**Commercial applications of conducting polymeric materials**

a. For making field effect transistors and Schottky barrier diodes

Examples : Polyactylene,
Polythiophene,
Polypyrole

b. For making large area light emitting device (LED) displays.

Examples : Poly (p-phenylenevinylene),
Poly (p-di ethynylenephenylene),
Poly (arylenevinylenes),
Poly (p-pyridines),
Poly (p-pyridinvinilenes),
Polythiophenes

c. For making photoconductors.

Examples : Poly (N-vinylcarbazole),
Poly (vinylpyrene)
Poly (2-vinycarbazole)

Thus the modern polymers play an important role not only in the field of biomaterials but also in the optoelectronics.

Figure 11.9 shows the structures of polymer light emitting devices.

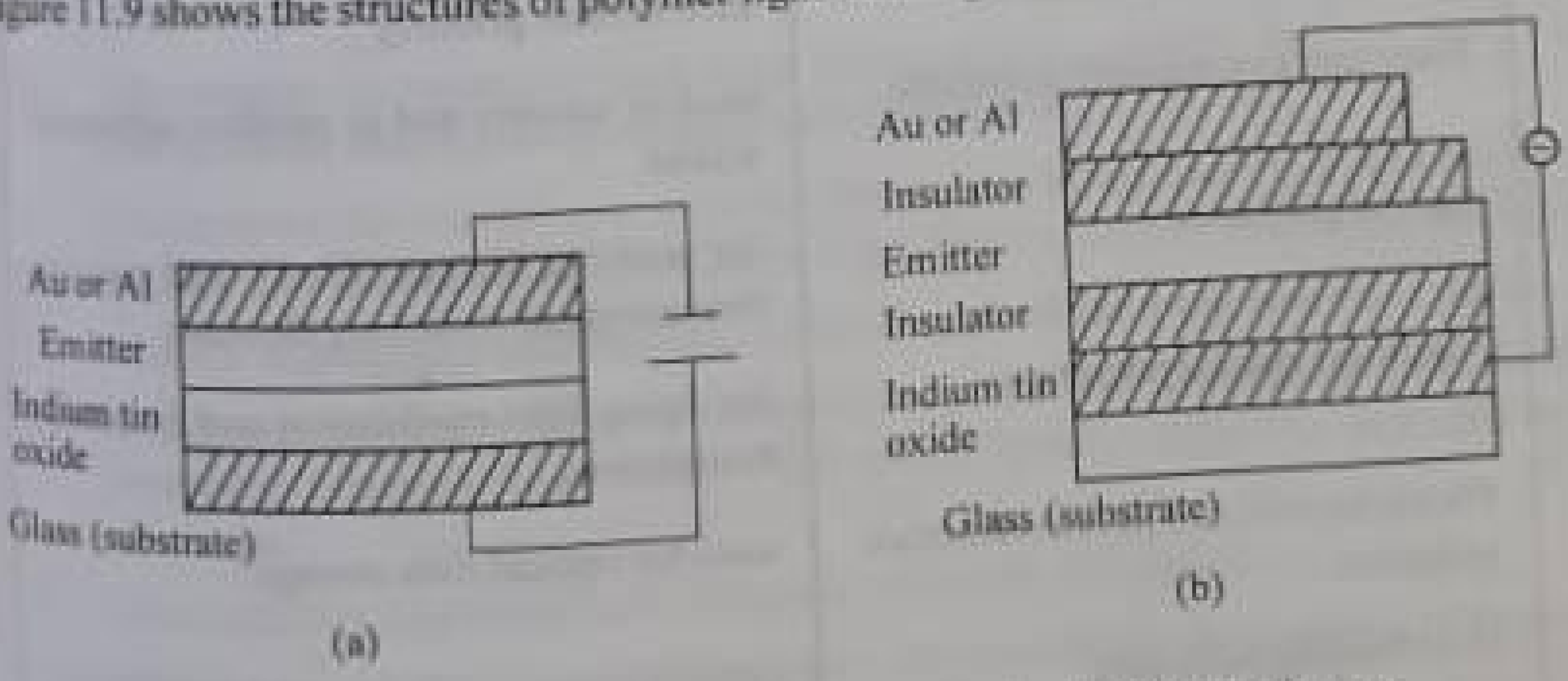



**Figure 11.9** a) Single layer light emitting device b) SCALE device

Figure 11.9 (a) and (b) show the various light emitting device structures available with conducting polymer as the light emitter. Light emitting polymer layer is sandwiched between a cathode and an anode, Indium tin oxide is used for the anode and gold or aluminium is used as the cathode. The indium tin oxide is coated on glass by spin coating and aluminium is

a. Fe 62%, Ni 34% and Cr 4% alloy is mainly used as a resistance wire and has maximum working temperature of 700°C.

b. Ni 80% and Cr 20% alloy is used for heaters and has a maximum working temperature of 1150°C.

c. The alloy consisting of chromium, nickel and cobalt has high strength and corrosion resistance even at temperatures upto 1200°C. Normally chromium based alloys are called heat resistant alloys which are used in high temperature applications.

In various heat engines and energy conversion devices like MHD generators and nuclear reactors, high temperature materials are used.

## 11.10 Thermoelectric materials

Thermoelectric materials are used to construct thermocouple. In a thermocouple, a voltage is induced between the hot and cold junctions of two dissimilar metals which increases with increasing temperature differences between hot and cold junctions. If we connect thermocouples in series, then that system can act as a voltage generator. Now a days thermocouples are widely used for temperature measurement, refrigeration, heating and generation of electrical power.

A good thermocouple which developes more voltage is defined by its figure of merit 'Z' such that

$$Z = \frac{S^2\sigma}{K}$$

where S is called thermoelectric power which is the thermoelectric voltage developed per unit degree rise of temperature. This is a constant in each metal. Further according to Wiedemann-Franz Law, in metals the ratio between thermal conductivity 'K' and electrical conductivity '$\sigma$' is directly proportional to absolute temperature.

$$\text{i.e.,} \quad \frac{K}{\sigma} = \frac{1}{3}\left(\frac{\pi k}{e}\right)^2 T$$

$$\text{or} \quad \frac{K}{\sigma T} = \frac{1}{3}\left(\frac{\pi k}{e}\right)^2 = L$$

where L is called Lorentz number and it is a constant. Its value depends upon the absolute temperature of the metal. So at a particular temperature $\frac{K}{\sigma}$ is a constant. The possibilities of increasing Z are very limited. Similarly common semi conductors like germanium and silicon have high thermal conductivity and so there are some semiconductors alloys in which larger thermoelectric effects occur than in metals. Bismuth and Antimony tellurides or selenides have high figure of merit.

and rejection greater than 80 dB over a 60 kHz band and a pass band attenuation of less than 1 dB over a 0 - 300 MHz range. ST - quartz SAW resonator can also be used to design IF

**4. Oscillators**

SAW oscillators have been produced operating in the frequency range 20 MHz to 1 GHz with transducers operated at their fundamental. They have high frequencies without multipliers, freedom from satellite modes, rugged good short term stability and are easily frequency modulated. The single mode oscillator is used in military applications. The conventional SAW oscillator consists of a quartz delay line with sufficient gain to exceed the delay line insertion loss.

**5. SAW pressure and temperature sensors**

The temperature and pressure dependence of acoustic wave time delay leads to SAW oscillator frequency variation. Thus a simple SAW oscillator can be designed as a sensitive sensor for either temperature or pressure. A small SAW substrate (from $Li\,Nb\,O_3$) is thinned over a small region to create a miniature flexible diaphragm. If the SAW propagation path is made to pass over the top of this diaphram, the effects of temperature and pressure induced strain due to a medium (gas or liquid) confined to the diaphragm's bottom side will be sensed as changes in SAW phase and time delay. By connecting electroacoustic transducers at each end of the SAW path to an electronic amplifier with sufficient gain, a SAW diaphragm sensor oscillator is created where frequency varies with pressure and temperature of external medium. If the SAW propagation path covers a sufficiently small portion of the diaphragm surface, the effects of pressure and strain will be uniform over the path. The output of the SAW diaphragm sensor can be processed by the more accurate frequency counter to get higher accuracy in the measurement of temperature and pressure. It has pressure sensitivity on the order of 1 kHz / psi and temperature sensitivity in the range 2 - 5 kHz/°C. Hence pressure resolution of 0.001 psi and temperature resolution of 0.001 °C can be easily achieved with this sensor.

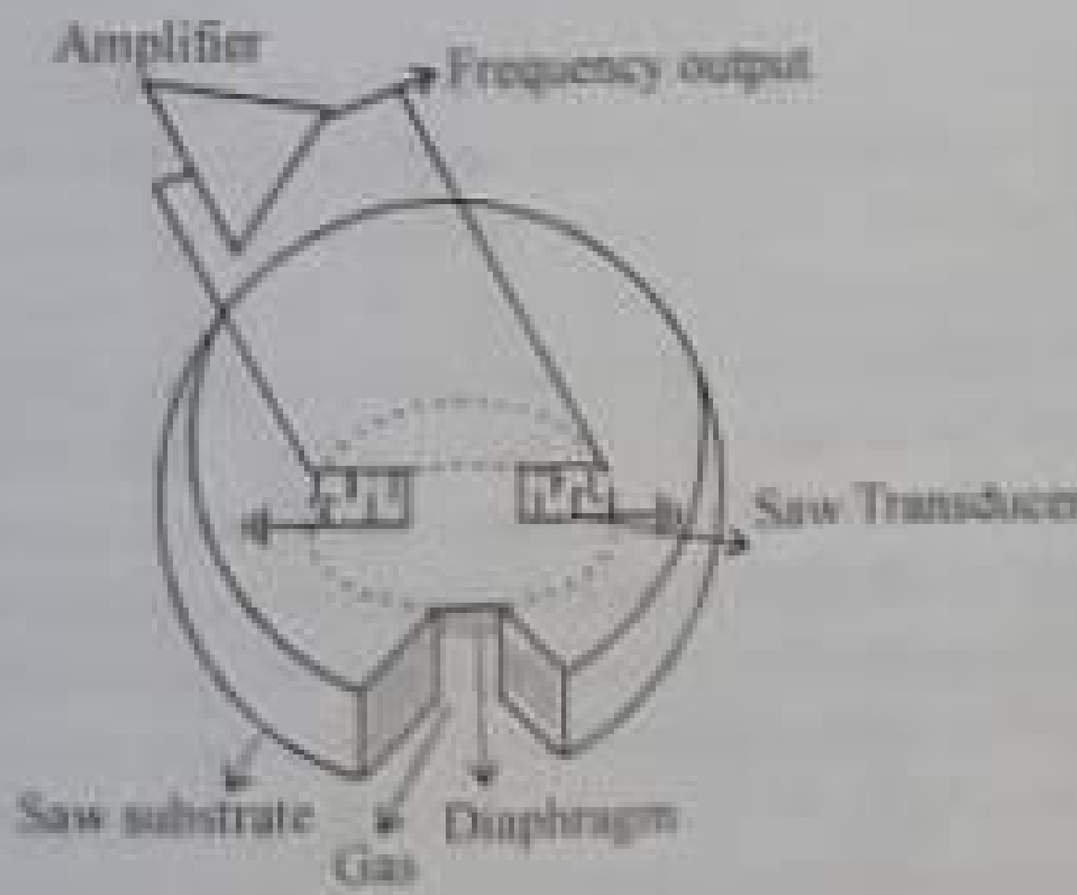



**Figure 11.5** SAW pressure sensor

**TABLE 11.1** Important fibers used in FRP and their properties

| | Fiber type | Density kg/m³ | Young's modulus G Pa | Strength G Pa | Maximum operational temperature 5 °C |
|---|---|---|---|---|---|
| 1. | E glass | 2500 - 2600 | 69 - 72 | 1.7 - 3.5 | 350 |
| 2. | Boron | 2400 - 2600 | 365 - 440 | 2.3 - 2.8 | 2000 |
| 3. | Carbon (high modulus) | 1960 | 517 | 1.86 | 600 |
| 4. | Carbon (high strength) | 1800 | 295 | 5.6 | 500 |
| 5. | $Al_2O_3$ | 3250 | 210 | 1.8 | 1250 |
| 6. | Nicalon SiC | 2800 | 45 - 480 | 0.3 - 4.9 | 1300 |
| 7. | $SiO_2$ | 2200 - 2500 | 75 | 5.9 | 1100 |
| 8. | Nylon 66 | 1200 | < 5 | 1 | 150 |
| 9. | Polyster | 1380 | < 18 | 0.8 | 150 |
| 10. | Kevlar 49 | 1450 | 135 | 3 | 250 |

