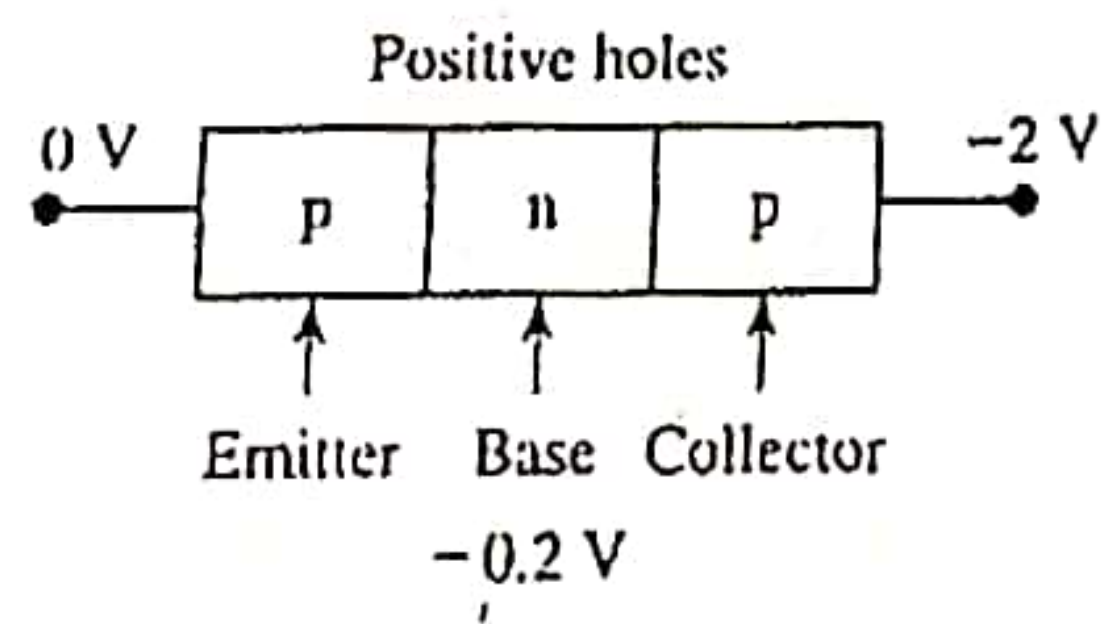


Fig. (a)

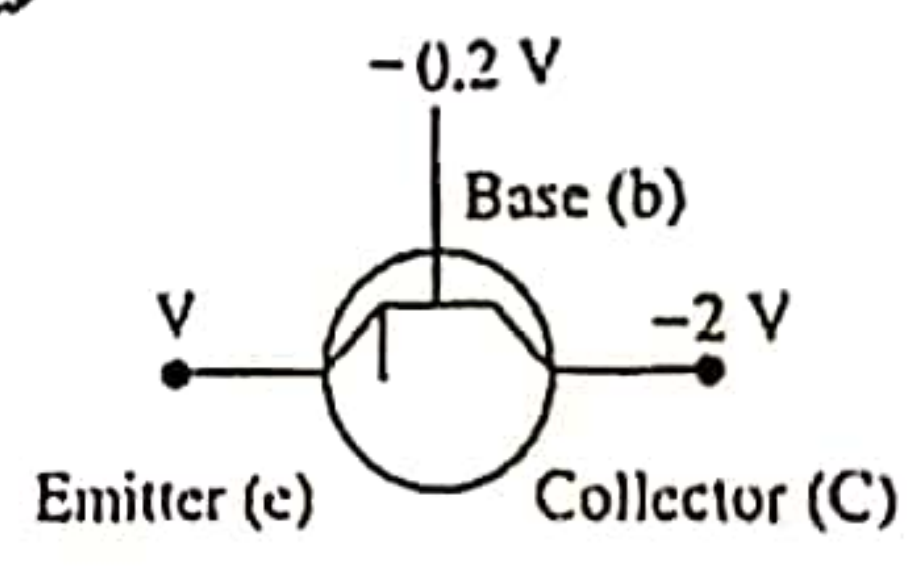


Fig. (b)

Fig. 5.29 Typical bias voltages for p - n - p transistor

Applications of transistors: Transistors are most widely used as 1) amplifiers and oscillators in radio, T.V, computers and hi-fi circuits, photo transistors, solar cells, detectors for ionizing radiations, thermistors and tunnel diodes.

5.9.3 Transistor as an Amplifier

Transistor can be used as an amplifier where the circuit has common emitter i.e., common to both base and collector. The base emitter is the input signal and the collector current is the

output signal. If the base current is increased, the base becomes more negative and increases the movement of positive holes to the collector. In a typical transistor a change in the base current produces a change 50 times as great as collector current producing current amplification factor 50. A small change in the input current to the base produces a much larger change in the collector current and causes amplification of original signal. The voltage for the collector and base are obtained from one battery by using higher resistance R_1 than resistance R_2 [Fig. 5.30 (a) & (b)].

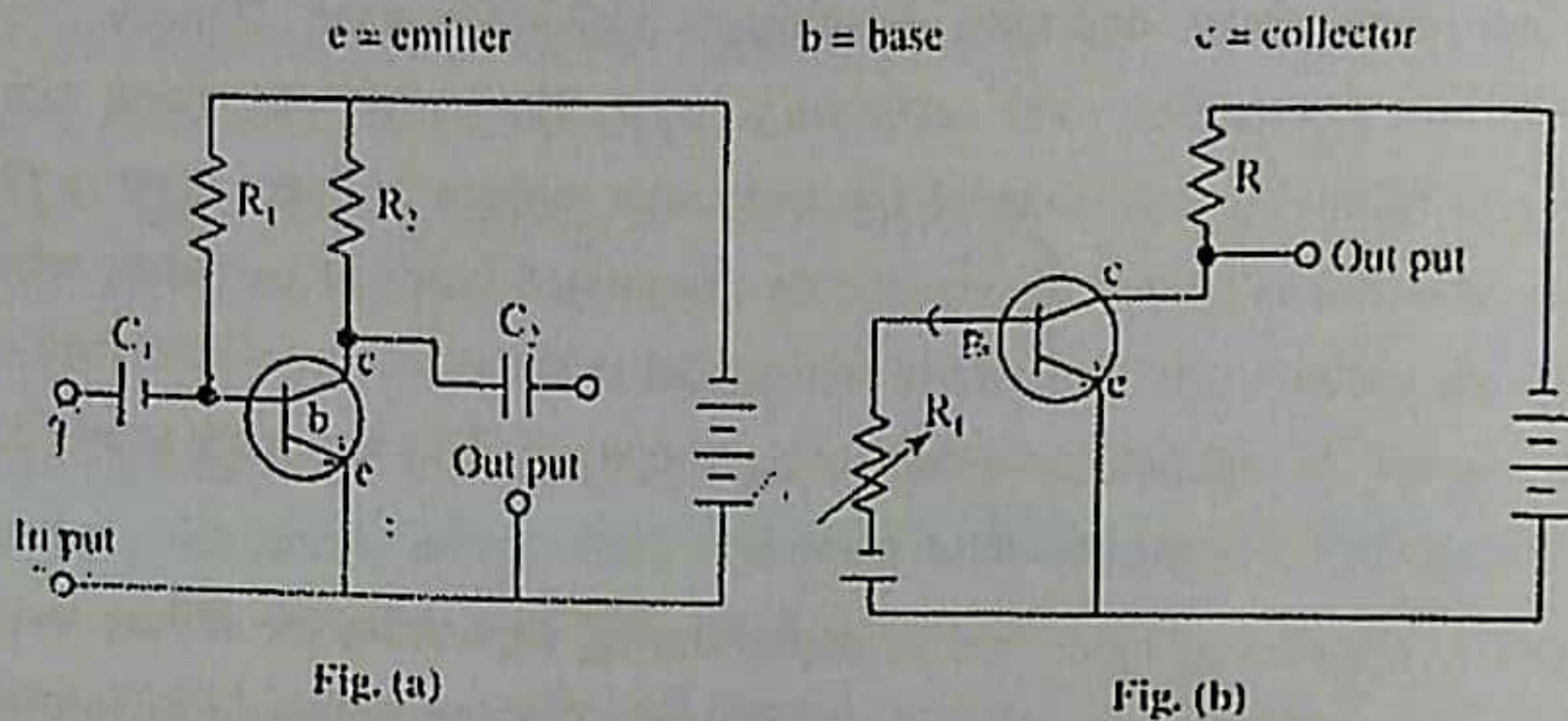
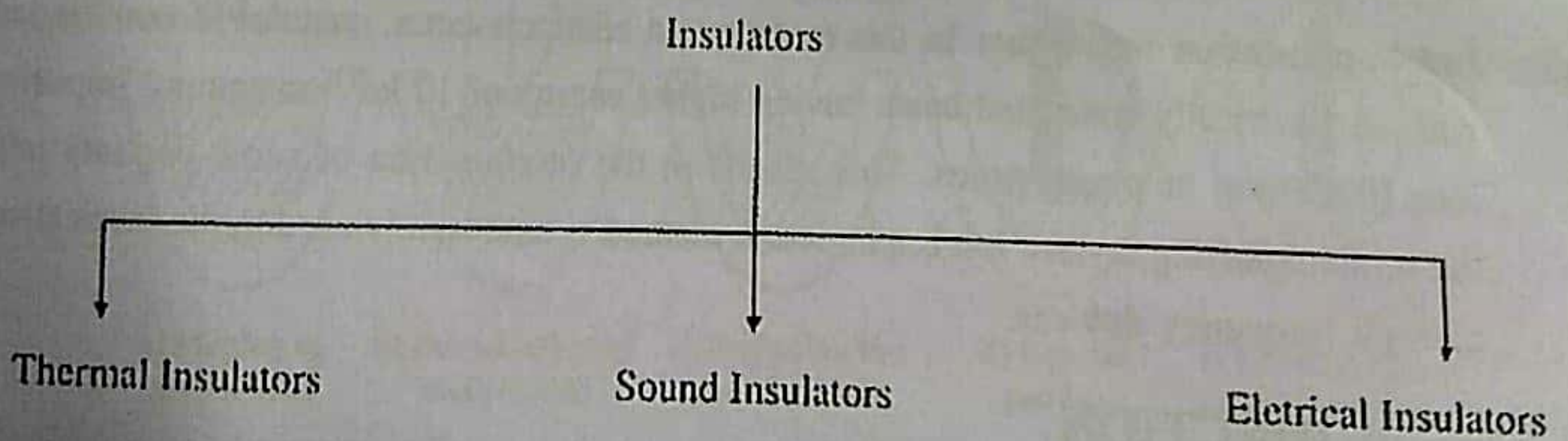


Fig. 5.30 Common emitter amplifier circuits

5.10 INSULATORS

The substances which are capable of retarding or prohibiting the flow of heat or electricity or sound through them are known as Insulators or Insulating materials.

Insulators can be broadly classified into 3 categories



5.10.1 Electrical Insulators or Dielectrics

The materials which are used to prevent the loss of electricity through certain parts in an electrical system are known as electrical insulating materials or dielectrics. These materials

apart from acting as electrical insulators can also store electric charge. Hence these materials have two functions i.e., insulation and storage of charge.

5.10.2 Characteristics of Electrical Insulators

a) A good electrical insulator possesses low electrical conductivity or high resistivity. Resistivities of insulators range between 10^9 to 10^{20} ohm-cm at room temperature.

b) A good insulating material should have a low dielectric constant. Dielectric constant is the capacity or ability of a material to store charge. However, a high dielectric constant is desirable for dielectrics used in capacitors, since a greater amount of energy can be stored in relatively thin insulation. Dielectric constant is expressed as the ratio of the capacitance of a capacitor containing the dielectric material to the capacitance of the same capacitor with vacuum as the dielectric. Thus

$$\epsilon = C / C_0$$

where, ϵ = dielectric constant

C = capacitance of the system with the material inserted

C_0 = capacitance of the system with vacuum between the capacitor plates.

c) Dielectric strength is the ability of the insulating material to resist puncture or rupture due to electrical field intensity. It is commonly expressed in volts per mm thickness of the material. Dielectric strength depends upon the thickness of an insulating material and on the length of time during which the voltage is applied. An increase in thickness increases the necessary breakdown strength. Further moisture, elevated temperature, ageing and mechanical stresses usually tend to decrease the dielectric strength of the material.

d) Dielectric losses of an insulating material may be caused by

i) the absorption of electrical energy and

ii) leakage of current through the material

This is due to the fact that

i) the absorption of electrical energy, under an alternating field gives rise to dissipation of the electrical energy in the insulating material.

ii) the leakage of current through the insulating material takes place as a result of conduction, specially at higher temperatures.