**Advantages of FRP**

1. It has high strength to weight ratio.
2. It has low cost tooling.
3. Intricate and large shapes are possible in one piece. Since it can be fashioned more easily than a metal it is used in making complicated machine parts.
4. Excellent environment exposure resistance can be obtainable.
5. It has excellent electrical properties.
6. It has higher heat resistance.

**Disadvantages**

1. The material cost is so high.
2. The strengths perpendicular to fiber orientations are low.
3. It has low rate of heat transfer and dissipation
4. It has lower flexural modulus than steel and requires higher thickness for equal stiffness.

For high temperature applications, polyimides are used as matrices in carbon fiber reinforced plastics. High temperature thermoplastic systems (polyethersulfone and polyetheretherketone) have much greater toughness, strain capability and adequate high temperature properties than thermosets. Similarly HTA, an amorphous resin of the poly sulfone group exhibits adequate high temperature properties.

| | | | | | |
|---|---|---|---|---|---|
| 1960s | : | Microalloyed steels | 1966 | : | Fiber optics |
| late 1970 | : | Discovery of amorphous silicon | 1976 | : | Twisted Nematic liquid Crystals for display devices |
| 1978 | : | Optical fiber communication | 1980 | : | Shape memory polymers |
| 1984 | : | Discovery of quasi periodic crystals | 1986 | : | Discovery of high temperature super conductors |
| 1987 | : | High temperature glass FRP and Al and Ti MMCs | 1989 | : | High temperature super conductor with higher transition temperature around 165 K. |
| 1990 | : | Applications of smart materials and shape memory alloys | 1991 | : | Conducting polymers and light emitting polymers. |
| 1997 | : | Applications of smart materials and shape memory polymers | 2000 | : | Soliton based optical fiber communication at 1.55 μm |

In this chapter, let us see some of the newly developed materials and their properties and uses.

## 4.2 Metallic glasses

The dream of an engineer to have materials with high strength, good magnetic properties, better corrosion resistance and ease of fabrication will be realised through metallic glasses and a total industrial revolution would have been brought about.

Metallic glasses are metal alloys which have no long range atomic order. To achieve this structure a suitable alloy must be quenched so rapidly that the random liquid like structure is retained in the solid. Generally a glass is an amorphous, brittle and transparent solid. It is not a metallic and does not exhibit ferromagnetism. Similarly metals are malleable, ductile and exhibit crystalline properties. Metallic glasses share the properties of both metals and glasses. They are amorphous alloys with an atomic configuration similar to that of the molten liquid that is there is no translational symmetry. Further they are all strong, ductile, malleable, opaque and brittle. Unlike glasses, the glass transition temperature for metallic alloys is about 20°C to 30°C instead of several hundred degrees. The glass transition temperature is the temperature at which the liquid like atomic configuration can be frozen into a solid. A major advantage of metallic glasses is that they can be produced easily and cheaply because they are produced directly from the molten alloy. The technique is called 'splat' quenching (very rapid quenching at the rate of $10^6$ K/second). The molten alloys are very rapidly cooled by highly conducting massive rollers rotating at high speeds to give ribbons of metallic glasses.

5. Many metallic glasses based on titanium, niobium, lanthanum and molybderum have been found to be superconducting. These would be used in producing high magnetic fields and for magnetic levitation of trains.

6. Further since the metallic glasses are not affected by irradiation, they seem to be ideal material for containers in disposal of radioactive waste.

7. The random ordering in metallic glasses gives very high corrosion resistance. Particularly chromium and phosphorous based metallic glasses (iron-chromium-phosphorus-carbon alloys) have high corrosion resistance and they can be used in marine cables, chemical filters, inner surfaces of reactor vessel, orthopaedical implants and surgical clips.

Thus if metallic glasses could be produced in bulk like ordinary castings, perhaps all the present engineering materials will be replaced by metallic glasses.

## 11.3 Fiber reinforced plastics (FRP) and fiber reinforced metals (FRM)

It is a composite material. We know that the composite materials have been developed to get improved or desired properties in them. Nowadays fiber reinforced plastics (FRP) play an important role in the machine parts where we require high strength, high modulus, heat resistance and light weight. The fiberous glass is used in reinforced plastics in the form of rovings, chopped strands, milled fibers, yarns, non woven mats and woven fabrics. Most commonly used reinforcements are (i) random chopped strand mat, bonded together with a resinous binder (polyster), (ii) mat from continuous strands, deposited in a swirl pattern and loosely bonded together with a resinous binder, (iii) filament type thin mats, (iv) preforms, (v) woven fibrous glass clothes, (vi) parallel stranded glass fibers and (vii) short stranded fibers. The glass fibers having a vinyl silane-epoxy surface treatment on the fibers are used. This treatment gives best dry and wet strength. E type glass which is one of the important glass fiber material which uses boric acid rather than soda ash as one of the component of the melt. Mostly polyster resin is used as plastic. Epoxy and phenolic resins are also used. Table 11.1 gives the important fibers used in FRP and their properties. The glass reinforced plastic is the one in which glass fibers provide strength while the polymer reduces brittleness. It is used in motor car bodies, chemical vats, sinks, etc. Carbon fiber reinforced plastics have greater resistance to fatigue and lower density. The fibers are made from synthetic textile fibers treated in such a way that the side groups are entirely removed. The carbon fiber reinforced plastics are used in aeroengines, high pressure rotor and stator blades since they can withstand higher thrusts. Silica and Boron fiber reinforced plastics have high strength and low density. But these are all costlier than glass or carbon fiber reinforced plastics.

In the twin roller system, molten alloy is passed through two rollers rotating in opposite directions. In the melt spinning system molten alloy jet impinges on a fast rotating roller. In the melt extraction system a fast moving roller sweeps off molten droplet into a strip from a solid rod. Theoretically the pure metals require extremely high cooling rates to make them glassy and this is beyond the present day technology. First class of metallic glasses arised from transition metal (Fe, CO, Ni) - metalloid (B, Si, C, P) type. So that they are called metal - metalloid glasses. Now we have metal - metal glasses which are nickel - niobium, magnesium - zinc, copper - zirconium and hafnium - vanadium alloys. Unlike metal - metalloid glasses, in the metal - metal glasses there is no restriction on composition. Normally iron - boron alloys require cooling rates of over a million degrees per second to become glassy. But palladium - copper - silicon and palladium - nickel - phosphorous alloys require the cooling rate of hundred degrees per second.

**Applications**

1. Eventhough metallic glasses are non crystalline, they are ferromagnetic. The lack of long range ordering results zero bulk magnetic crystal anisotropy on an average. Due to that, they possess low magnetic losses, high permeability and saturation magnetisation with low coercivity. Thus they resemble the very soft magnetic alloys. When we compare with permalloys these have extreme mechanical hardness, excellent initial permeability and zero magnetostriction. So these are used in tape - recorder heads, cores of high power transformers and magnetic shields.

   Examples : $Fe_{75} P_{15} C_{10}$, $Fe_{24} Zr_{76}$, $Ni_{60} Nb_{40}$

2. Metallic glasses possess high strength and tensile strength. For example $Fe_{80} B_{20}$ has its tensile strength around 3.6 GPa. Its hardness is also very high. For $Fe_{40} Mo_{40} B_{20}$, the hardness (HV) = 1950 kg/mm$^2$. Thus they are superior than common steels. This is based on their structure since the random ordering does not have any lattice defects like dislocations and grain boundaries. This makes them useful as reinforcing elements in concrete, plastic or rubber. Strong ribbons of metallic glasses can be used for simple filament winding to reinforce pressure vessels or to construct large fly wheels for energy storage.

3. They have higher workability. Thus they can be cold worked upto half their thickness without cracking. They are very pliable and can be bent back all the way through 180° over thin razor blades without breaking. This fact is also utilized to make different kinds of springs.

4. Metallic glasses have high electrical resistance with nearly zero temperature coefficient of resistance. Only at very low temperatures there is a sharp variation in resistance. So these are used to make accurate standard resistances, computer memories, magneto resistance sensors and cryothermometers ( thermometers measuring very low temperatures).

The surface acoustic wave is launched on the surface of a substrate material through piezoelectric effect. The energy of the wave is exponentially decaying into the material and is generally confined to within a few wavelengths of the surface. The material which can generate and guide surface acoustic waves are called SAW materials. Ideally one wants zero temperature coefficient of delay and high piezo electric coupling from SAW materials. The first order temperature coefficient of delay is given by

$$\frac{1}{\tau}\frac{\partial \tau}{\partial T} = \left(\frac{\ell}{v_s}\right)^{-1} \frac{\partial}{\partial T}\left(\frac{\ell}{v_s}\right) = \frac{1}{\ell}\frac{\partial \ell}{\partial T} - \frac{1}{v_s}\frac{\partial v_s}{\partial T} = \alpha - \frac{1}{v_s}\frac{\partial v_s}{\partial T}$$

where $\tau = \ell / v_s$ is the delay time, $\ell$ is the distance between input and output end in the material, $v_s$ is the SAW velocity and $\alpha$ is the coefficient of thermal expansion. ST - cut quartz has zero temperature coefficient of delay and its cost is low. Further we can make large substrates from it. But its coupling is very low. The Li $Nb O_3$ crystal with 41.5° orientation cut, and Li $Ta O_3$ have good coupling and moderate temperature sensitivity. Particularly piezoelectric substrates for SAW filters and delay lines with 131° rotated Y - cut X propagating crystalline lithium niobate plates are widely used. It has large electrochemical coupling coefficient. Now YZ Li $Nb O_3$, YX quartz and $Bi_{12}$ Ge $O_{20}$ are popular SAW substrate materials. Table 11.2 shows the different SAW materials and their properties like propagation loss in vacuum, temperature coefficient of velocity and time delay.