Hence an ideal insulator should have minimum dielectric losses.

e) Dielectric materials should have low porosity. This is due to the fact that high porosity increases the moisture holding capacity, which adversely affects the electrical properties.

f) Insulators used must resist the heat as well as temperatures encountered. Hence an ideal insulator should have least thermal expansion and contraction.

g) Good insulating materials should be chemically inert to acids, alkalies, oils, solvents, moisture, gas fumes etc.

h) Due to continued working at elevated temperatures, certain insulators become weak and less serviceable, particularly in contact with oxygen or air of the surroundings. This phenomenon is called thermal ageing of an insulator.

5.10.3 Classification of Insulators

According to the American Institute of Electrical Engineers all insulating materials are divided into three classes according to their constitutions. They are :

- a. Gaseous insulators
- b. Liquid insulating materials and
- c. Solid insulating materials

5.10.4 Important Electrical Insulating Materials and their Applications

a) Gaseous insulators :

Dielectric gases are used both as insulants and heat transfer mediums. The major problem associated with them are abnormalities in dielectric behaviour at high pressures, temperature instability, and fire hazards. Taking into consideration the dielectric strength, dielectric loss, chemical stability, corrosion resistance etc., they may be classified as follows :

Table - 3 : Insulating Materials and their Applications

<i>Insulator</i>	<i>Properties</i>	<i>Engg. Applications</i>
1. Simple gases i) Air	Most important of all dielectric gases. It acts as a reliable insulating material when voltages are not very high. However oxygen in air causes oxidation, which reduces the life of an electrical equipment.	It provides insulation between overhead transmission lines without any cost.

<p>ii) Nitrogen</p>	<p>It is a chemically inert dielectric.</p>	<p>Used in transformers to replace harmful oxidising atmosphere. Nitrogen under high pressure is used as dielectric in certain types of electrical capacitors.</p>
<p>iii) Hydrogen</p>	<p>It is of special interest due to its lightness and coolant property. Organic insulations in contact with hydrogen are less susceptible to ageing because there is no oxidizing effect.</p>	<p>Used as a coolant in electrical machines like large turbogenerators, synchronous condensers etc.</p>
<p>iv) Carbondioxide</p>	<p>The dielectric strength of CO_2 is comparable with that of air.</p>	<p>CO_2 is used as an insulant in certain types of fixed capacitors and is also used as a pre-impregnant for oil filled high voltage apparatus such as cables and transformers.</p>
<p>2. Electronegative gases like SF_6 and CCl_4</p>	<p>They have high dielectric strength as compared to N_2 and air. For eg : the dielectric strength of sulphur hexafluoride(SF_6) is 2.35 times and of carbon tetrachloride (CCl_4) is 6.33 times that of air. These gases are also non-inflammable and non-explosive. SF_6 is non toxic,stable when heated upto 800°C. However presence of sulphur in SF_6 molecule yields corrosion effects under some conditions.</p>	<p>SF_6 is used in electrical devices like capacitors, cables etc.</p>

b) **Liquid insulating materials :**

Insulating liquids are used for purely dielectric purposes in order to eliminate air or other gases, or as an insulating and heat transfer medium. Usually liquid insulants are used in conjunction with solid insulants. These can be broadly classified as follows :

<i>Insulator</i>	<i>Properties</i>	<i>Application</i>
<p>i) Mineral oils</p>	<p>These are obtained from crude petroleum. Their electrical properties and resistance to thermal oxidation are greatly influenced by the presence of non-hydrocarbon compounds, oxygen, sulphur, nitrogen etc. These are used in the temperature range of -50°C to 110°C.</p>	<p>They find extensive applications as insulating oils in cables, capacitors, transformers, switch gears etc.</p>
<p>ii) Askarels</p>	<p>These are synthetic insulating liquids which are non inflammable and which under the influence of electric arc does not decompose to produce inflammable gases. These are also used in the temperature range of -50°C to 110°C. Most widely used askarels are chlorinated hydrocarbons i.e. chlorinated diphenyl, pentachloride diphenyl, trichloro diphenyl, hexachloro diphenyl, trichloro benzene.</p> <p>Further askarels possess excellent fire resistance, high dielectric strength, dielectric</p>	<p>Askarels are used as transformer fluids. In practice, the askarels are usually used to impregnate cellulosic insulating material such as paper or pressboard etc.</p>

3. *Cork* : It possess good porosity and compressibility. Apart from good thermal resistance it also impart water resistance. It is used in lining of cold storages, bottle stoppers, refrigerators etc.
4. *Cellular rubber* : This possess large number of cellular cavities, and used for heat insulation in cold storage and refrigerators.
5. *Vermiculites* : These are mica like minerals and used as heat insulators for furnaces and used also as sound insulators.

5.11 MAGNETIC MATERIALS

Ferro and Ferri magnetism: Ferromagnetism is the basic mechanism by which certain materials such as iron form permanent magnets or attached to magnets. When compared with other types of magnetism, ferromagnetism is the strongest type, produces forces strong enough to be felt. Common example of ferromagnetism is a refrigerator magnet used to hold notes on a refrigerator door. These materials that can be magnetized by an external magnetic field and remain magnetized after external field is removed are permanent magnets which are either ferro magnetic or ferri magnetic. Only few substances are ferro magnetic. Common examples are iron, nickel, cobalt and their most of alloys. lodestone is naturally occurring mineral that is magnetic. The term ferro magnetism was used for any material that could exhibit spontaneous magnetism, a net magnetic moment in the absence of an external magnetic field.

5.11.1 Origin of Magnetism

One of the fundamental property of an electron is that it has a magnetic dipole moment. i.e., it behaves like a tiny magnet. This dipole moment comes from the quantum mechanical spin of electrons. The spin of an electron can be in one or only two states with magnetic field either pointing up or down. The spin of the electrons in atoms is the main source of ferro magnetism along with the contribution from the orbital angular momentum of the electrons about the nucleus. When all these magnetic dipoles in a piece of matter are aligned (pointing in the same direction). Their individually tiny magnetic fields add together to create much larger.

5.11.2 Classes of Magnetic Materials

Origin of magnetism lies in the orbital and spin motions and how electrons interact with one another. The best way to introduce the different types of magnetism is to describe how materials respond to magnetic field. In some materials there is no collective interaction of

atomic magnetic moments, whereas in other materials there is a very strong interaction between atomic moments.

The magnetic behaviour of materials is grouped into the following type.

1. Dia magnetism
2. Para magnetism
3. Ferro magnetism
4. Ferri magnetism
5. Anti ferro magnetism

1. **Dia magnetism:** It is due to the non-cooperative behaviour of orbiting electrons when exposed to an applied magnetic field. Dia magnetic substances have all orbitals filled and no unpaired electrons. When the field is zero, magnetization is zero and they are temperature independent. Ex: quartz, calcite etc.

2. **Para magnetism:** This class of materials have some atoms or ions have net magnetic moment due to unpaired electrons in a partially filled orbitals. The magnetism is zero when the field is removed. Ex: Mont morillonite (clay), Biotite (silicate), Pyrite (sulphide).

3. **Ferro magnetism:** The atomic moments in these materials are very strong interactions, which are produced by electron exchange forces and result in parallel alignment of atomic moments. The electron exchange force is due to the relative orientation of spins of two electrons.

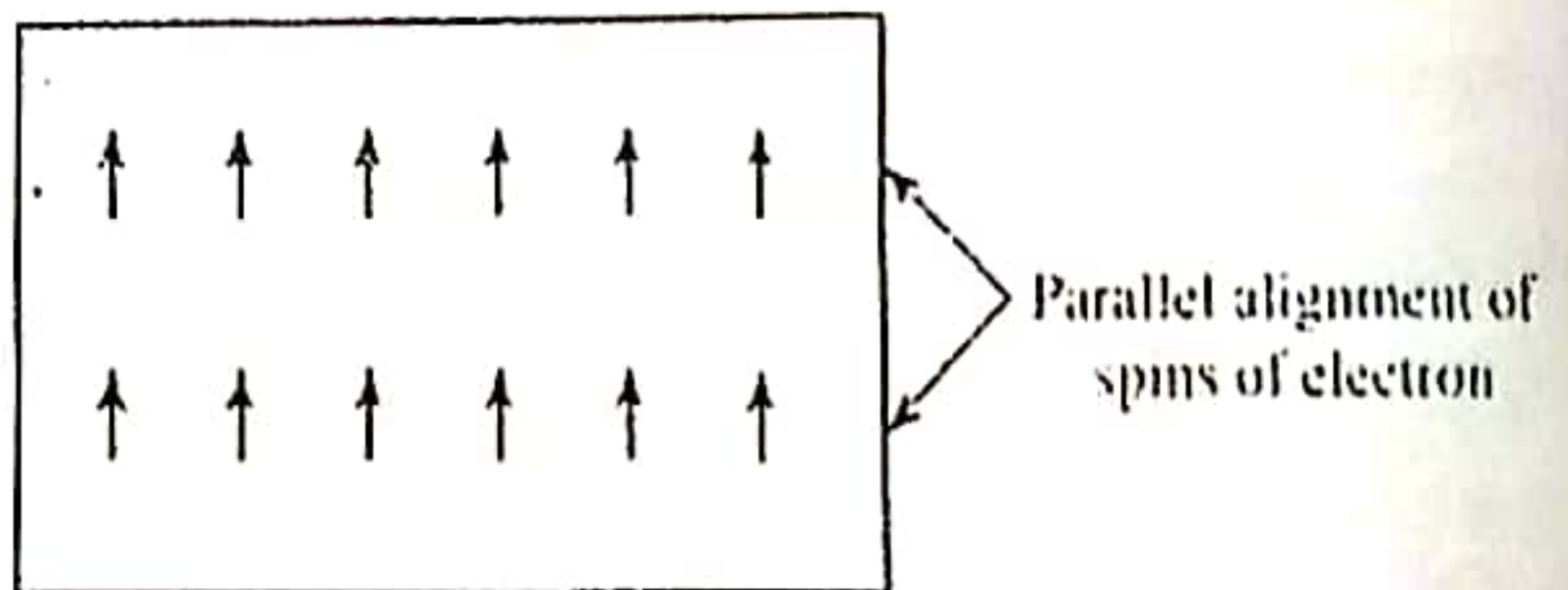


Fig. 5.31 Ferro magnetism

The distinctive characteristics are spontaneous magnetization and magnetic ordering temperature. Ex: Fe, Ni and Co

4. **Ferri magnetism:** As a result of crystalline structure of ionic compounds such as oxides, more complex magnetic ordering occurs and one type magnetic ordering is called ferri magnetism.

The magnetic structure consists of two magnetic sublattices (called A and B) separated by oxygen. The exchange interactions are carried out by oxygen anions producing super exchange interactions resulting anti parallel alignment of spin between A and B sub lattice [Fig. 5.33]. Ferri magnetism is similar to ferro magnetism in its behaviour.

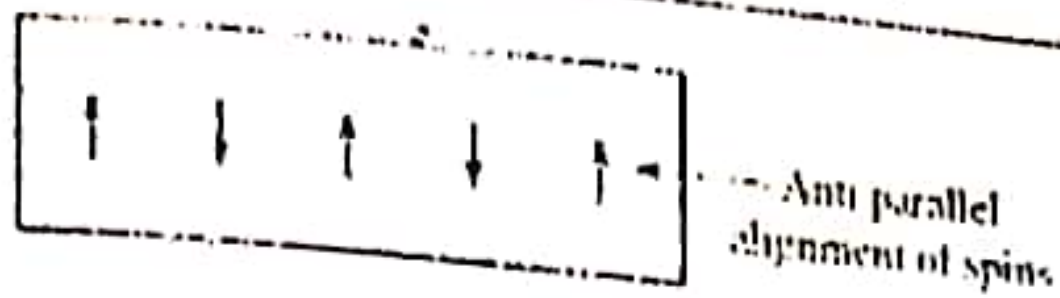


Fig. 5.32 Ferri magnetism

5. **Anti ferro magnetism:** If two sub lattices A and B have exactly opposite sub lattice moments, where the net moment is zero, it is called anti ferro magnetism. Eg: Haematite
The anti parallel alignment of electrons is shown in Fig. 5.33

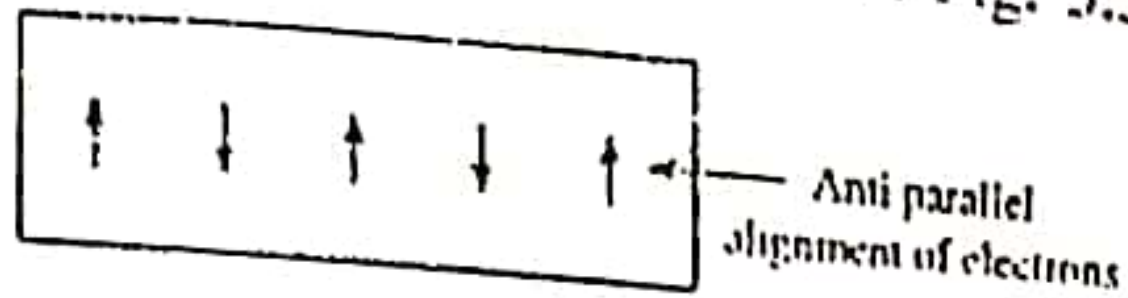


Fig. 5.33 Anti ferro magnetism

The following are the magnetic properties of minerals

Magnetic properties of minerals

S. No.	Minerals	Composition	Magnetic order	T_c °C
1	Magnetite	Fe_3O_4	Ferri magnetic	575 - 585 °C
2	Haematite	Fe_2O_3	Anti ferro magnetism	675 °C
3	Jacobsite	$MnFe_2O_4$	Ferri magnetic	600 °C
4	Magnesio ferrite	$MgFe_2O_4$	Ferri magnetic	440 °C
5	Troilite	FeS	Anti ferro magnetic	305 °C
6	Iron	Fe	Ferro magnetic	770 °C
7	Nickel	Ni	Ferro magnetic	358 °C
8	Cobalt	Co	Ferro magnetic	1131 °C
9	Wairauite	$CoFe$	Ferro magnetic	986 °C

5.11.3 Ordering of Magnetic Ions in Ferri Magnetic Lattice

The figure 5.34 shows the ordering of magnetic ions in a ferri magnetic lattice with arrows pointing down being longer than those pointing up to indicate the relative size of the spin - up and spin - down moments. The result is a net magnetic moment in the down spin direction.

The anti parallel magnetic moments in both ferri magnetic and anti ferro magnetic materials can be explained by the super exchange behaviour that occurs in oxide materials. Using MnO as an example, in its crystal oxygen ions O^{2-} sit between manganese ions Mn^{2+} as shown schematically in figure 5.35.

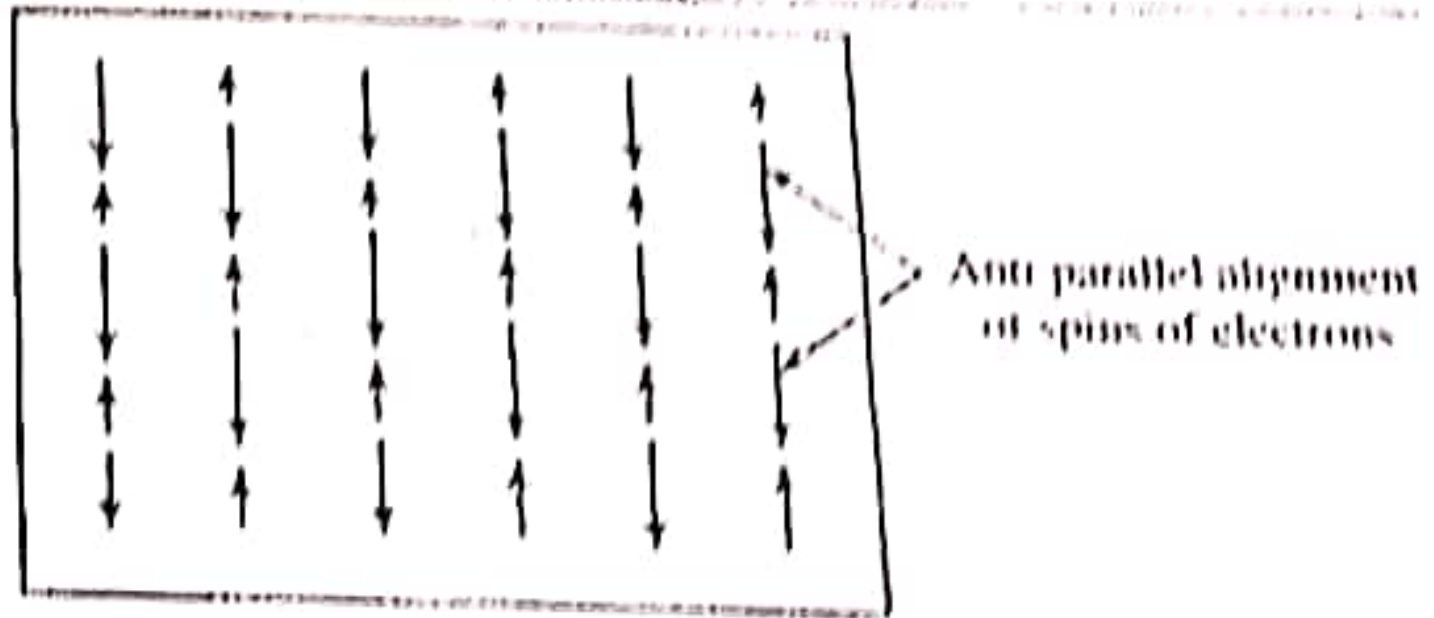


Fig. 7.34 Magnetic ordering in a ferri magnetic material

Due to the different energy levels of the Mn and O orbitals, and for the bonding between the two to occur, the spin direction of one electron in Mn^{2+} is flipped to match that of electron in the oxygen ion, thus forcing magnetic moments on either side of the molecule to be anti parallel to each other.

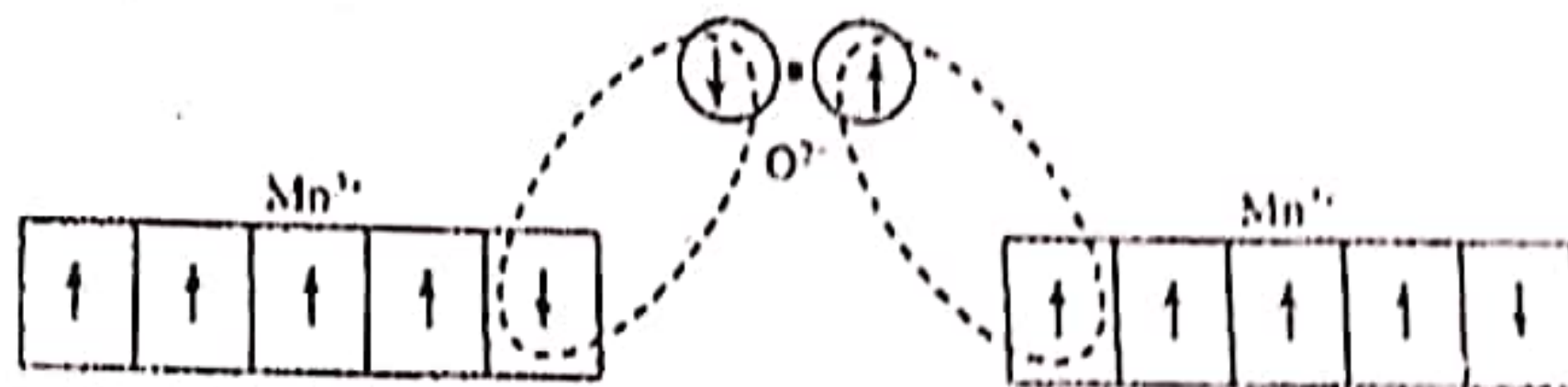


Fig. 5.35

- a) Initial transition of super exchange behaviour in MnO where the magnetic moment of one electron of the left side Mn^{2+} is flipped due to the down spin of the electron in the outer most orbital of the O^{2-} ion to which it bonds.

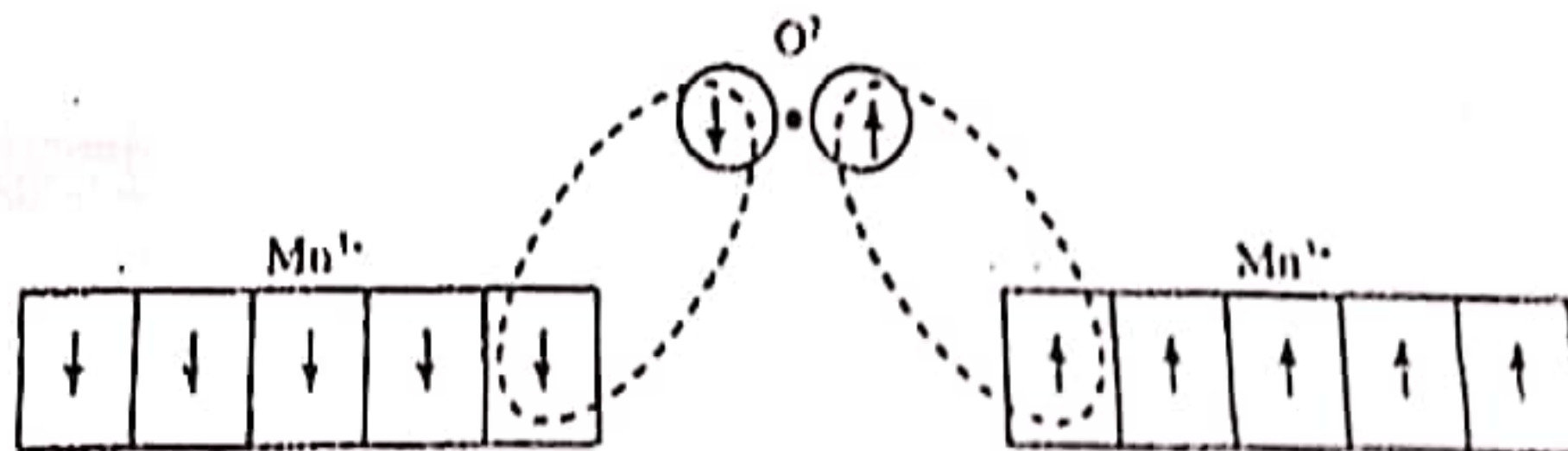


Fig. 5.36 Super exchange behaviour

- b) The result of super exchange behaviour, the e^- in Mn are rotated to be anti parallel to the right side of Mn^{2+} to match the spins of the bonding orbitals of the O^{2-} ion macroscopic field. Only atoms with partial filled shells can have a net magnetic moment. These unpaired dipoles simply called spins tend to align parallel to an external magnetic field produces an effect called para magnetism. The dipoles tends to align spontaneously, giving rise to spontaneous magnetism.

Most ferrites are ferri magnetic and like ferro magnetism ferri magnets retain their magnetization in the absence of a magnetic field is strong.

Applications: Ferro magnetism is very important in industry and modern technology and is the basis for many electrical and electro chemical devices such as electro magnets, electric motors, generators, transformer and magnetic storage such as tape recorders and hand discs.

5.11.4 Ferri Magnetism

Ferri magnetism is considered as a combination of ferro magnetism and anti ferro magnetism because of many similarities between them. Ferri magnets exhibit spontaneous magnetic moment (i.e., a magnetic moment even in the absence of magnetic field).

Ferri magnetic materials are differentiated from ferro magnetic and anti ferro magnetic materials by arrangement of their magnetic moments. The most widely used ferri magnetic materials are ferrites with general formula $MOFe_2O_4$, where M is a divalent ion such as Mn^{2+} , Fe^{2+} , Co^{2+} or Ni^{2+} .

Ferri magnetic materials contain magnetic moment aligned antiparallel to one another as illustrated in the (Fig. 5.36), similar to antiferromagnetic materials. However instead of having zero net magnetic moment, different numbers of unpaired electrons in the component transition metals do not cancel out one another resulting in a spontaneous magnetization.

Hence the ordering of spins of different types of magnetism can be summarised as follows.

Ferro magnetic

↑ ↑ ↑ ↑ ↑ ↑ ↑ → Below T_C spins are aligned parallel in magnetic domains

Anti ferro magnetic

↑ ↓ ↑ ↓ ↑ ↓ ↑ → Below T_C spins are aligned anti parallel in magnetic domains

Ferri magnetic

↑ ↓ ↑ ↓ ↑ ↓ ↑ → Below T_C spins are aligned anti parallel but do not cancel

Para magnetic

↑ ↓ ↑ ↑ ↓ ↑ ↓ → Spins are randomly oriented

5.12 HALL EFFECT AND ITS APPLICATIONS

Hall effect is the production of a voltage difference across the electrical conductor, transverse to an electric current in the conductor and a magnetic field perpendicular to the current. It was discovered by Edwin Hall in 1879.