**Table 11.2** Different SAW materials and their properties

| Material | Orientation | Coupling efficiency $k^2$ | Velocity, $v_s$ m/s | Temp. coefficient of velocity, $\left(\frac{1}{v}\right)\frac{\partial v}{\partial T}$ $K^{-1}$ | Temp. coefficient of delay time, $\left(\frac{1}{\tau}\right)\frac{\partial \tau}{\partial T}$ $K^{-1}$ | Propagation loss in vacuum dB/μs |
|---|---|---|---|---|---|---|
| Li $NbO_3$ | Y Z | 0.0504 | 3488 | –87 | 94 | 0.88 |
| $Bi_{12}$ Ge $O_{20}$ | (111) | 0.0169 | 1708 | ... | ... | 1.45 |
| Li $Ta O_3$ | Y Z | 0.0068 | 3230 | –31 | 35 | 0.94 |
| Quartz | Y X | 0.0022 | 3159 | 38 | –24 | 2.15 |
| | ST X | 0.0014 | 3158 | 14 | 0 | 2.62 |

In the table 'k' is the electromechanical coupling constant and $k^2$ is a measure of coupling efficiency. From this table one can identify Li $Nb O_3$ as a best SAW substrate because of its high coupling constant and low insertion loss.

**Applications of SAW Devices**

The surface acoustic wave (SAW) devices are performing similar functions of bulk acoustic wave devices like delay lines, frequency filters, dispersive delay lines and oscillators. Hence SAW devices are also established in the same fields like communications and radar since both depend on the same basic property - the ability to store energy/information on the slowly propagating acoustic wave.

**Merits of SAW devices**

1. The accessibility of the surface wave has lead to novel monolithic devices capable of performing more sophisticated signal processing functions than bulk wave devices.
2. The saw devices have bandwidths of several hundred megahertz and dynamic ranges extending towards 100 dB.
3. These provide VHF - UHF signal processing functions not readily available by other means.
4. They have high data rates and large data handling capacity. Information storage capacity is directly proportional to time bandwidth product. In SAW devices the time bandwidth product is about $10^3$.
5. These are thin film devices and hence size and weight are small.

Let us see their applications in detail.

**a. Delay lines and Memories**

Delay line is a device by which one can delay the signals. To achieve longer delays with good pulse response we must utilize ultrasonic delay lines instead of electrical delay lines. In SAW delay lines, the electrical signals is converted into slowly moving surface acoustic wave by means of a transducer and then it is reconverted into electrical signal by other transducer. With these devices, delays of upto 20 milliseconds have been achieved.

**Uses**

1. It can be used as memory stores for the temporary storage of data. That is the input information can be stored in binary form like semiconductor charge coupled device (CCD).
2. It can be used to hold the displayed information in CRT data displays and TV displays.
3. In radar it is used to hold the transmitted pulse for comparison with the returned target pulse or to provide delayed pulses which simulate a target return for purposes of calibrating the radar range. In the radar case long delay is associated with increased range since the time bandwidth product determines the pulse compression capabillity of the radar. By transmitting long pulses of large energy larger ranges can be reached before signals fall bellow the level of detectability. Thus for a given target resolution (bandwidth ) larger time delay capability in the delay line translates into increased radar range. SAW delay lines have sufficient time delay to store these long pulses before they can be compressed.

Fiber reinforced metals (FRM) have high strength and ductility and are manufactured by molten metal infiltration and coating of fibers with a layer of metal. So a fiber bundle is placed in contact with the metal which is then heated to its melting point.

Coating of carbon fibers on pure Nickel (Ni - 50% C) or Aluminium (Al - 60%C) increases the strength of the base metal even at very high temperatures.

## 11.4 Metal matrix composites (MMC)

For aerospace applications, an unique combination of properties can be achieved using discontinuous silicon-carbide reinforced aluminium metal matrix composites (MMC). These are light as aluminium, but have significantly higher strengths and specific stiffness. These can be easily forged, superplastically formed, and precision machined into complex shapes. These are mainly used in aerospace structures, inertial guidance systems and light weight optical assemblies. These composites are produced via powder metallurgy techniques to combine and consolidate rapidly solidified aluminium powders and high strength SiC whiskers. Fiber reinforced titanium metal matrix composites offer significant improvements in stiffness. Magnesium MMCs have increased strength and wear resistance over unreinforced Mg alloys.

## 11.5 Surface Acoustic Wave (SAW) materials

Sound waves can be propagated in solid medium as longitudinal waves, shear or transverse waves, surface waves, extensional waves and flexural waves. Surface acoustic waves or Rayleigh waves are propagated on the surface of solids whose dimensions are large in comparison with the wavelength. The oscillations of the particles are restricted to a surface layer about one wavelength thick. Both longitudinal and transverse components occur and the surface becomes 'wavy'. The velocity of surface acoustic waves is given by

$$V_s = \alpha\left(\frac{K}{\rho}\right)^{1/2}$$ where $\alpha = 0.93$ for metals and K is the bulk modulus of the material.

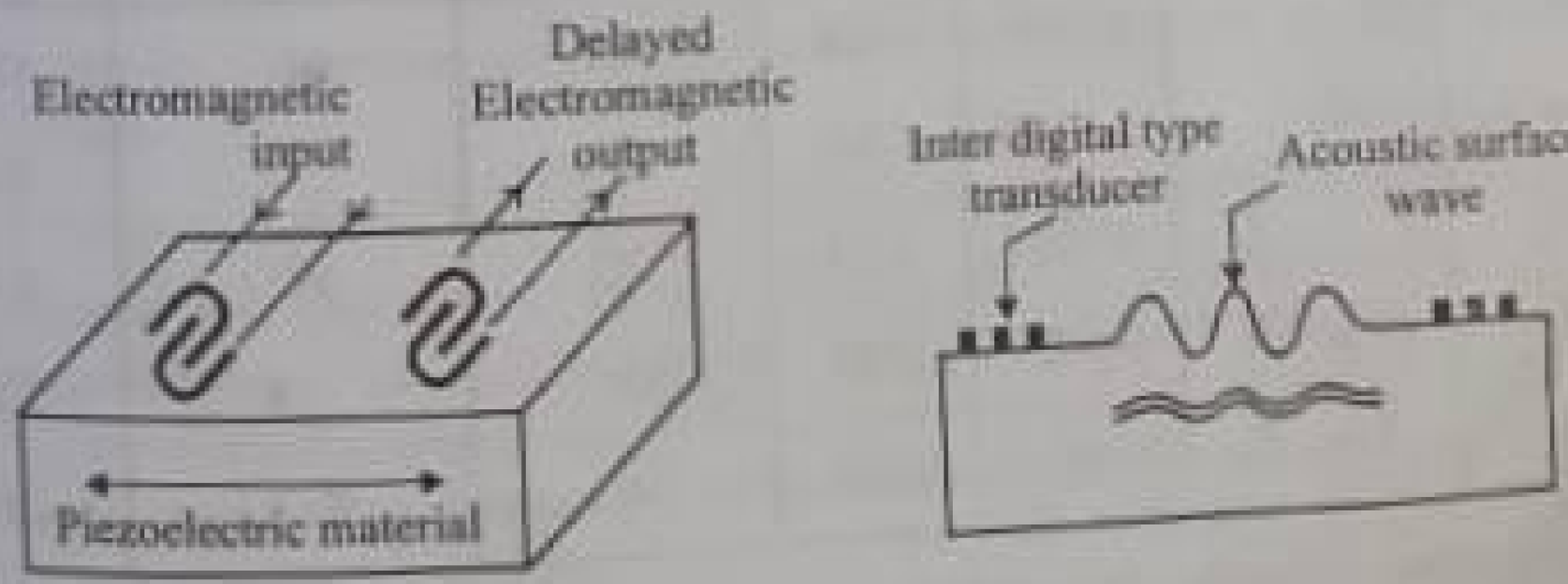



Figure 11.1 Schematic representation of the launching and propagation of a surface acoustic wave

4. In real time imaging systems it may be desirable to store a line or frame of picture information for processing to reduce the channel capacity required to transmit the picture. Using SAW delay lines we can achieve this.

5. Some types of processing the data sequence in question must be multiplied by some function of time and the product must be integrated over the time duration of the sequence, as in calculating cross correlation, Fourier transforms and other transformations (like convolution) are involving integrations. It is then necessary to store the entire data sequence in order to perform these operations. For this we must use SAW delay lines.

**b. Frequency filters**

Frequency filters have a variety of roles in signal processing. They may be incorporated simply to prevent unwanted signals entering the signal processor; they may form a vital part of the signal processor giving processing gain through the filter's ability to integrate by virtue of its storage capability; they may be present to identify frequency components as required for spectral analysis. The high value of Q in SAW filters is obtained from quartz and lithium niobate. But lithium niobate has excessive temperature dependence. Frequency sorting and selective filters are of particular significance processing signals.

**Frequency Selection**

First the input signal is passed through a SAW Fourier transformer and is then gated in the time domain. After that it undergoes an inverse Fourier transform. The position in time of the gate determines which frequency components are removed or passed. Resolution is determined by the dispersive delay time of the delay lines in the transformer and by the width of the gate (Figure 11.2).