When a current carrying semiconductor is kept in a magnetic field the charge carriers of the semiconductor experience a force in a direction perpendicular to both the magnetic field and the current. At equilibrium a voltage appears at the semiconductor edges. The simple formula for the Hall coefficient given above becomes more complex in semiconductors, where the carriers are generally both electrons and holes which may be present in different concentration and have different mobilities. For moderate magnetic fields the

$$\text{Hall coefficient is } R_H = \frac{p\mu_h^2 - n\mu_e^2}{e(p\mu_h + n\mu_e)^2}$$

or equivalently

$$R_H = \frac{(p - nb^2)}{e(p + nb)^2}$$

$$\text{with } b = \frac{\mu_e}{\mu_h}$$

Where n is the electron concentration, p = the hole concentration

μ_e = the electron mobility

μ_h = the hole mobility and e = elementary charge

For large applied fields the simple expression analogous to that for a single carrier type holds.

Applications:

1. Hall probes are used as magnetometers to measure magnetic field.
2. Hall effect devices suitable for laboratory instruments.
3. Hall effect sensors have mass application and analog - to - digital converters.
4. A Hall effect thruster is used in space craft application.
5. Industrially Hall effect joysticks are used to control hydraulic valves, scissor lifts, cranes mining trucks etc.

4.1 NANO MATERIALS

The materials like metals, ceramics, polymeric materials or composite materials with dimensions and tolerances in the range of 1 nm to 100 nm are called nanomaterials. A nanometer (nm) is one billionth (10^{-9}) of a meter is a unit of measurement. One meter is equal to 39 inches or 3 feet, $\frac{1}{100}$ of a meter is called centimeter (cm), $\frac{1}{1000}$ of a meter is called millimeter (mm), $\frac{1}{10,00,000}$ of a meter is called micron or micrometer, which is a scale of most integrated circuits and microelectromechanical systems. $\frac{1}{100,00,00,000}$ of a meter (one billionth of a meter) is called nanometer (nm) which is a scale of size of a single small molecules.

Nanometer is used to measure the objects which are very small in size. For eg. the size of hydrogen atom is 0.1 nm, water molecule is less than one nanometer, RBC is 5000 nm and human hair is 50,000 nm. The limit of human eye's visibility is 10,000 nm. The diameter of a carbon nanotube is 1.3 nm.

The significance of nanomaterials is due to their small size. They exhibit unique properties (different from those observed in bulk materials) like melting point reactivity, reaction rates, electrical conductivity, colour, transparency etc. Nanomaterials may be biological, inorganic or organic by their origin. A nanoparticle is defined as a small object that behaves as a whole unit in terms of its transport and properties and exhibit a number of special properties relative to bulk materials.

4.1.1 General Methods of Preparation

There are basically two major types of approach for the preparation of nanomaterials.

1. **Top-down approach:** In this method bulk materials are converted to powder and then to nanoparticles by making use of lithographic methods. This method is used in the microelectronic industry.

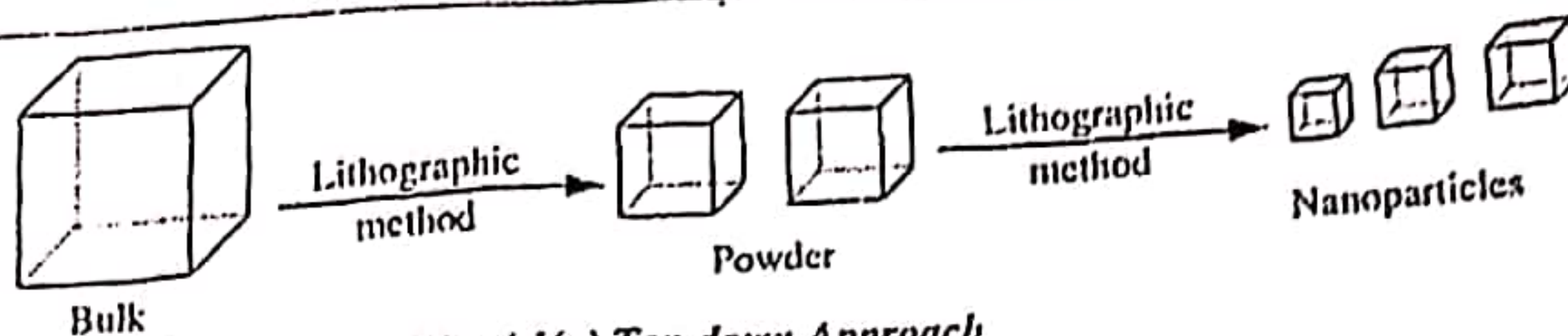


Fig. 4.1(a) Top-down Approach

2. **Bottom up approach:** In this method very small particles like individual molecules or atoms are assembled to get clusters which in turn are aggregated to get nanoparticles. This method is used to prepare a new class of nanomaterials. Eg: Fullerenes and polymer nano composites are prepared by this method.

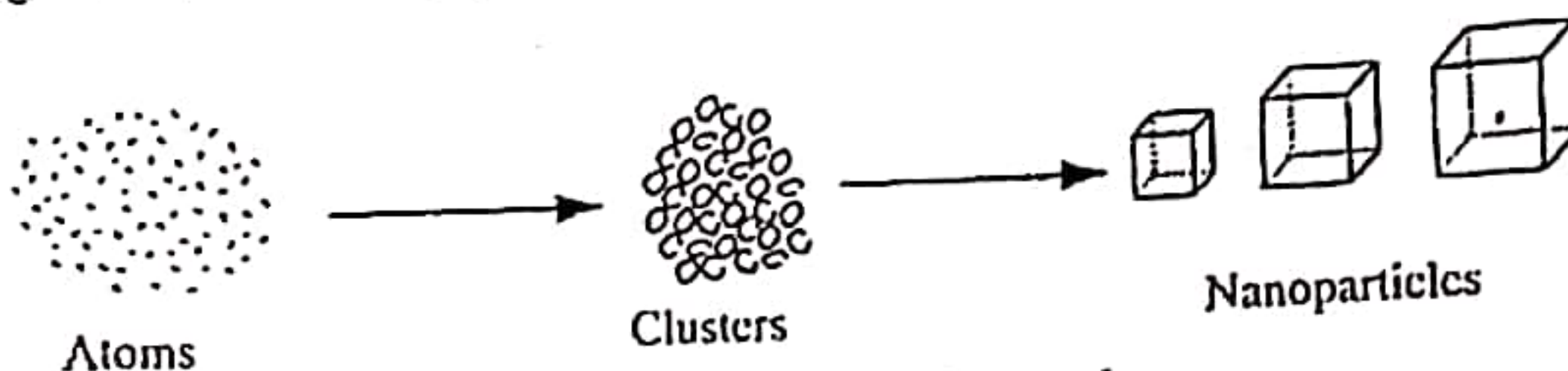


Fig. 4.1(b) Bottom up Approach

4.1.1.2 Sol-gel method

Sol-gel preparation is bottom-up approach for the synthesis of nano materials and it is very long known since 1980s. The versatility of this technic has been rediscovered in the early 1970s when glasses were produced without high temperature melting processes. A sol is a colloidal or molecular suspension of solid particles of ions in a solvent. A gel is a semi-rigid mass that forms when the solvent from sol begins to evaporate and particles or ions left behind begin to join together in a continuous network. Sol-gel processing is wet chemical technic that uses a sol to produce an integrated network i.e., gel. Metal oxides or metal chlorides undergo hydrolysis and polycondensation reactions to form a colloid which is a system composed of nano particles dispersed in a solvent. The solvent evolves towards the formation of an inorganic continuous network containing a liquid phase (gel). Formation of a metal oxide involves connecting the metal centers with oxo (M-O-M) or hydroxo (M-OH-M) bridges generating metal-oxo or metal-hydroxo polymers in the solution. After a drying process the liquid phase is removed from the gel and calcination is performed in order to enhance the mechanical properties. Alcohol is used as a solvent.

Advantages of sol-gel method: 1. Able to get uniform and small size powder. 2. Can get new microstructure and composition at low temperatures. 3. Can produce uniform multi component systems. 4. Better control over the reactions.

4.1.1.3 Chemical reduction method

This method also belongs to bottom-up approach. Metal nano particles particularly silver nanoparticles are prepared by this method.

Preparation of silver nanoparticles:

For the preparation of silver nanoparticles silver nitrate solution (from 1 ppm to 6 ppm) and 8% w/w sodium dodecyl sulphate (SDS) are used as metal salt precursor and metal stabilizing agent respectively. Hydrazine hydrate (2-12 ppm) and citrate solution (1 ppm) are used as reducing agents. The transparent colorless solution will be converted to pale yellow and pale red colour which indicates the formation of silver nanoparticles. To remove the excess silver ions the solution is washed with deionizer water under nitrogen stream for three times. The nanoparticles are purified by centrifugation. A dried powder of nano silver is obtained by freeze drying. The nano particles are characterized by UV and X-Ray crystallography.

General preparation is carried out by mixing the metal salts with phase transfer agents and reducing reagents. Different types of phase transfer reagents are used for the preparation of different metal nanoparticles.

Metal salt solution + metal salt precursor + stabilizer + reducing agent → stand for sometime → nanoparticles separate → purification → centrifugation → freeze drying → metal nanoparticles.

Applications:

Nanoparticles like silver, gold, platinum etc., are prepared by this method.

4.1.1.4 Brunauer-Emmett-Teller (BET) method

Nano crystalline particles of $\text{Co}_x\text{Fe}_{(3-x)}\text{O}_4$ are synthesized by combustion reaction method using iron nitrate, cobalt nitrates and urea with Asa's fuel without template and subsequent heat treatment. The process is simple and inexpensive since it does not involve intermediate decomposition or calcination steps. The maximum reaction temperature range 850-1010 Degree centigrade and combustion lasts for 30 seconds for all systems. The materials are washed with deionised water and the byproducts are rinsed off producing pure nanoparticles.

4.1.1.5 Transmission Electron Microscopic (TEM) method

This is a shape controlled method for the synthesis of colloidal platinum nanoparticles which is potentially important in the field of catalysis. Catalytic reactivity depends on size and shape of the particles. A solution of potassium platinum chloride (0.00001M) is prepared

in water and treated with 0.2 ml of 0.1M sodium polyacrylate. The resulting solution is bubbled with Ar gas for 20 min. The Pt ions are reduced by bubbling hydrogen gas for 5 min. The reaction vessel is sealed and left overnight. The solution turns light golden and nanoparticles are purified and separated.

4.1.2 Properties of Nanomaterials

Nanoparticles are specific in their behaviour because the physical behaviour of particles change with decreasing size of the particle. The particles are always aggregated due to high energetic adhesive forces close to the surface, hence the surface of a nanoparticle is never naked.

The following are some of the important properties of nanomaterials.

1. Properties based on size of the particles:

By varying the size of the material, properties like melting point, solubility, colour, transparency and catalytic behaviour of nanomaterials vary. Let us consider a material which is not nanomaterial exhibit ordered electronic spin on the surface and disordered electronic spin inside because the number of atoms inside is more than outside the material. When the material is reduced to smaller nanosize, the number of atoms on the surface increases when compared to number of atoms inside the material, thereby increasing the ordered electronic spins inside the nanomaterial. Nanoparticles or nanocrystals possess ordered electronic spins inside and outside the material exhibiting magnetism.

- a) The magnetic properties increase with decrease in size of the materials due to increased orderly electronic spins.
- b) Melting point of the nanomaterials increases, when compared with other material depending on the size of the particles.
- c) Solubility of nanomaterials is more than other materials due to the decreased size.
- d) Colour: The physical property colour is again size dependant. As the size of the particle decreases the colour of the material changes. For eg. bulk gold looks yellow but 12 nm nanosized gold particle looks red, due to the decreased size of the particle and intum different scattering of light.
- e) Transparency: Transparency of nanomaterials is more than the other materials due to decreased size of the particles and increased transmission of light.
- f) Catalytic behaviour: Due to increased surface area, the catalytic activity of the nanomaterials is more than other materials.

2. Properties based on composition of nanomaterials:

The composition effects of the nanomaterials influence both physical and chemical properties of nanomaterials as given below.