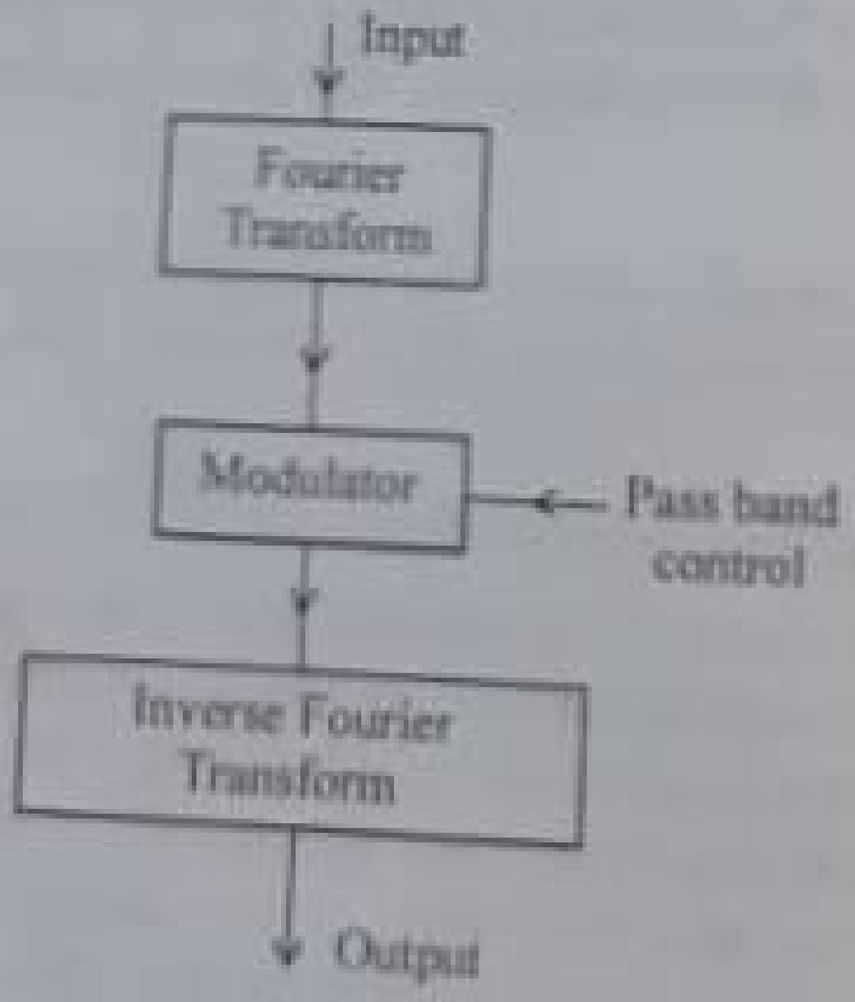



**Figure 11.2** Frequency sorting using SAW devices

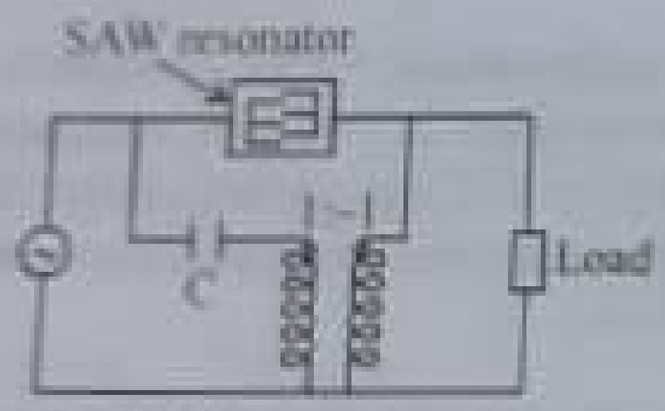
where $m$ is an integer and $\lambda_s$ is the resonance wavelength. Experimental measurements at 35 MHz showed that for arrays of Aluminium strip reflectors on YZ - Li Nb $O_3$, $\in$ is found to be - 1.5 for electrically connected strips and + 1.1 for electrically isolated strips. To improve performance of the resonator for filtering applications several resonators can be coupled either electrically or acoustically.

**d. Narrow band filters employing SAW Resonators**

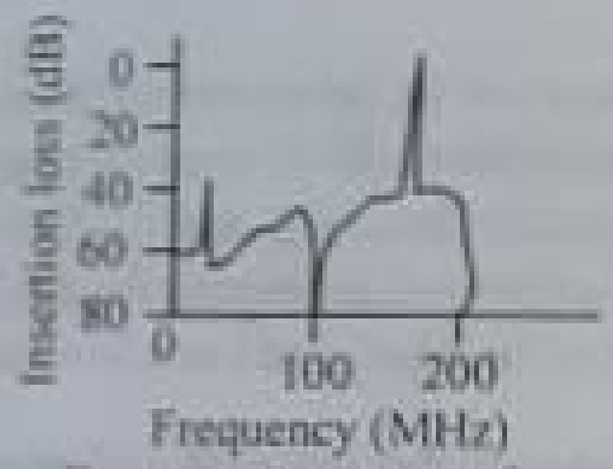
Using SAW resonators on Li Nb $O_3$ or ST quartz we can design narrow band pass filter (BPF) and narrow band elimination filter (BEF) in VHF and UHF ranges with high Q.

**SAW BPF (figure 11.4(a))**

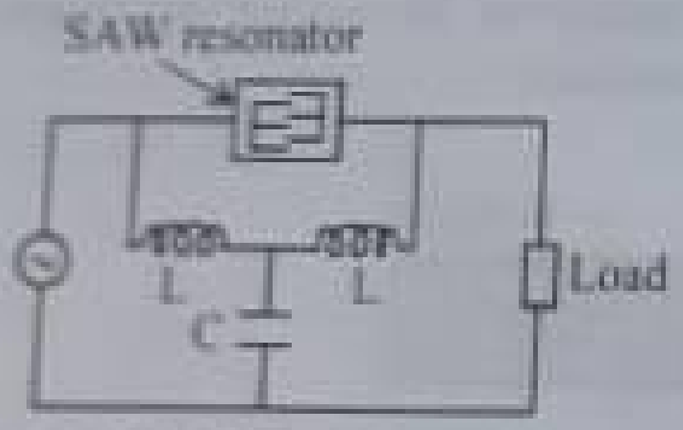
Using SAW resonators as impedance elements low loss SAW BPF can be constructed since here there is no energy conversion from electric to acoustic or vice versa.



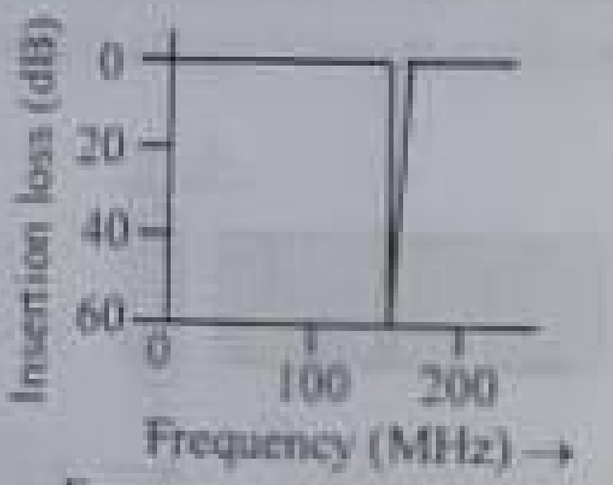

(a) SAW BPF configuration




Frequency response of a two cascaded BPF using ST-quartz SAW resonators in 950Ω system




(b) SAW BEF configuration




Frequency response of a four cascaded BEF using LiNb O SAW resonators in 950Ω system

**Figure 11.4** SAW resonators

But in crystal resonator BPF, large loss will occur due to this energy conversion. In the circuit $C$ is the transducers capacitance. By parallel resonance the SAW resonator takes a very high impedance (about 1000Ω) at pass band frequency. The pass band attenuation for a two cascaded ST - quartz SAW BPF is 3 dB at 153 MHz with a 3 dB width of 43 kHz and an out of band rejection of more than 45 dB over 0 - 200 MHz range. Li Nb $O_3$ SAW resonator can also be used to design BPF.

**SAW BEF (figure 11.4(b))**

We can design narrow BEF with SAW resonators by replacing the capacitive elements in LC network. The frequency response of a four cascaded BEF using Li Nb $O_3$ SAW resonators is shown in figure 11.4(b). The BEF has a 153.5 MHz center frequency, a stop

**c. Surface acoustic wave resonators**

The SAW resonator is the surface wave equivalent of the crystal resonator. Now it is used extensively for stable frequency sources and filters. Particularly it is more attractive for narrow band filtering applications. It has high Q (2 - 10000) and low insertion loss (≤ 5dB). It is rugged smaller in size and has fundamental operating frequencies (30 - 1000 MHz) an order of magnitude higher than for crystal resonators. One can visualize the SAW resonator as a crystal resonator in which the acoustic energy is confined to one surface of the substrate and reflectors placed on this surface define the boundaries of a SAW resonator cavity in the same way that the top and bottom surfaces of a crystal define the cavity of a conventional volume wave crystal resonator. The requirement of thin and comparatively fragile disks limit the crystal resonators usefulness at high frequencies. The corresponding limit for the SAW resonator is set by the ability to define fine lines for reflectors and transducers.

**Design**

SAW resonators can be fabricated in three basic configurations. 1. One - port, with a single interdigital transducer (IDT) used as a resonant impedance. 2. Two port, with input and output IDT's outside the cavity and 3. Two port with the IDT's inside the cavity. The latter configuration is the most promising for device applications since it requires no external balancing circuits (i.e., bridges) and has a low insertion loss.

Figure 11.3 shows the schematic diagram of the basic two port SAW resonator structure. A Fabry-Perot cavity is formed by two distributed acoustic reflectors and input - output is accomplished with two intracavity interdigital transducers. The proper functioning of SAW resonator is characteristed by the following parameters:

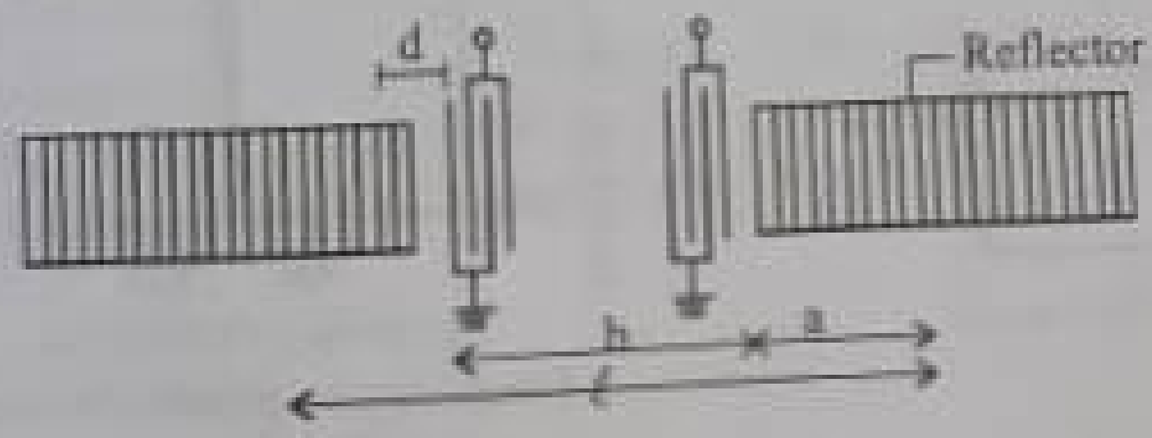



**Figure 11.3** Schematic diagram of basic two port SAW resonator

1. The acoustic amplitude reflection factor of the reflectors in both magnitude and phase, 2. the cavity length '$\ell$' equal to the sum of the distance b between the reflectors and the depth of energy penetration 2a into the reflectors and 3. the position 'd' of the transducers in the cavity to achieve optimum coupling to the standing wave. If $\epsilon$ is the fractional impedance discontinuity (positive or negative) and d is the distance from the first edge of the reflector to the middle of the first transducer electrode then

$$d_{opt} = \begin{cases} m\lambda_s/2 & \text{for } \epsilon > 0 \\ \left(\frac{m}{2} - \frac{1}{4}\right)\lambda_s & \text{for } \epsilon < 0 \end{cases}$$

material has been aluminium oxide-alumina which is coming under the pure oxide ceramics. It is white and can be manufactured by cold pressing powder in a die with subsequent sintering. But it has lower value of tougness and thermal shock resistance. Further it has low thermal conductivity. The modern alumina ceramic contains a proportion of Zirconium oxide Zirconia, which toughens the material. Further it has higher value of thermal shock resistance and thermal conductivity. (ii) In mixed ceramics oxide plus carbide and nitride are mixed. These have better thermal shock resistance than pure oxide ceramics, in addition to being harder and able to retain their hardness at high temperatures. (iii) The third class of ceramic tool material is that based on silicon nitride. Silicon nitride has a very low coefficient of thermal expansion which reduces the stresses set up between the hotter and cooler parts of an insert, so its thermal shock resistance is excellent. Sialon ceramics are silicon nitride plus alumina.