- a) **Colloidal properties:** The colloidal nanoparticles are called *coercing colloids*. The colloidal properties of coercing colloids is more than the colloidal solutions like optical properties, electrical, magnetic and gel properties.
- b) **Chemical reactivity:** Nanomaterials possess high chemical reactivity than other materials.
- c) **Reaction rates:** High reaction rates were observed with nanomaterials when compared with other materials.

3. Properties due to surface of nanomaterials:

The surface of nanomaterials is always agglomerated with particles due to high energetic adhesive forces due to the properties like dispersibility, conductivity, optical properties and catalytic behaviour.

- a) **Dispersibility:** The nanomaterials exhibit good dispersibility.
- b) **Conductivity:** The energy gap between the valence band and conducting band in a semiconductor is proportional to the inverse of the square of the size due to quantum confinement where the spatial domain of the electronic wave function is about the size of the nanoparticle. Hence discrete energy states exist instead of continuous energy bands as that of bulk semiconductors resulting in the absorption of wavelengths characteristic of the composition and size of the nanoparticle. The nanomaterials can be used as good conducting, semiconducting and insulating depending on the structure of nanomaterial.
- c) **Catalytic behaviour:** The nanomaterials possess very good catalytic activity due to increased surface area of contact than other materials. In crystalline particles, the place where two faces of a crystal are in contact is called edge and the place where two or more faces come together is called a point. These edges and points are the seat of pronounced catalytic activity. Because the crystalline nanoparticles contain enormous number of edges and points, their catalytic activity is maximum.

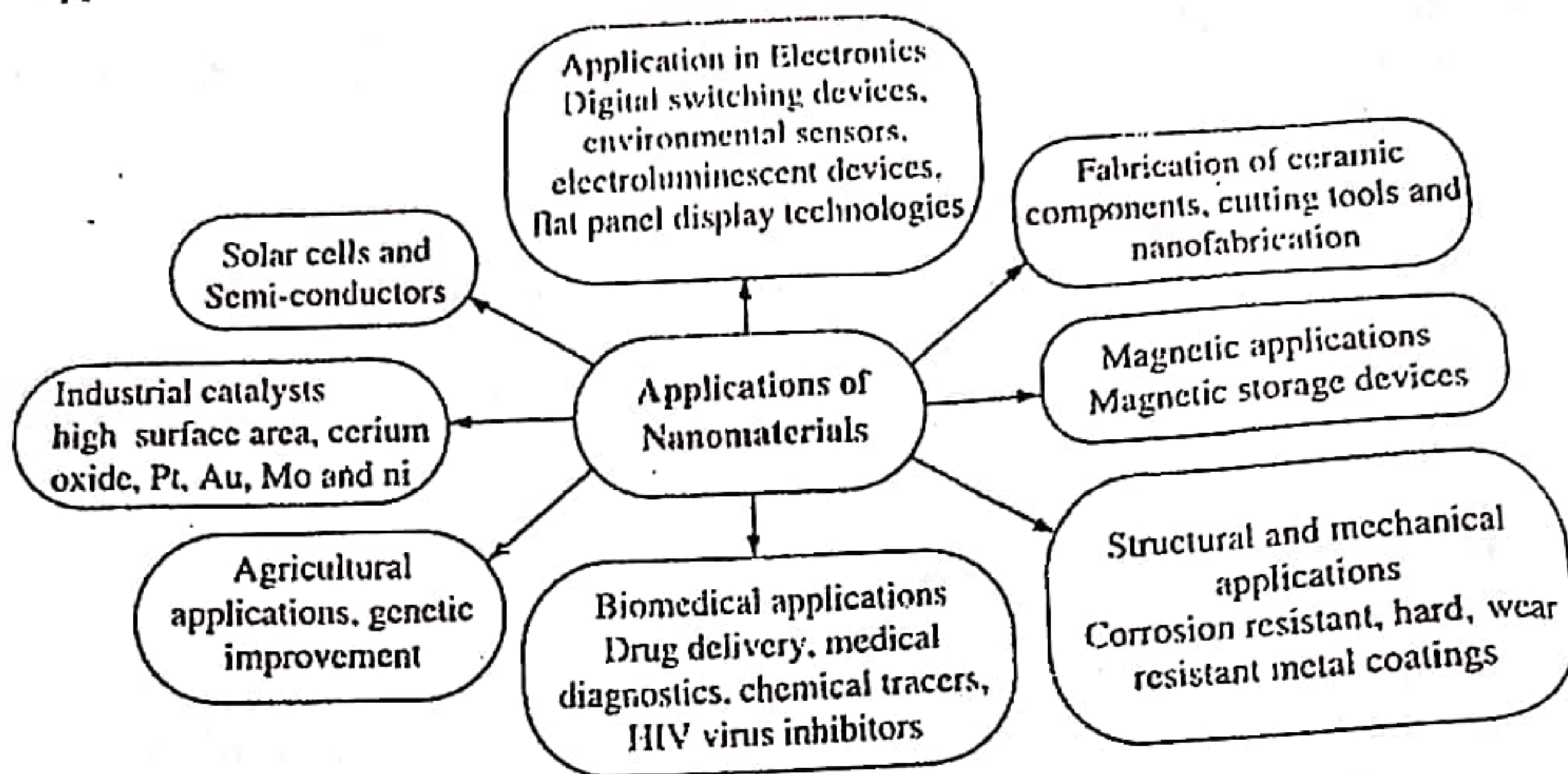
4.1.3 Engineering Applications of Nanomaterials

Nanomaterials are an emerging field of material science technology, where vast engineering applications of these nanomaterials in a wide range of fields. Some of these engineering applications are listed below.

1. **Electronics:** A variety of applications of nanomaterials in the field of electronics are there. Some of them are mentioned below.
 - a) **Commercial digital switching devices,** integrated in 10^{12} devices on a single chip are fabricated.
 - b) **High sensitivity and high selectivity environmental sensors** to sense gaseous chemicals like CO, NO, NO₂ and O₃ in high traffic environments are fabricated.

- c) The nanomaterials find good application in making light emitted electroluminescence devices, which find application in flat panel display technologies like T.V., Computer monitor, Colour changing fabrics etc.
2. **Magnetic applications:** Newly synthesised magnetic nanoparticles from iron and palladium, have been found to self-arrange automatically and these materials are extensively used in the manufacture of magnetic storage devices producing terabyte storage capabilities.
3. **Biomedical applications:** The following are the applications of nanomaterials in biomedical field.
- Drug delivery of biomedical drugs which are bounded to magnetic nanocrystals to the region of body where the drug is required is carried out. For example, rare tumour causing cells can be targeted by nanocrystals, then captured and removed from blood stream.
 - Medical diagnostics is a field which extensively use nanocrystals silica coated iron oxide nanocrystals with embedded magnetic colloidal particles are sent into bloodstream where the antibody reacts and binds with the target hormone and move rapidly which can be separated and detected from blood sample. DNA detection through colorimetric technique by using oligonucleotide functionalised gold nanocrystals is developed.
 - Structural and mechanical material applications are as follows:
 - Coating nanocrystals of metals with ceramics is carried nanostructuring by getting the benefits of ceramics (corrosion resistant, hard and wear resistant) and metals (ambient ductility). These coatings are superior coatings.
 - Fabrication of ceramic components is easier through nanostructuring. By nanoscale distribution of tungsten in the matrix containing tungsten carbide improves the life and performance of cutting tool materials.
 - Industrial catalysts should contain high surface area and capacity to make any material attach to their surface. Cerium oxide, platinum, gold, molybdenum, nickel nanoparticles are extensively used as catalysts.
 - Because of high tensile strength, light weight and flexible nature some nanomaterials like CNT (Carbon Nano Tubes) are extensively used in aircraft industry.
 - Nanomaterials like fullerenes are used extensively in making consumer goods like sports goods, cleaning products and fabrics etc.
 - Agriculture is another field where nanomaterials find their use in delivery of genes and drugs to animals for health and genetic improvement and in delivery the biodegradable chemical for plant nourishment is adopted.

Applications of Nanomaterials can be summed up as follows:



Applications of Nanomaterials

4.1.4 Fullerenes

A fullerene is any molecule composed entirely of carbon in the form of a hollow sphere, ellipsoid or tube. Spherical fullerenes are also called buckyballs as they resemble the balls used in football (soccer). Fullerenes are similar in structure to graphite which is composed of stacked graphene sheets of linked hexagonal rings, may also contain pentagonal or heptagonal.

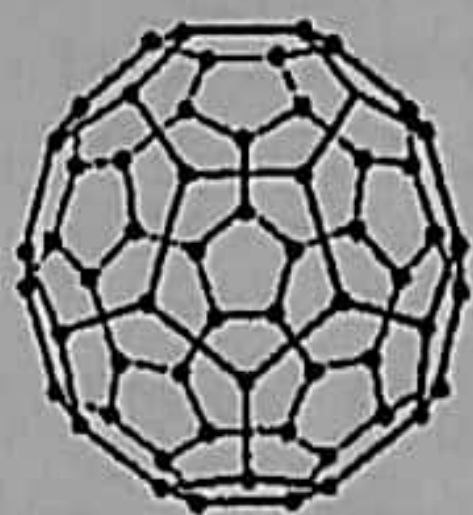
The first fullerene molecule was prepared in 1985 by Richard Smalley et al at Rice University, USA. They were awarded Noble prize in 1996 for their work. The name fullerene was given as a homage to Buckminster Fuller, whose geodesic domes the molecule resembles.

Types of fullerene:

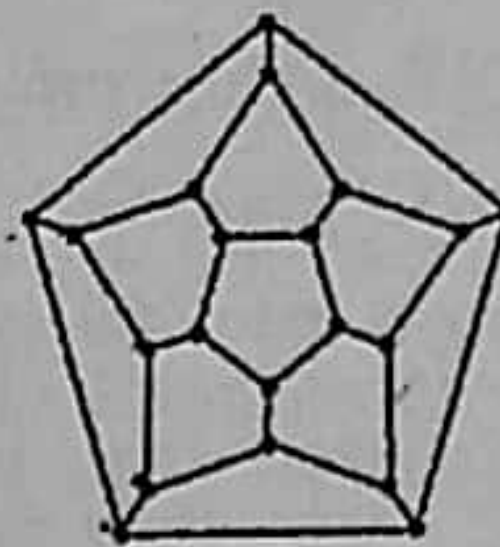
Due to structural variations fullerenes exist in the following different types.

- Buckyball clusters:** The smallest is C_{20} (unsaturated version of dodecahedrane) and most common is C_{60} .
- Carbon nanotubes:** Hollow tubes of very small dimensions having single or multiple walls. Potential applications in electronic industry.
- Megatubes:** Larger in diameter than nanotubes and prepared with walls of different thickness. Potentially used for the transport of a variety of molecules of different sizes.

- d. **Polymers:** Chain, two dimensional and three dimensional polymers are formed under high-pressure, high temperature conditions.
- e. **Nano 'onions':** Spherical particles based on multiple layers surrounding a buckball core. Proposed for lubricants.
- f. **Linked ball and chain dimers:** Two buckballs linked by a carbon chain. The different individual fullerenes based on composition is listed below.
- i. **Buckminster Fullerene** is the smallest fullerene molecule containing pentagonal and hexagonal rings (Fig. 4.2) in which two pentagons share an edge. It is naturally occurring fullerene found in soot. The structure of C_{60} is called truncated icosahedron which resembles football containing twenty hexagons and twelve pentagons with a carbon atom at the vertices of each polygon. The vander Waals diameter of C_{60} is 1.1 nm and its average bond length is 1.4Å. Silicon bucky balls have been created around metal ions.



(a) Fullerene/buckyball



(b) C_{20} fullerene (dodecahedral graph)

Fig. 4.2 Buckminster fullerene

- ii. **Boron buckyballs:** A type of buckyball which uses boron atoms instead of a carbon atom is discovered in 2007. The B_{80} structure with each atom forming 5 or 6 bonds is more stable than C_{60} buckyballs.

The smallest fullerene is dodecahedral (C_{20}).

Metallofullerenes are a class of novel nanoparticles, comprises 80 carbon atom (C_{80}) forming a sphere which encloses a complex of three metal atoms and one nitrogen atom, and they find potential use in diagnostics, therapeutics and organic solar cells.

Preparation of fullerenes:

A common method used to produce fullerenes is to send a large current between two nearby graphite electrodes in an inert atmosphere. The resulting carbon plasma arc between the electrodes cools into sooty residue from which many fullerenes can be isolated. The fullerenes are extracted from soot using multi step procedure.

Properties: Fullerenes are stable with sp^2 hybridized carbon atoms. The reactivity of fullerenes is increased by attaching active groups in their surfaces. The characteristic reaction of fullerenes is electrophilic addition at 6-6 double bonds which reduce the angle strain by

changing sp^2 hybridised carbon to sp^3 hybridised carbon. When other atoms trapped inside fullerenes to form inclusion compounds is known as endohedral fullerenes
Eg: Tb_9NeC_{60} (egg shaped fullerene).

When a metal is used as an inclusion compound it is called metallo fullerene. For eg: steel.

Solubility: Fullerenes are sparingly soluble in many solvents. Common solvents for fullerenes are toluene, CS_2 .

Quantum mechanics: Wave-particle duality is exhibited by fullerenes as a result several sculptures symbolizing wave-particle duality are created.

Chirality: Some fullerenes are inherently chiral because they are D_2 -symmetric and have been successfully resolved.

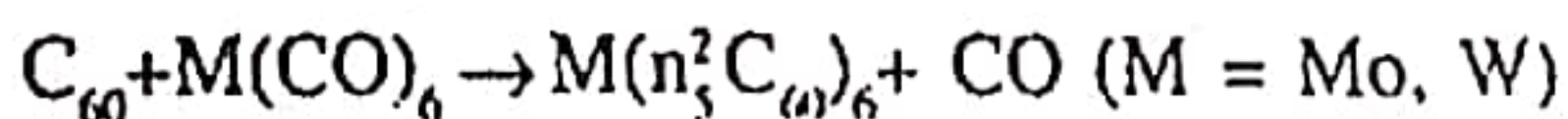
Hydrogenation: C_{60} exhibits a small degree of aromatic character, undergoes addition with hydrogen to polyhydro fullerenes.

Halogenation: Addition of F, Cl and Br occur for C_{60} under various conditions, produce a vast number of halogenated derivatives. For ex. $C_{60}Br_8$ and $C_{60}Br_{24}$.

Addition of oxygen: C_{60} can be oxygenated to epoxide $C_{60}O$ and ozonisation of C_{60} in orthoxylene at 257K gives ozonide $C_{60}O_3$ which can be decomposed into 2 forms of $C_{60}O$ and the same decomposition at 296 K gives epoxide.

Free radical reaction: When C_{60} is mixed with a disulphide, the radical $C_{60}SR$ is formed spontaneously, whose stability depends on steric factors.

Metal complexes were produced with C_{60} fullerenes by using metals Mo, W, Pa, IG and Ti.



Applications

- 1. As a fuel:** Buckyballs are efficient medium to make hydrogen fuel.
- 2. Medicine:** Buckminster fullerene inhibit the HIV virus. C_{60} inhibits a key enzyme in the human immunodeficiency virus known as HIV-1 protease which could inhibit the reproduction of HIV virus in immune cells. When impregnated with He, C_{60} buckyballs can be used as chemical tracers in human body.
- 3. Solar cells:** The optical absorption properties of C_{60} match solar spectrum, hence finds its application in solar cells.

4.2 LIQUID CRYSTALS (LCs)

(Liquid crystals (LCs) are matter in a state that has properties between those of conventional liquid and those of solid crystals) For example, a LC may flow like a liquid, but its molecules may be oriented in a crystal like way (Fig. 4.4). (There are many different types of LC phases which can be distinguished by their optical properties). (Liquid crystals can be found naturally and in technological applications) (Many proteins, cell membranes and tobacco virus are the natural LCs). (Most contemporary electronic displays, solutions of soap and various related detergents are synthetic LCs).

LC behaviour was first observed by Friedrich Reinitzer at Charles University, Prague in derivatives of cholesterol which now belong to cholesteric liquid crystals. The name 'liquid crystal' was coined by Otto Lehman in 1904. Later liquid crystals became a topic of research into the development of flat panel electronic displays to replace the cathode ray vacuum tube in televisions from 1962 onwards.

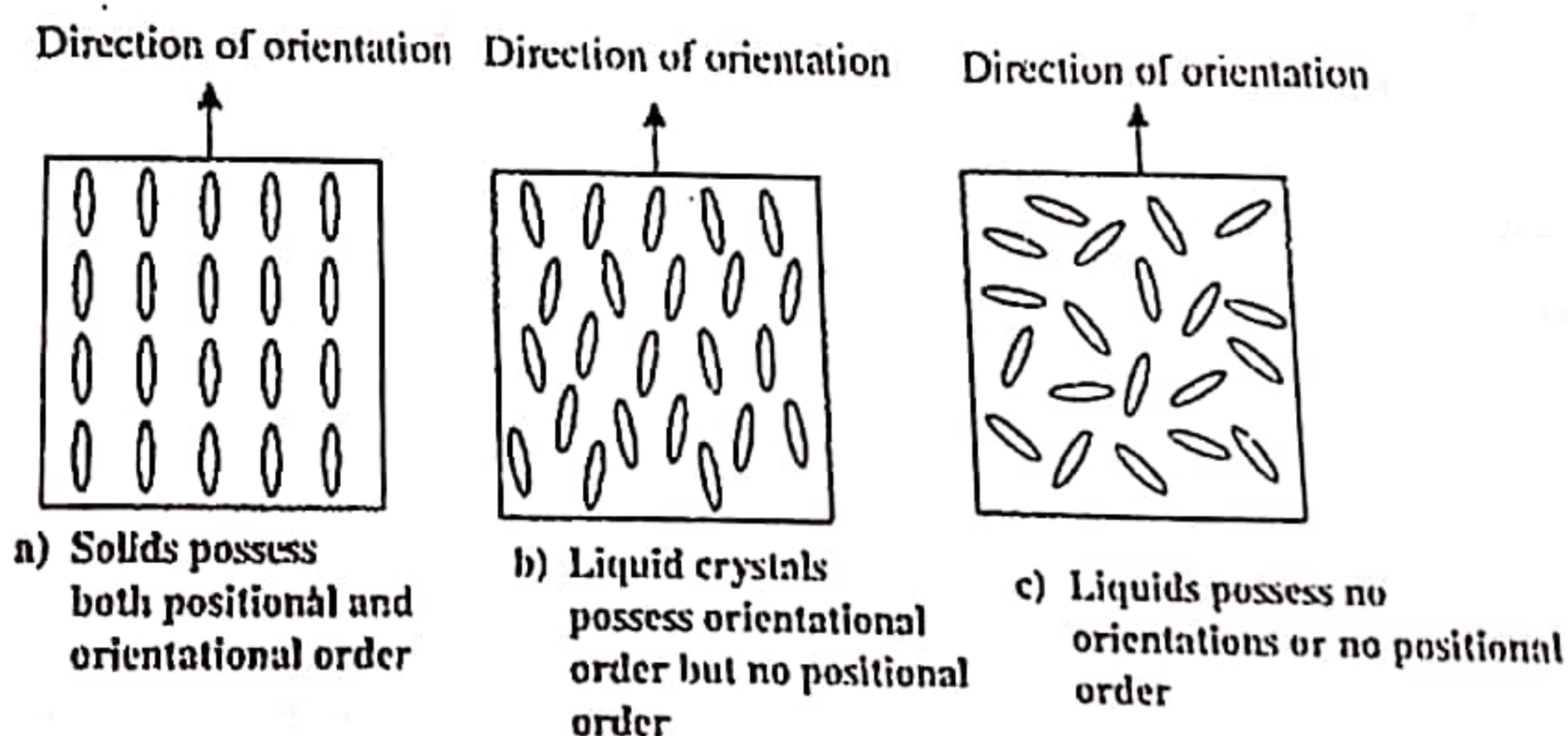


Fig. 4.4 Positional and orientational order in solids, liquid crystal and liquids

4.2.1 Types of Liquid Crystals

LCs can be divided into three types:

1. Thermotropic LCs exhibit a phase transition into LC phase as the temperature is changed.
2. Lyotropic LCs exhibit a phase transition into LC phase when both temperature and concentration of LC molecules in solvent changes.
3. Metallotropic LCs are constituted by both organic and inorganic molecules. They exhibit phase transition into LC phase when temperature, concentration, and organic-inorganic composition ratio changes.

4.2.2 Thermotropic Liquid Crystals

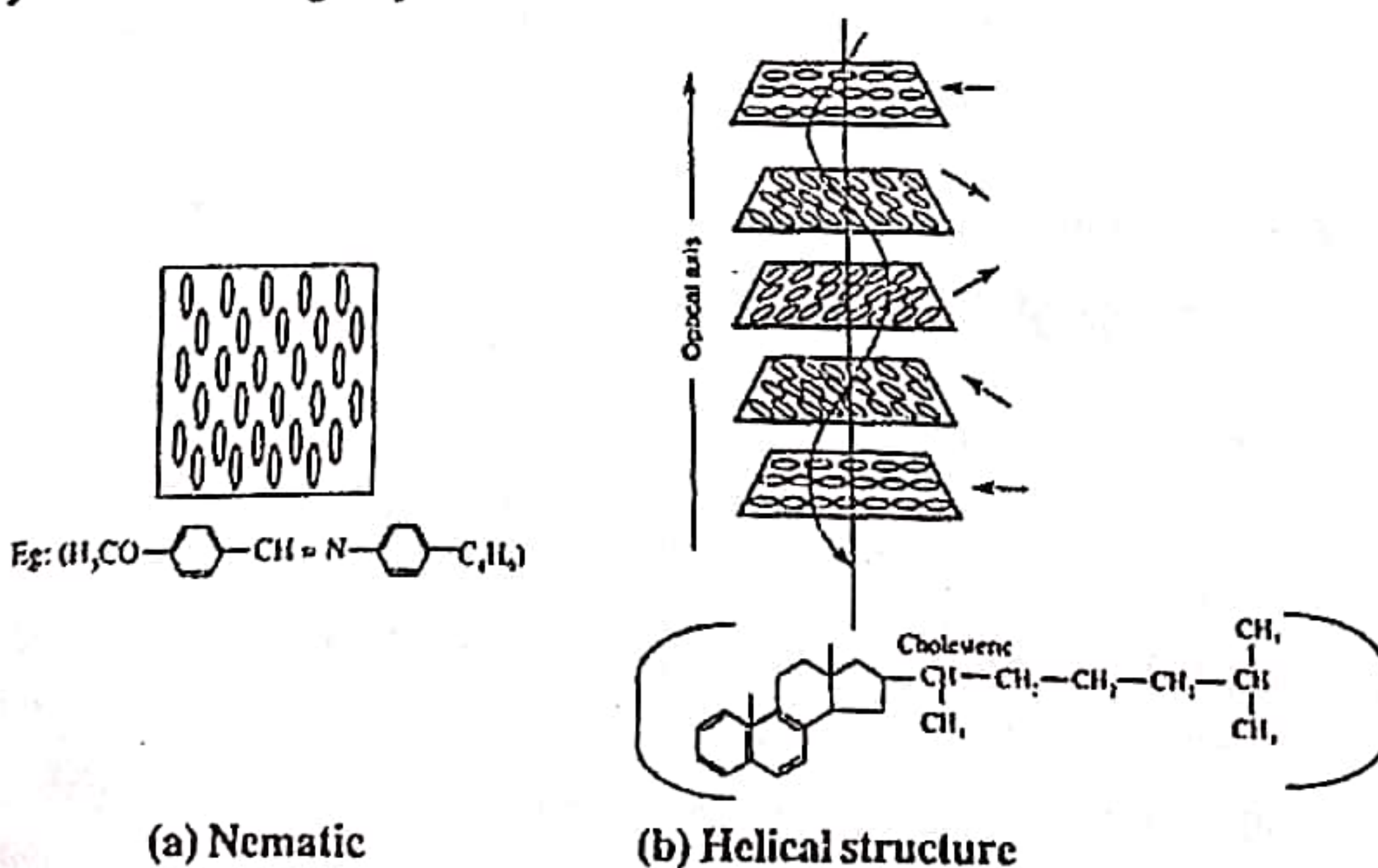
Thermotropic phases are those that occur in a certain temperature range. If temperature is too high thermal motion may destroy the ordering of LC phase; pushing the material into a conventional isotropic liquid phase. The following are some of the phases as the temperature is changed. The liquid crystalline phase of thermotropic crystals can be observed by carefully lowering or raising the temperature of liquids and solids respectively. Thermotropic liquid crystals are formed from organic molecules with rod-like shape, rigid and planar ring structures.