The present day use of ceramics for steel machining is largely confined to tuning of hardened or low alloy steels and both pure oxide and mixed ceramics are used. Nitride ceramics find their most suitable application in rough-turning the intermittent operations whereas pure oxide ceramic is likely to give the longest tool life in semiconducting good quality castings under stable continuous cutting conditions. For finishing operations mixed ceramic is the best choice. The mixed ceramic is also used for high speed machining of heat resistant steels. Thus ceramics can offer increased metal removal rates, extended tool life and an ability to machine hard work piece materials.

The ceramic ultrasonic transducers are used to produce ultrasonic waves at very high frequencies (–100 MHz) and are designed at any shape with a given fundamental frequency. These are acting as SAW materials and soner transducers. To day we have fine ceramics as the active ceramics.

**Modern applications of fine ceramics**

Fine ceramics are synthesized ceramics from highly refined new material, vigorously controlled composition and strictly regulated forming and sintering. These have specialized functions. Table 11.3 shows the applications of fine ceramics.

b. Bone cements are made from acrylic resins and methylmethacrylate acrylic copolymer.

c. Porous polysulfone with the coating of Co - Cr - Mo is used for orthopaedic implants. Carbon reinforced polysulfone which is a light weight, high strength composite material used for bone implants and silicone for breast implants. Silicone gel and silicone solid are also used for the same.

d. Polyethylene is used for short term indwelling. Porous high density polyethylene is used for dental and cortical implants.

e. The other polymeric biomaterials are polyurethane vinylchloride and PTFE.

**iii. Ceramics**

a. Ceramic implants ($Al_2O_3$ with some $SiO_2$ and alkali metal oxide) are used to make femoral head. This is made from powder metallurgical process.

b. Apatite ceramics are new bioactive ceramics. These are regarded as synthetic bone, readily allows bone ingrowth, better than currently used alumina ($Al_2O_3$).

The general formula is $M_5 X (YO_4)_3$

where

M - divalent cation such as $Ca^{2+}$ or $Sr^{2+}$

X - an univalent anion such as $OH^-$ or $F^-$

Y - Trivalent species such as P or occasional As which forms an ortho oxyanion

c. Synthetic hydroxyapatite is the raw material for dental and orthopaedic purposes.

d. Porous ceramics (alumina containing an organic flock filler) are used for mitral valve prosthesis and are injection moulded polypropylene.

e. Further we have bioglass, ceravital and AW glass. Bioinert bioceramics, especially join alumina, include carbon titania and zirconia. These are used in the synthesis bones and implants.

## 11.7 Ceramics

Ceramic materials are those materials which consist of phases which are compounds of metals and non metals. Ceramics are hard, strong and dense. These are completely stable even at high temperatures and are chemically inert. They have high compression strength and possess excellent dielectric properties. Already we have seen that the different types of ceramics and their uses as insulating materials in dielectric materials. Now let us see some of the ceramic tool materials with superior properties. In recent years, there have been significant developments in such materials available today : (i) The traditional ceramic tool

also used as sonar transducer but it has excessive temperature dependence. The composite of 95% Ba $TiO_3$ and 5% Ca $TiO_3$ is one of the low cost sonar transducer with reasonable ability at low power levels. The sonar transducer made from the composite of 95% Ba $TiO_3$ 4.5% Ca $TiO_3$ and 7.5% Co C $O_3$, called NRE - 4 has good high drive characteristics but weak piezoelectric effect. PZT - 4 and PZT - 8 have curie temperature around 300°C. But Ba $TiO_3$ and its composites have curie temperature around 115°C.

## 11.6 Biomaterials

Biomaterials science is that branch of biomedical engineering that is concerned with the materials aspects of medical devices. Any material, metal, ceramic plastic or organic brought into contact with the fluids cells and tissues of the living body comes within the domain of biomaterials science. Developments in biomaterials are the result of an interesting combination of technologists and scientists including bioengineers, biochemists, surgeons, physicians, orthopaedic researchers and cardio vascular scientists. Polymers - and ceramics are just now arriving in the field of biomaterials. They have high compatibility, high strength and corrosion resistance. Medical ceramics are emerging as replacements for some metals for structural or wear applications in implants. Typically these implants are used to strength or replace portions of a bone or joint. Bone joins readily with some ceramic surfaces.

### i. Metals and alloys

a. Bone screws are made from stainless steel (ASTMF - 138 and ASTMF - 139) wrought bar or strip. These have high tensile strength and modulus of elasticity. Stainless steel wires and plates are also used in implant devices.

b. Cobalt based alloy with titanium and stainless steel are used as implant metals. Protasul from cast alloy of Co - Cr - Mo is used to make stem and head of implanted hip endoprosthesis. The improved version, protasul - 10 from Co - Ni - Cr - Mo alloy is an important hip joint alloy. ASTMF - 75 (H - 21, Vitallium, Zimmalloy, Co - Cr - Mo + 0.35 C max, cast, with elongation + 8%), ASTMF - 90 (Co - Cr - W + Low carbon, wrought, elongation 30%) are the important ones.

c. In some cases, stainless steels are used to make stems of implanted prosthesis.

d. ASTMF - 136 (Ti - 6Al - 4 V, EL I alloy, forged) is a high strength alloy which is also used in implant devices. It has high strength/weight ratio, high corrosion resistance and high biocompatability.

### ii. Polymers

a. Endoprosthetic development is made by the use of ultra high molecular weight polyethylene (UHMWPE) with and without reinforced carbon fibers. The carbon reinforcement improves strength. This material can be taken as an impeoved bearing material for joint replacement prosthesis. This is frequently used to replace a diseased or injured joint. Long term stability depends on the strength and integrity of the carbon - polyethylene bond.

### iii. Sonar transducers

Sonar stands for sound navigation and ranging. Sonar is the name given to the use of radar techniques in which ultrasonic waves replace electromagnetic waves. Wartime applications of sonar are mainly concerned with submarine location but peaceful uses are those such as depth finding and fish location. For these purposes, a short ultrasonic signal is sent in a definite direction under the water. Whenever something different from water is there in the way of the signal, the sound would be reflected from it as an echo. This can be detected by an ultrasonic receiver. The time interval between the reflected signal and the initial signal is noted and from it the distance of the obstruction is determined. Sonar system is also used for under water communications. This is because ultrasonics can be focussed into a narrow beam and thus can penetrate the sea water to long distances as there is very little loss of energy and it avoids interference due to propeller noises and noises caused by the ship moving through water.

Sonar transducers are of the low Q type. The transducer consists of a hollow piezoelectric ceramic structure with end masses and usually a bias rod through the center (figure 11.6). The end masses act to lower the resonance frequency of the structure and to provide better acoustic matching between the ceramic and its fluid load. The rod provides a bias compressive stress to prevent fracture of the ceramic element in tension as it is driven at high dynamic stress. The ceramic element is either a hollow radially poled tube or a series of parallel connected axially poled rings.

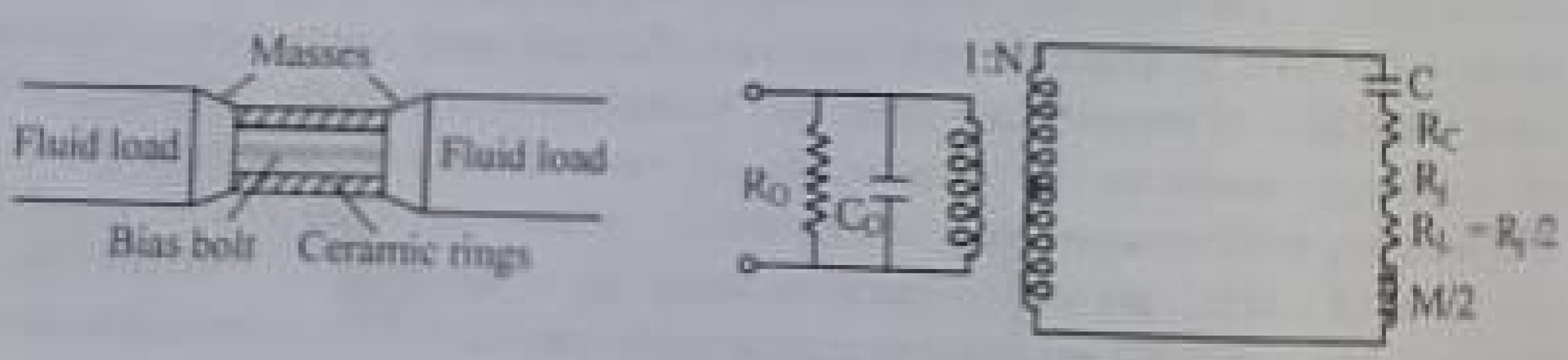



**Figure 11.6** Equivalent circuit for symmetric sonar - type transducer

The equivalent circuit for equal end masses M and equal fluid loads at each mass is also shown in figure 11.6. Actual transducers usually are fluid loaded on only one side and the end masses can be adjusted independently to change 'Q' of the transducer. The stiffness and compliance of the bias bolt, the compliance of the end masses and the mass of the ceramic elements are neglected in the simplified electrical equivalent circuit. The resistance $R_L$, $R_C$ and $R_E$ represent the acoustic load (mass loading neglected), internal mechanical losses in the ceramic and other mechanical losses respectively. The resistance $R_D$ represents internal dielectric losses which depend upon the dielectric constant of the material. Further $R_C$ and $R_D$ are dependent upon the input voltage and the stress developed in the ceramic respectively. The transducer ratio N gives the force equivalent of voltage. C and $C_D$ are the transducers capacitances. PZT - 8, PZT - 4 and PZT - 5A are sonar transducers. Among these PZT - 8 is more advantage than others since it requires low driving electric field and produces low dielectric loss. PZT - 4 has high coupling characteristics. Further Ba $TiO_3$ is

## 11.8 Cermets

Cermets are the composite materials consist of combination of metals and ceramics. The metal acts as a binder. These are made by powder metallurgy; the sintering temperature is above the melting point of the metal powder. In the finished cermets, the metal contributes high toughness and thermal shock resistance, while the ceramic contributes higher refractory properties, creep resistance, superior chemical stability and abrasion resistance. These properties are depending upon the ratio of combination of metal and ceramics. Generally two types of cermets are available based on the type of ceramics used.

a. Oxide cermics based cermets, in which ceramics are bonded by iron, chromium and tungsten.

b. Carbide ceramics are bonded by iron, nickel and cobalt.

**Uses**

1. Due to their higher hardness, these are used to cut and shape many refractory materials such as glass, procelain and high temperature resistant brittle alloys which are considered to be unmachinable.
2. These are also used to manufacture cutting tools and dies in metal working industry and rotating drills in the mining industry.
3. Further high speed, heavy duty cutting tips and inserts are made from cermets.