Examples of thermotropic liquid crystalline substances are cholesteryl benzoate, exhibit liquid crystalline state at 145.5–178.5 °C, P-azoxyanisole at 116–135 °C, and P-azoxy phenetole at 137–167 °C.

There are three distinct phases in which thermotropic crystals exist.

- a) Nematic phase
- b) Cholesteric phase
- c) Smectic phase

a) Nematic liquid phases: Nematic in Greek means thread like. Nematic liquid crystals are less ordered, they point in the same direction, characterised by the total loss of positional order and a near normal flow behaviour similar to its liquid phase with simple structure as shown below (Fig. 4.5(a)) $y-\text{C}_6\text{H}_4-x-\text{C}_6\text{H}_4-y''$ where $x = \text{azo } (-\text{N}=\text{N}-)$, azoxy $(-\text{N}=\overset{\text{O}}{\parallel}\text{N}-)$, ester $(-\overset{\text{O}}{\parallel}\text{C}-\text{O}-)$ and Schiff's bases $(-\text{CH}=\text{N}-)$. y and y'' are smaller groups.



(a) Nematic

(b) Helical structure

Fig. 4.5 Schematic representation of liquid crystals

b) **Cholesteric liquid crystals:** The name of these liquid crystals originated from the fact that many derivatives of cholesterol form this structure and the molecules are chiral. The structure of these crystals are similar to nematic liquid crystals, but each plane of the molecules is twisted slightly in relation to plane above and below. The molecules are aligned parallel to a preferred direction as in nematic phase. When proceeding in a direction normal to the plane, the preferred direction rotates continuously, the result is helical structure (Fig. 4.5(b))

c) **Smectic liquid crystals:** In Greek smectic means soap. The substances that form smectic phase are soap like. In smectic LCs there is a small amount of orientational as well as positional order. The molecules form planes perpendicular to the axes of the molecules and they tend to point along the director. There are three types of smectic phases based on the orientation of the director.

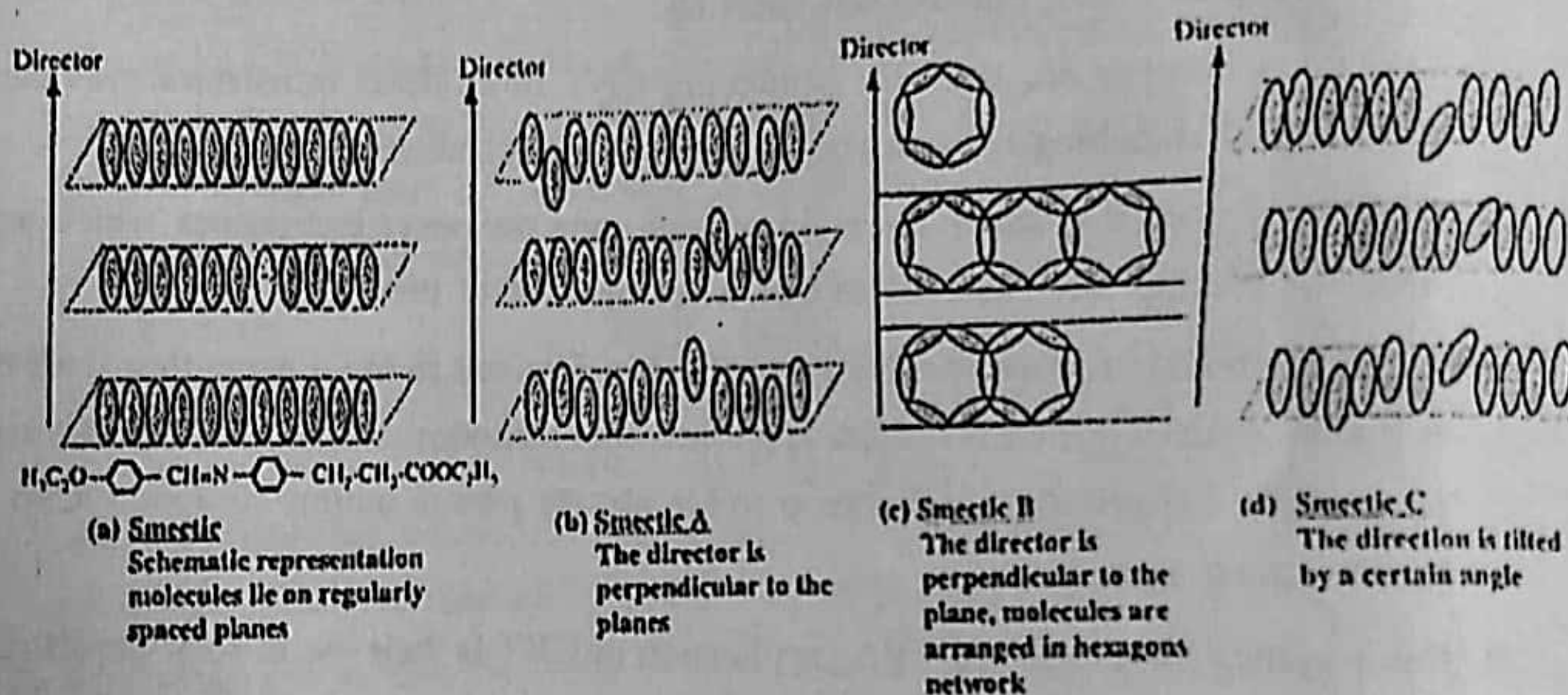


Fig. 4.6 Schematic representation of smectic mesophases

Smectic A: The long axes of the molecules are parallel to a preferred direction which may be normal to the planes. Fig. 4.6(b).

Ex: Diethyl 4, 4' - azoxydibenzoate.

Smectic B: The director is perpendicular to the smectic plane with the molecules arranging themselves into a network of hexagones within the layer Fig. 4.6(c)

Ex: N, N' - Terephthalylidene-bis-(4-n butylaniline) (TBBA)

Smectic C: The long axes of the molecules are disordered and parallel to a preferred direction which may be tilted by a certain angle. Fig. 4.6(d).

Ex: 4, 4'-di-n-dodecyloxy-azoxybenzene.

4.2.3 Lyotropic Liquid Crystals

Some compounds are transformed to a liquid crystal phase, when mixed with other substance (solvent) or when the concentration of one component is increased. Such compounds which exhibit liquid crystallinity on mixing with a solvent or changing its concentration are called lyotropic liquid crystals. Lyotropic liquid crystals are amphiphilic in nature as they contain both lyophilic (solvent attracting) and lyophobic (solvent repelling) parts in the same molecule (Fig. 4.6(a)). When treated with a solvent the lyophobic ends come closer whereas the lyophilic ends are directed away forming micelle. The micelle are formed only at a particular concentration critical micelle concentrate (CMC). Beyond CMC, when the solution is heated to a particular temperature, the size of micelle increases, collapses and separates out as a liquid crystal. Thus the solvent-solute interactions play a vital role in such systems. Lyotropic liquid crystals are two types broadly 1. Lamellar phases and 2. Hexagonal phases.

1. **Lamellar lyotropic liquid crystals:** These are characterised by layers of well defined thickness but no order within the layers (Fig. 4.7(b)) and water is sandwiched between. Lamellar phase is called neat phase or G-phase.
2. **Hexagonal lyotropic liquid crystals** possess hexagonal arrays like upforming cylinders with the water molecule by the formation of polar heads as outer shell (Fig. 4.6(c)). Sometimes inverted hexagonal phases are formed with tails point away from the centres of the hexagons.

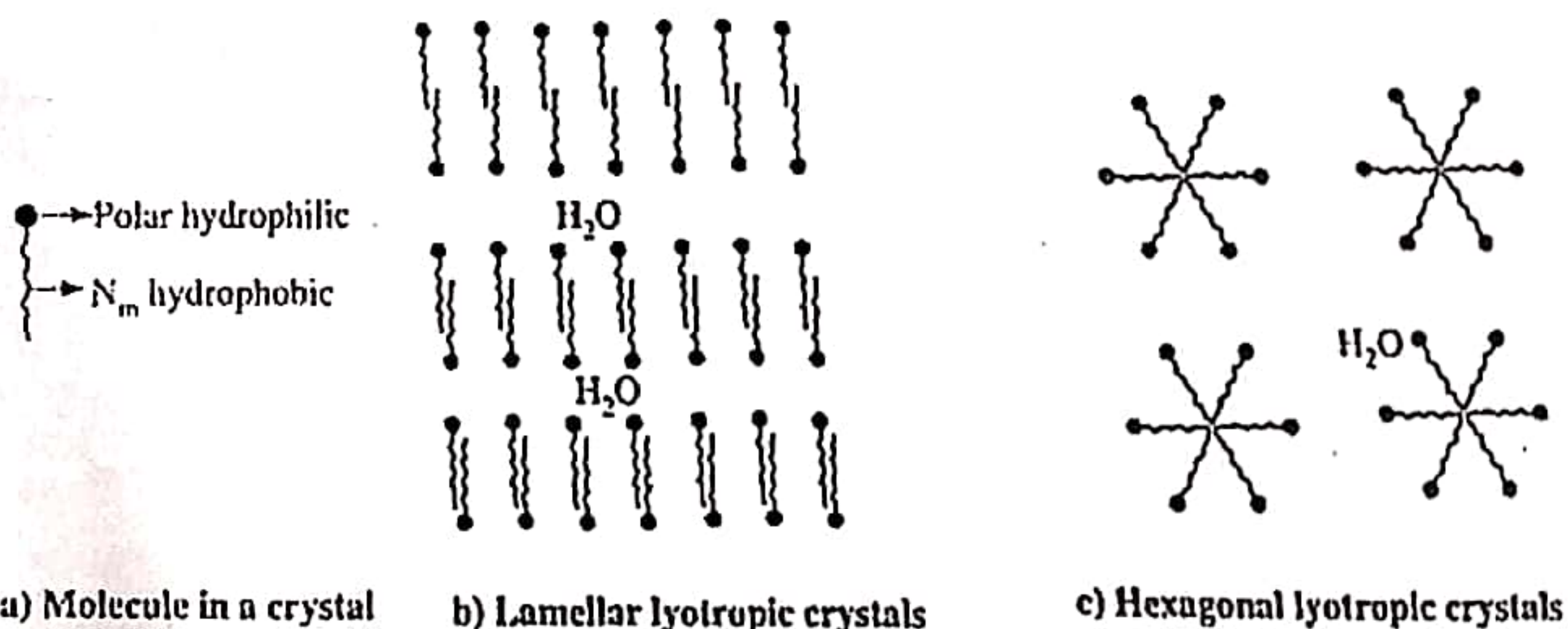
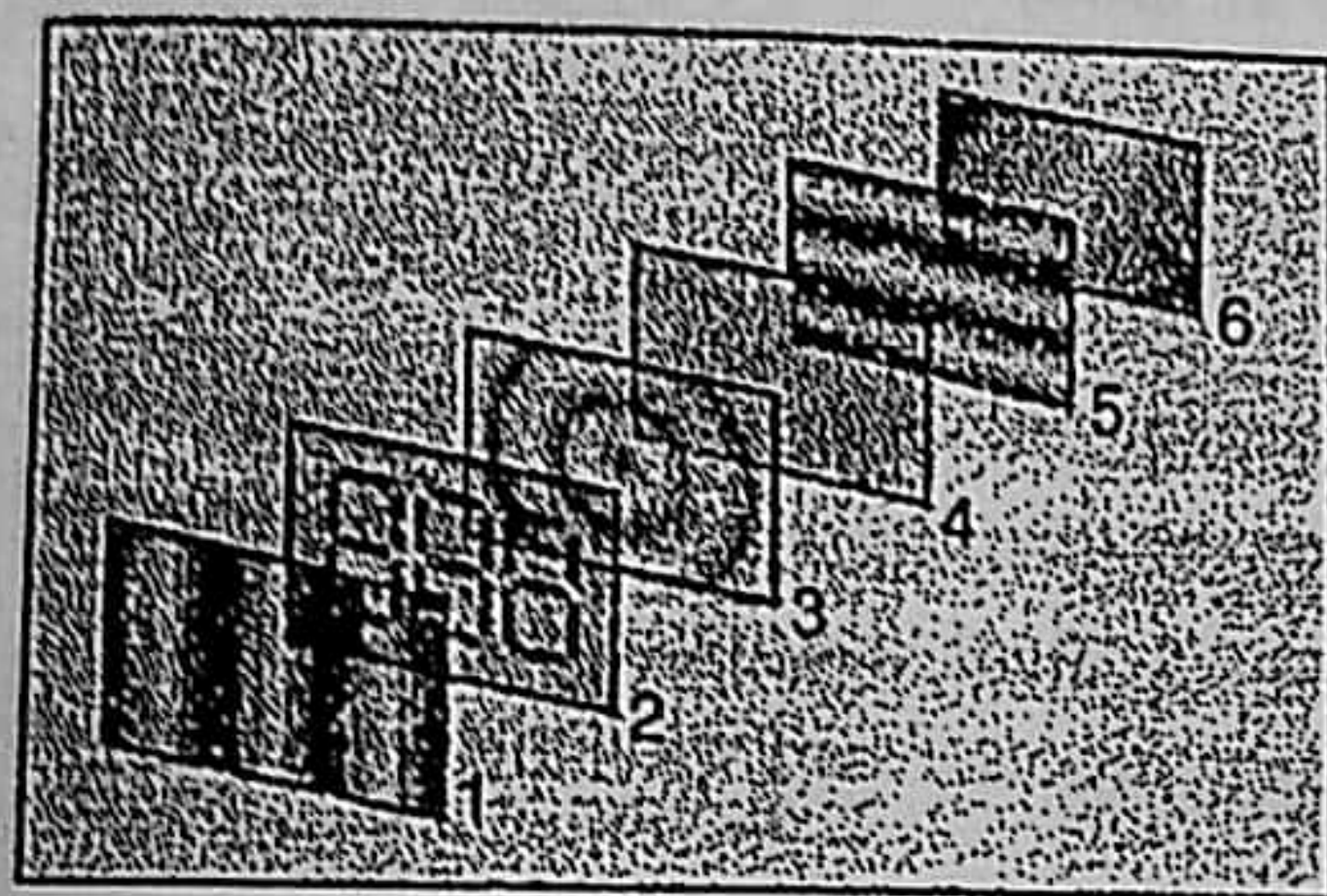