## 11.9 High temperature materials

The high temperature materials used in machine parts and structural components should have high thermal shock resistance and high creep resistance. Thermal shock resistance is a property of a material which indicates its ability to be subjected to rapid temperature changes without physical failure. So by means of this property a material can retain its shape and not distort, crack or shatter, due to a sudden change in its temperature. Creep is a time dependent strain occurring under stress. Creep can take place and lead to fracture at stress stresses much smaller than those which will break the object when loaded quickly. Normally creep rate is enormous at high temperatures. Creep resistance is a property by which the material can withstand stresses without fracture at high temperatures and during quick loading. To obtain creep resistance at high temperatures, we must use metal with high melting point and FCC structure with low stacking faulty energy. To improve the creep resistance in high temperature materials, dispersion hardening method is adopted. For high temperature applications, the fine grained materials and materials with grain boundaries are not useful since they have very weak creep resistance and generally the coarse grained materials are more useful since they show a better creep resistance.

Refractory oxides such as MgO and $Al_2O_3$ have high melting points and so they are very suitable for high temperature use. Further these materials should not react with the materials that they are in contact with. The Austentic stainless steels are used for continuous service upto 1100°C. It contains 74% iron, 18% Chromium and 8% Nickel. The commonly used high temperature alloys are iron-base, nickel base and cobalt-base alloys :

The semiconductor alloys such as 75% of $Bi_2Te_3$ + 25% of $Bi_2Se_3$ and 50% of $Bi_2Te_3$ + 50% of $Sb_2Te_3$ have lower thermal conductivities but substantially high electrical conductivities. Similarly lead telluride semiconductor (where lead is the n - type semiconductor and tellurium is the p type semiconductor) with 61.9% of Pb + 38.1% of Te is a very good thermoelectric material. For the electrical power generation or refrigeration, the maximum thermoelectric efficiency is about 10% only.

## 11.11 Electrets

Electrets are ferroelectric materials and are electrostatic analog of permanent magnets in that they possess a gross permanent electric dipole moment. They are manufactured from certain types of waxes, plastics and ceramics. When these waxes are subjected to high electric fields ($\approx 10^6$ V/m) they are polarised in their molten state and retain a permanent polarization after solidifying eventhough the external polarising filed is removed. Some barium titanate ceramics and carnauba waxes can be polarised in this way. A number of new electret applications are based on the piezoelectric or pyroelectric effects in polarised polymers. The interest in polymer electrets is due to the fact that these show extremely good charge storage capabilities and are available as flexible thin films. Polytetrafluoroethylene and polyvinylidene fluoride are important polymer electrets.

**Applications**

a. These are used in capacitor microphones. Here there is an electret diaphragm with metal layer at its top for electrical connection purpose. Further there is an air gap in between the back metal plate and bottom end of the electret diaphragm. If a sound wave impinges on diaphragm, it undergoes deflection and hence change in thickness of air gap is produced. The output voltage developed which is taken between the top metal layer and bottom metal back plate through a load is directly proportional to the frequency of sound waves. The same technique is also used in earphones. Here alternating voltage applied between the top and bottom of the earphone produces sound waves. Thus these are acting as electroacoustic transducers in an efficient manner with higher sensitivity and fidelity.

b. An electret recorder is a in which events lasting as little as 0.1 micro second are stored as electrets on the surface of plastic foil by a puncture of a thin air gap. The foil is not damaged and can be erased after readout.

c. These are also used in gas filters which use carona charged electret fibers to capture submicron particles by electrostatic attraction.

d. Further these are used in motors, relay switches, optical display systems, electrophotography and radiation dosimeters.

e. In medical field, electrets are used in so many ways. It was shown that foil electrets placed in contact with bones of animals in vivo cause accelerated growth of callus necessary for fracture healing. Moreover electret bondages pur on skin incisions considerably improve the tensile strength of the wound over a given period of time and thus speed the healing process.

2. $Sm\,Co_5$ belongs to $AB_5$ group intermetallic compound. It has large energy product $(B_r H_c)$ and so it is used for making permanent magnets.
3. $U\,Be_{13}$, $Nb_3\,Ge$ and $Y\,Ni_2\,B_2\,C$ are high Tc superconductors.
4. Similarly Ga As is also an intermetallic compound resembles germanium (mimics Ge) and is used for making LEDs and laser diodes.
5. Most of the titanium alloys like $Ti\,Al$, $Ti_3\,Si$, Ti - 6Al - 4V are intermetallic compounds.

Pure titanium is in the α-phase and nonheattreatable. It has hexagonally close packed structure (α phase) upto 882°C and converts into BCC structure (β phase). Above 1675°C, particularly when the alloy is in α - β phase, it has high strength/weight ratio, high corrosion resistance even at high temperatures, high rigidity/weight, good fatigue strength and toughness and low thermal expansion. By adding aluminium or tin, the strength of titanium is increased. It increases the value of α-phase temperature. By adding vanadium, the ductility and plasticity are increased. Thus Ti - 6Al - 4V alloy is in the α-β phase and has improved mechanical properties. Aluminium is acting as an α-stabiliser. Meanwhile vanadium acts as a β-stabiliser. *Ti - 6Al - 4V* alloy is widely used in aerospace applications and dental and artificial implants.

## 11.15 Shape memory alloys

Certain alloys such as nickel-titanium (Nitinol) and polymers like polyurethane can switch from a temporary shape to a parent shape above a certain transition temperature. Below that temperature the shape memory alloy (SMA) or shape memory polymer (SMP) can be bent into various configurations. Shrink-wrap is the familiar example of SMA and SMP. Shape memory alloys are known to change their stiffness characteristics with change in operating temperature. This effect is used in the vibration control.

SMAs are also used in activating springs which open and close the control valves. SMA wires can be embedded in structures at critical locations that are the likely sites for a crack propagation. Upon initiation of a crack, the SMA wires are energized which in tern provide local stiffening and thus prohibit further propagation of crack. Most of the SMAs are in martensite condition, then attain the temporary deformed shape on cooling and on heating the martensite converts into austenite condition. SMAs are sensitive to magnetic fields. This effect is used in actuators and relays. Ni Mn Ga ternary alloy is sensitive to magnetic field producing strain.

## 11.16 SMART materials

SMART materials or intelligent materials or active materials are the materials which respond with a change in shape upon application of externally applied driving forces. The shape change is appeared in the form of elongation of the material. Similarly there are electro and magneto rheological fluids in which there is an increase in viscosity on the application of external magnetic or electric field.

f. Now-a-days so many piezoelectric transducers and pyroelectric devices are manufactured from electrets.

## 11.12 Nuclear engineering materials

The materials used in nuclear reactors may be classified into the following main groups

i. Fuel Materials
ii. Moderator Materials
iii. Fuel Cladding Materials
iv. Control Materials

### i. Fuel materials

a. **Uranium :** Uranium is very reactive and easily oxidised. In pure form it is heavy, hard and nickel like metal. It retains its hardness at much higher temperatures. In natural uranium, the following isotopes are present :

Uranium - 238 (99.3%) and Uranium - 235 (0.7%). Uranium 238 is a fertile material. But it can be converted into fissionable material as Plutonium - 239 by neutron bombardment. Uranium - 235 is a fissionable material. It is used as a fuel in most thermal reactors. Enriched uranium which contains slightly increased percentage of uranium - 235 in natural uranium is also used as fuel. Uranium Oxides or carbides are also used as Nuclear fuels in some reactors.

b. **Plutonium :** Plutonium - 239 is very reactive, easily oxidised and highly toxic. It is a concentrated nuclear fuel and is not found in nature. It is produced from uranium - 238. It can undergo fission chain reaction even by fast neutrons. So plutonium reactors would not use moderator to thermalize the fast neutrons.

c. **Thorium :** It is a radio active material. Thorium - 232 is a fertile material. It can be converted into fissionable Uranium - 233 by neutron bombardment. Thorium is less susceptible to irradiation damage. In pure form it is soft and weak. In India, thorium is available in Kerala sea shores.

### ii. Moderator materials

Moderators are used to thermalize the fast neutrons and by that way the fission yield can be increased. Any reactor with moderator is a thermal reactor. Nuclear fuel rods are surrounded by moderator material. Deuterium ($D_2O$) and graphite are very good moderators since they have high moderating ratio. Beryllium is the best metallic moderating substance as it occupies small spaces and has low absorbtion cross section for neutrons. Moderators are also helpful in controlling and stabilizing the reactor power level during its operation. In some reactors moderators can also act as coolant and reflector.

### iii. Fuel cladding materials

Fuel cladding materials are used to improve the mechanical strength of fuel rods and to increase their corrosion resistance. They should not absorb any neutrons and should be stable even at high temperatures. They should possess higher thermal conductivity. For thermal

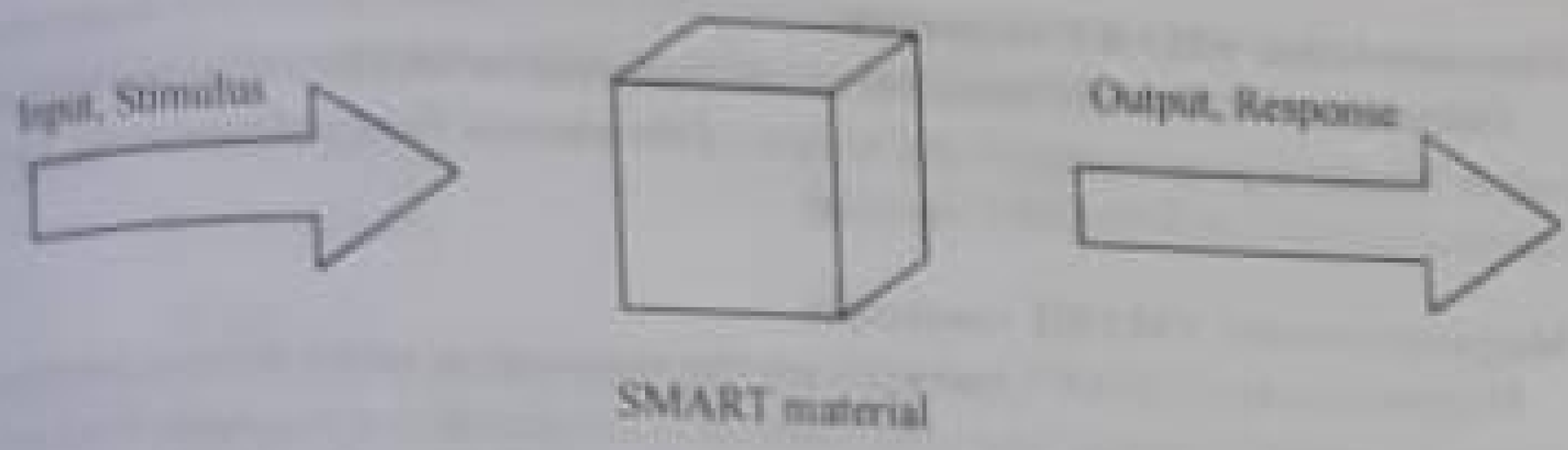



**Figure 11.7** Principle of working of a SMART material

Figure 11.7 shows the principle of working model of a SMART material or active material. The input or stimulus can be in the form of change in temperature or change in magnetic field. The material then intrinsically responds with an output which is in the form of change in length, change in viscosity or change in electrical conductivity of the material.

Further the SMART materials can also be used as sensors where a strain applied on the material is transformed into an electrical signal that allows the computation of the strain levels in the system. Similarly they act as actuators where a stimulus like voltage results in strain output.

SMART structures contain the following five components : i) sensing the data ii) transmission of data iii) command and control unit iv) data instructions and v) action devices as shown in figure 11.8.

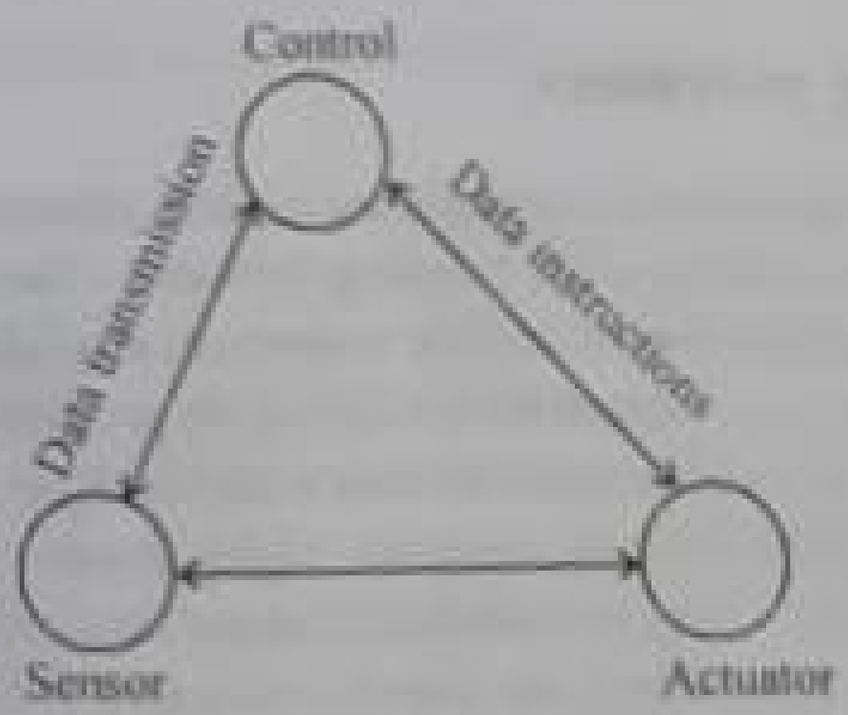



**Figure 11.8**

**Classification of SMART materials**

**i. Piezoelectric SMART materials**

Piezoelectric SMART materials act as energy converters from mechanical (strain) into electrical (charge or voltage) and vice versa.

reactors aluminium, magnesium beryllium and zirconium are preferred. For high power reactors zirconium and stainless steel are used since they can withstand at high temperatures.

**iv. Control materials**

The power level of the reactor or neutron flux in the reactor is controlled by inserting control rods which are high neutron absorbers. These are made from boron, silver and cadmium.

## 11.13 Nanophase materials

### 11.13.1 Introduction

Nanophase materials or simply nano materials are the nano structured materials having a characteristic length less than 100 nm. These are recently developed new materials having so many new properties. These have a three dimensional structure with a domain size smaller than 100 nm. These are characterised by a large number of grain boundary interfaces in which local atomic arrangements are different from those of the crystal lattice. A cluster of nano particles contains less than $10^4$ molecules or atoms corresponding to a diameter of only a few nanometre. Thus one can conclude that particle's size in nano materials is about 1 nm. With these small sized particles one can get the different properties (electronic, optical, electrical, magnetic, chemical and mechanical) which are different from the bulk materials. Having a size between the molecular and bulk solid state structures, the nano particles have hybrid properties. They have nonlinear optical and magnetic properties.

### 11.13.2 Preparation of nanomaterials

Nanocomposites consist of nano particles dispersed in an continuous matrix, creating a compositional heterogeneting of the final structure. The nanocomposites usually involves ceramic or polymeric matrix and are not restricted only to thin film. The nano materials are produced by gas phase processes and aerosol processes. Gas phase processes contain no impurity : i.e., pure nano materials can be developed. Aerosol processes are used to create complex chemical structures which are useful in producing multi component materials such as high-temperature superconductors. Thin film of nano particles are produced at a lower cost. Further the deposition rate of particles is very high being a nonvacuum technique. Mostly in aerosol processes, chemical vapour deposition techniques are adopted.

### 11.13.3 Applications

1. There are two types of applications. The structural applications are based on the mechanical properties of the nano structured or nanophase materials. These are used to produce super plastic ceramics and extremely hard metals.
2. Functional applications are based on the transformation of external signals such as the filtering of the incident tight, the change of electrical resistance in different gas concentrations and luminescent behaviour when electrically activated.
3. These are used to produce very tiny permanent magnets with high energy product $(B_r H_c)$. Thus these are used in high density magnetic recording.

4. These have lower melting point, high solid state phase transition pressure, lower Debye temperature and high self diffusion coefficient, high catalytic activity and lower ferroelectric phase transition temperature.
5. One can make alloy from immiscible materials and high $T_c$ superconductors.
6. Quantum wells, quantum dots and quantum wires having quantum confinement are produced from semiconductor nanomaterials which are acting as computer storage (memory) materials with high density.
7. Nano materials have a large volume function of grain boundaries or large ratio between surface area and volume. This property is used to get improved mechanical properties like higher hardness in ceramics.
8. These have very high magnetoresistance.

## 11.14 Intermetallic compounds

Intermetallic compounds are the materials having the behaviour of metals and ceramics which arises from their metallic and ionic or covalent nature. In the case of alloys of two metals, the bonding is purely metallic. But in the intermetallic compounds of two metals, the bonding is partly metallic and the remaining is ionic or covalent. They have high elastic modulus, high melting point and high electrical and thermal conductivities like metals. But they have poor ductility, high resistance to oxidation and corrosion like ceramics. However by adding small alloying elements like boron, manganese and niobium, the ductility can be increased to certain extent.

To day we have metal-metal type, metal-nonmetal type, metal-metal-metal type based on composition. During the formation of intermetallics, one must take care of the following i) Principle of space filling ii) Principle of symmetry and iii) Bonding formation. For example in the case of first intermetallic compound Cu Zn, the valence electron concentration is different in both the metals. Further in the case of Cs Au, it behaves as an insulator eventhough it contains two metals. This in the case of intermetallic compounds metal-metal combination need not be a metallic. Intermetallic compounds are brittle. So that the formality is very poor. But this can be eliminated by addition of some other elements. In the case of $Ni_3$ Al, the ductility can be increased by addition of boron. Similarly in Ti, Al with Nb and in Ti Al with Mn one can get proper ductility.

**Applications of intermetallic compounds**

1. The β compound Ni Ti (Nitinol) is an important shape memory alloy. The shape memory effect is produced when Ni Ti is deformed into a shape at low temperature martensite condition and it regains its original shape when the deforming stress is removed and heated above the martensitic transformation temperature. The martensitic transformation in Ni Ti alloy is a thermoelastic martensitic transformation. The shape memory alloy is used in orthopaedic devices for pulling fractures together, artificial hearts, pipe fittings, pipe couplings, servo-mechanisms for driving recording pens, switches, activators and thermostats.

**ii. Electrostrictive SMART materials**

Electrostrictive SMART materials are the materials in which mechanical change (i.e., change in length) is proportional to the square of the electric field and vice versa. LiNbO$_3$ acts as an electrostrictive SMART material.

**iii. Magnetostrictive SMART materials**

Magnetostrictive SMART materials are the materials in which there is a mechanical change (i.e., change in length) when the material is subjected to a magnetic field and vice versa. Terfenol-D or ferrites are the examples of magnetostrictive SMART materials.

**iv. Shape memory alloys**

These will undergo phase transformations which will produce shape changes when they are subjected to a thermal field. It deforms to its 'martensitic' condition with low temperature and regains its original shape in it, 'austenite' condition when heated (high temperature) Example : Nitinol (TiNi alloy).

**v. Sensor based optical fiber SMART materials**

Using intensity, phase, frequency or polarisation modulation, they can measure strain, temperatures, electrical/magnetic fields, pressure and other measurable quantities. These are high quality sensors.

**vi. Other types of SMART materials**

Textile material like SMART T-shirt can detect a variety of signals from the human body and weather conditions so as to allow from greater comfort. Catalytic material can detect the progress of a reaction or distinguish the reaction of a product.

## 11.17 Conducting polymers

We know that the polymeric materials are usually characterised by a strong covalent bonds along the polymer chain, while bonding between chains are considerably weaker. Today there are very large numbers of organic monomers available to make organic polymers for getting a wide range of applications by modifying the properties of polymers. Eventhough the polymers are electrical insulators due to their wide bandgap, a low carrier mobility and a low melting point, using new synthetic methods, highly conducting doped polymers such as polyaceylene are developed. They have defects free polymer chain and have high electrical conductivity as that of copper. These are doped conjugated polymers. Thus the conjugated polymers act as conductors. Polaniline and polypyrole semiconducting conjugated polymers are converted into conducting polymers when they doped with sufficient concentrations. These are used as battery electrodes, conductive coatings for electrostatic speakers, capacitor electrolytes, transparent conductive coatings, interconnecting wires in IC circuits instead of copper. The transport of charge carriers in these conducting polymers involves the transport rate, scattering, trapping processes, recombination, tunneling and hopping.

## SUMMARY

1. Today new materials play important roles in the field of electrical, electronic, magnetic, optical, medical and communication engineering.
2. Metallic glasses are used in transformer cores, standard resistance and cryothermometers.
3. FRP and FRM are having high strength and low density.
4. SAW materials are the surface acoustic wave materials. They are widely used in delay lines and computer memories.
5. Biomaterials are used to make implant devices which are used to strengthen or replace the portions of a bone or joint.
6. Ceramics are the compounds of metals and nonmetals and are hard, strong and dense.
7. Fine ceramics are synthesized ceramics from highly refined new material, vigorously controlled composition and slightly regulated forming and sintering.
8. The oxide ceramics and nonoxide ceramics are used as saw devices, ultrasonic transducers, piezoelectric materials, high energy product magnetic materials and high Tc superconductors.
9. Cermets are the composite materials having metals and ceramics. They have high hardness and are used as cutting tool materials.
10. High temperature materials are having high creep resistance even at high temperatures.
11. Thermoelectric materials have high thermoelectric powers and are used for refrigeration, heating and generating electrical power.
12. Electrets are the ferroelectric materials having permanent electric dipole moment and are used in medical field as well as in gas filters to capture submicron particles.
13. Nuclear engineering materials are used as fuel, moderator and control materials.
14. Nanophase materials are nanostructured materials and are used as superplastic ceramics, extremely hard metals, high energy product magnetic materials and memories.
15. Intermetallic compounds have properties of metals and ceramics.
16. Shape memory alloys be can change their shape under the applications of thermal energy, electric fields and magnetic fields.
17. SMART materials or intelligent materials are the materials which can respond to mechanical stress, electrical stresses or magnetic stresses and they produce corresponding outputs.
18. Conducting polymers are used to make transistors, diodes, light emitting devices and photoconductors.

deposited on the top electrode by evaporation. Figure 11.9(a) shows the structure of a simple (single layer) light emitting device and it works under a forward d.c. bias. Figure 11.9(b) shows the efficient configuration of light emitting device called a Symmetrically Configured Alternating Current Light Emitting (SCALE) device which works under a.c. as well as forward and reverse d.c. bias.