Fig. 4.7 Lyotropic liquid crystals

4.2.4 General & Engineering Applications of LCs

1. **Liquid Crystal Display:** Liquid crystals find wide use in liquid crystal displays which rely on optical properties of certain liquid crystall substances in the presence and absence of electric field. In a typical device, a liquid crystal layer (typically 10 mm thick) sits between two polarizers that are crossed (oriented at 90° to one

another). (Fig. 4.8) The liquid crystal alignment is chosen so that its relaxed phase is twisted one. This twisted phase reorients light that has passed through the first polarizer, allowing its transmission through the second polariser (and reflected back electric field is applied to the LC layer. In this state the LC molecules do not reorient light, so that light polarised at first polariser is absorbed at the second polariser and the device loses transparency with increasing voltage. In this way the electric field can be used to make a pixel switch between transparent or opaque on command color LCD systems also use the same technique with color filters used to generate red, green and blue pixels. Similar principles can be used to other LC based optical devices.



- 1 - Vertical polarization filter
- 2,4 - Glass with electrodes
- 3 - Liquid crystals
- 5 - Horizontal polarization filter
- 6 - Reflector

Fig. 4.8 Structure of liquid crystal display

LC tunable filters are used as electro optical devices and in hyperspectral imaging.

2. Thermotropic chiral LC vary their pitch with change in temperature as a result the colour of the material changes as the temperature changes. They are used as thermometer for aquarium, swimming pools and infant baths and also to look for hot spots for failure analysis in semiconducting industry.
3. Liquid crystal lasers are used in casing medium for stable monochromatic emission.
4. When the temperature of cholesteric liquid crystal is changed over a particular range, these LCs exhibit colour change from red to violet. This important property is utilised in thermography (for measuring surface temperature), to indicate temperature variation by using colour differences, for following thermal diffusion, thermal mapping (like integrated circuits) and aerodynamic testing.
5. Medical applications of liquid crystals are for studying circulatory system, detection of tumours, skin and breast cancers.
6. Liquid crystals are also used in finding the efficiency of heat engines and testing of radiations.

4.3 SUPERCONDUCTORS

(A solid which offers no resistance to the passage of electricity through it, is called superconductor) This phenomenon was discovered by Dutch Physicist Kammerlingh Onnes in 1911, when he was measuring the resistivity of mercury below 4.2 K. The niobium alloys were the earliest superconductors to be studied elaborately. Superconductivity can be understood with the help of quantum physics.

(Charged particles in solids can travel only in fixed directions or levels. The electrons in a normal metallic conductor can collide with the metal atoms and shift themselves from one level to another, but the electrons in a superconductor are prevented from such shifts by a unique quantum effect. These electrons are confined to their original levels and therefore cannot collide with the atoms, and consequently must travel endlessly along fixed directions. Under such a circumstances, they head in one direction and continue to carry current endlessly.

(Superconductivity is exhibited by several metals, but only at low temperatures. The temperature at which the normal metal passes into superconducting state is called the superconducting transition temperature or critical temperature, denoted by T_c). The resistivity - temperature behaviours for superconductive and nonsuperconductive materials are differentiated below in the Fig. (4.9).

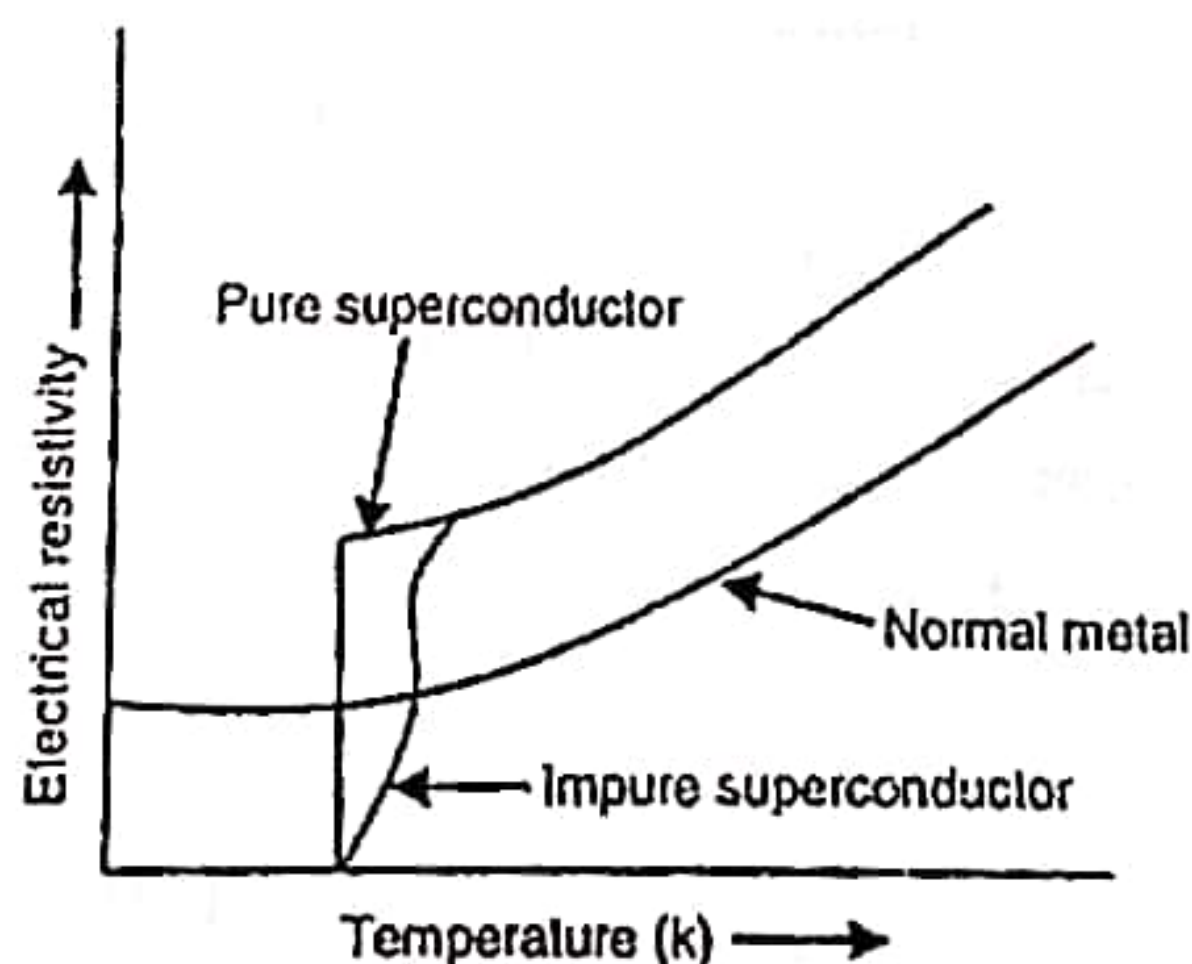


Fig. 4.9 Resistivity - Temperature behaviour of Superconductors

4.3.1 Types of Superconductors

Superconductors are divided into two types based on their magnetic response.

- a. Type I or Ideal superconductors
- b. Type II or Hard superconductors

Type - I superconductors are those which become completely diamagnetic in the superconducting state. These materials exhibit 'Meissner effect' i.e., the expulsion of magnetic flux from the interior of a piece of super conducting material as the material undergoes the transition to the super-conducting phase.

Type - II superconductors are those in which the ideal behaviour is seen upto a lower critical magnetic field beyond which the magnetization gradually changes and attains zero at an upper critical magnetic field.

Yttrium barium cuprate ($\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, where x is small)

This functions as a superconductor at a critical temperature (T_c) of 90 °K. The constituents of this material i.e., yttrium, barium and copper are in 1: 2: 3 molar stoichiometric ratio and hence are called as 1: 2: 3 superconductors.

Synthesis of 1: 2: 3 superconductor by ceramic method:

$\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ can be synthesised by solid state ceramic technique. This involves the following steps:

- Preparation of a homogeneous mixture of there oxides (Y_2O_3 , BaCO_3 and CuO) in their molar ratios.
- Heating them to obtain oxygen deficient superconductor in a muffle furnace.
- Annealing the above compound to room temperature to retain its composition, structure and superconducting properties.

4.3.2 Classes of Superconductors

Superconductors belong to different classes like

- | | |
|---|---|
| 1. elements | eg: Hg, Nb, La |
| 2. alloys | eg: La ₃ In, Nb ₃ Ge |
| 3. simple compounds | eg: Nb N |
| 4. molecular crystals | eg: $\text{C}_{60} \text{K}_x$ |
| 5. nonstoichiometric crystals
having defects | eg: TiO , NbO , $\text{Ba Bi}_{0.25} \text{Pb}_{0.75} \text{O}_3$ |
| 6. Ceramic | eg: mixed metal oxides |
| 7. Inorganic polymers | eg: $(\text{SN})_x$ |
| 8. Organic compounds | eg: charge - transfer compounds between electron donors (like derivative of tetrathiofulvalene) and electron acceptors (like tetracyanoquinodimethane). |

4.3.3 Properties of Superconductors

1. Superconducting materials are generally brittle in nature. This property limits their ability to be fabricated into useful forms such as wires.
2. At room temperature, the resistivity of superconducting material is greater than other elements.
3. A Superconductor exhibits perfect diamagnetism. Because of diamagnetic nature, superconducting materials strongly repel external magnets which leads to a levitation effects.
4. Thermoelectric effects of materials disappear in the superconducting state.
5. If a sufficiently strong magnetic field is applied below T_c (superconducting transition temperature), its superconducting property is destroyed.
6. When current is passed through the superconducting materials, the heating loss I^2R is zero.

$$| \because \text{Resistivity } \rho = 0 \text{ at } T = T_c; \therefore R = \rho \frac{l}{A} = 0; \therefore I^2R = 0 |$$

4.3.4 Applications of Superconductors

1. Superconductors can be used to perform logic and storage functions in computers. Superchips made of superconductors for computers can function 1000 times faster than currently used silicon chips.
2. Power can be transmitted through superconducting cables without loss as there is no I^2R loss in a superconductor.
3. A zero resistance combined with high current densities makes superconductors useful for strong electromagnets. They can be used for producing very strong magnetic fields of about 50 tesla, which is much larger than the field obtainable from an electromagnet.
4. Superconducting magnets capable of generating high fields with low power consumption are currently employed in scientific and research equipment. (They are used for magnetic resonance imaging (MRI) in the medical field as a diagnostic tool.)
5. Superconductors serve as gas sensors because their electrical resistivity sharply changes on contact with certain gases. For example $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ is a good sensor for alcohol vapours.
6. Some superconductors function as excellent catalysts for industrial chemical processes. For example $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and the related cuprates act as catalysts in oxidation dehydrogenation reactions.