The working principle of light emitting polymer device can be explained as follows: When a voltage is applied electrons are injected from one electrode and holes from the other into polymer layer. They migrate across the polymer layer and can meet up to form an exited state known as the singlet exciton which can decay by emitting a photon. The colour of the light emission is determined by the energy difference between the highest occupied molecular orbital (valence band) and lowest unoccupied molecular orbital (conduction band). Table 11.5 shows the recently developed high technology polymers and their applications.

**Table 11.5** High technology polymers and their uses

| | High technology polymers | Applications |
|---|---|---|
| 1. | Photoresists | used in Lithographs. |
| 2. | Conductive polymers | used as electrodes of battery and transparent conductive coatings. |
| 3. | Dielectric polymers | used for packaging and high voltage insulation. |
| 4. | Photoconductive polymers | used in laser printing |
| 5. | Piezo and pyroelectric polymers | used as sensors and to produce ultrasonic waves. |
| 6. | Optical polymers | for making lenses, fibers and passive thermooptical switching elements. |
| 7. | Nonlinear optical polymers | for doing light modulation and frequency conversion. |
| 8. | Photochromic and photo refractive polymers | used for optical data storage. |
| 9. | Hole burning polymers | used for optical multiplex and data storage. |
| 10. | Electroluminescent polymers, light emitting polymers and liquid crystalline polymers. | for making large area display. |

### 3. Orthorhombic system

In this system, three axial lengths of the unit cell are not equal but they are perpendicular to each other. (fig. 7.9 (c))

i.e., $a \neq b \neq c$ and

$\alpha = \beta = \gamma = 90°$

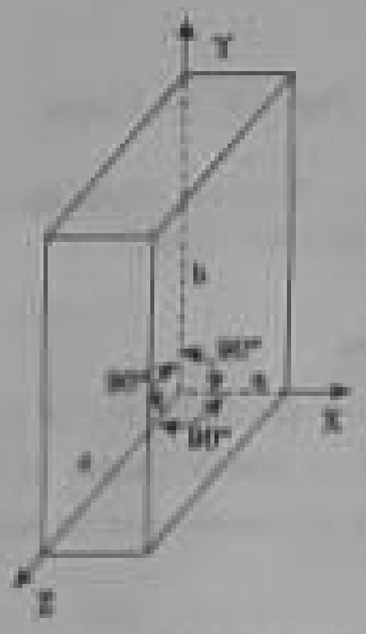



**Fig. 7.9 (c) Orthorhombic**

**Example:** Sulphur, Topaz.

### 4. Monoclinic system

In this system, three axial lengths of unit cell are not equal. Two axes are perpendicular to each other and third axis is obliquely inclined (fig. 7.9 (d))

i.e., $a \neq b \neq c$ and

$\alpha = \beta = 90°, \ \gamma \neq 90°$

**Example:** Sodium sulphite ($Na_2SO_3$).






**Fig. 7.9 (d) Monoclinic**

### Triclinic system

In this system, three axial lengths of unit cell are not equal all the three axes are inclined obliquely to each other (fig (e))

i.e., $a \neq b \neq c$ and

$\alpha \neq \beta \neq \gamma \neq 90°$

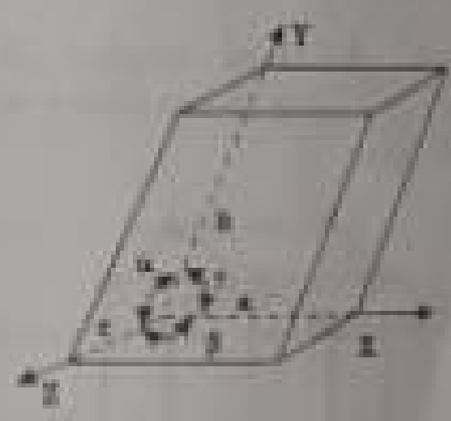



**Fig. 7.9 (e) Triclinic**

**Example:** Copper sulphate ($CuSO_4$).

Potassium dichromate ($K_2Cr_2O_7$)

Ferrous sulphate ($FeSO_4$).

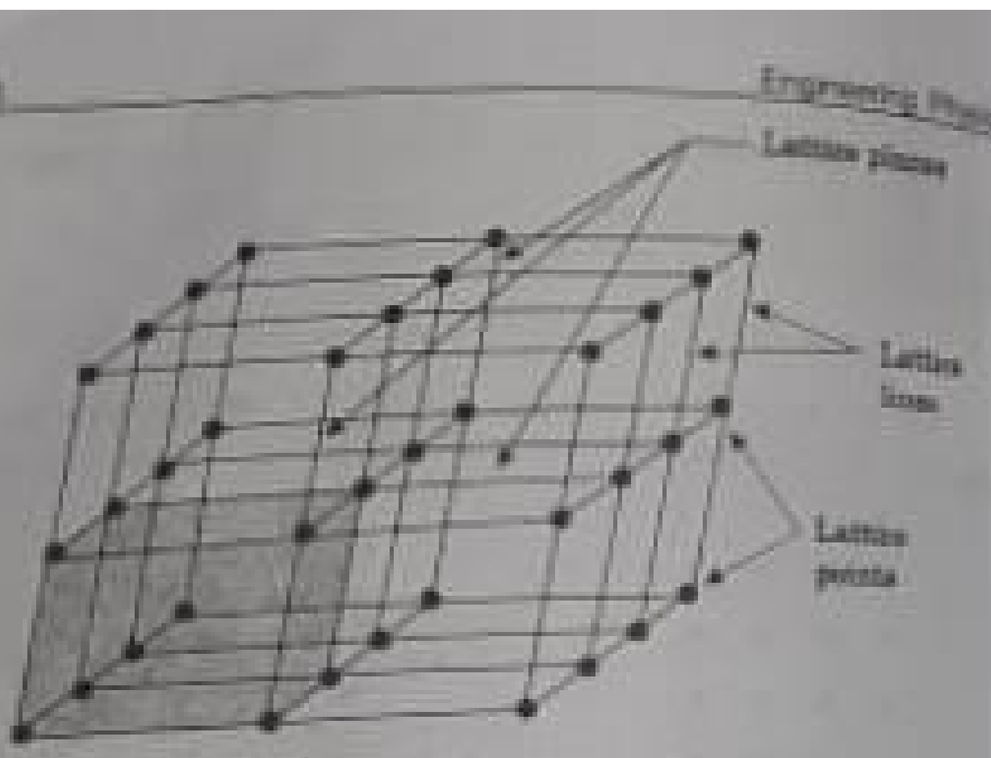



Fig. 7.4 Space lattice in three - dimension

## Basis

### Definition

**The crystal structure is obtained by adding a unit assembly of atoms to each lattice point. This unit assembly is called basis.**

### Explanation

A basis may be a single atom or assembly of atoms which is identical in composition, arrangement and orientation.

When the basis is repeated in a space lattice with correct periodicity in all three directions, then it gives the actual crystal structure.

Therefore, a space lattice combined with a basis gives a crystal structure.

i.e., Space lattice + Basis → Crystal structure

The basis combined with lattice points is shown in fig 7.5 which two atoms represented by circles of smaller and larger are added to one lattice point (represented by a black dot)

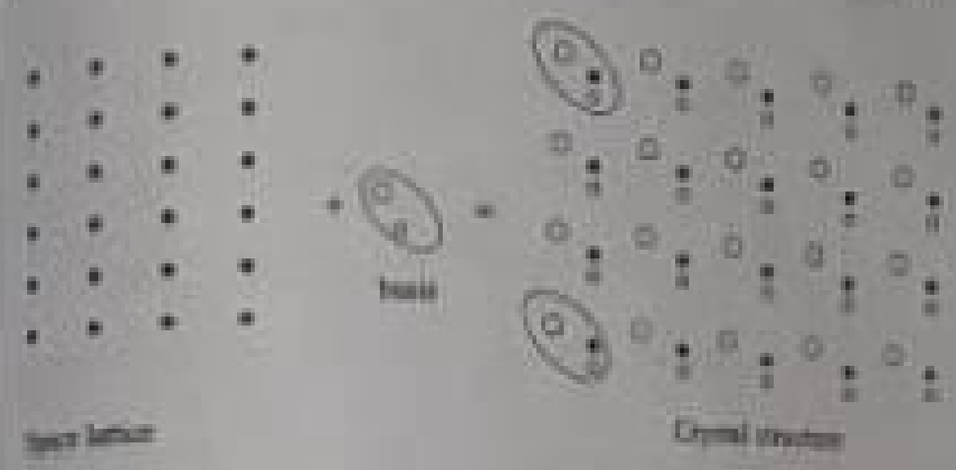



Fig. 7.5 Crystal structure is obtained when a basis is added to each lattice point

For many metals, the number of atoms in basis is one Lithium and Barium crystals, two or three or more

For example in NaCl and KCl each basis has two atoms a $CaF_2$ basis has three atoms. But, for many complicated crystals, the basis exceeds more than 1000 atoms.

Note
Space lattice refers to the geometry of a set of points in space whereas a crystal structure refers to the actual arrangement of atoms in space.

## SINGLE CRYSTALS UNIT CELL

Consider a two - dimensional space lattice as shown in fig 7.6

It is found that when a parallelogram ABCD is repeated an integral multiple of vectors $\vec{a}$ and $\vec{b}$ corresponding to AB and AD, the whole pattern (or array) is obtained.

| | |
|---|---|
| 7. These have high melting points and high boiling points since the ionic bonds are so strong. | The covalent compounds have comparatively low melting and boiling points since the covalent bonds are not as powerful as ionic bonds. |
| 8. Ionic solids are not so hard. | Covalent solids are hard. |
| 9. In crystalline state, the ions are arranged in the lattice by close packing and without directional character. Further the force between ions are equal in all directions. That is why, it is also called hetropolar bond. | The bond is formed in a direction where the shared two electron clouds are overlapping with each other and it has directional character. That is why, it is also called homopolar bond. |

**Examples**

NaCl, MgO, $Al_2O_3$ — Ge, Si, Diamond

**e) Metallic bonds**

It has been found that in metals, each atom loses all its valence electrons and becomes a positively charged ion. These free and mobile electrons form a kind of electron cloud or gas which permeates all atoms. In fact one may look upon a metal as consisting of an array of closely packed ions immersed in a sea of free electrons. The valence electrons are not bonded directly to an individual atom but they move freely in the sphere of influence of other atoms and are bound to different atoms at different times and that too for part of the time.

Thus a metallic bond results from the sharing of variable number of electrons by a variable number of atoms. Thus it may be looked upon as an unsaturated covalent bond which is due to the electrostatic attraction between the negative electron cloud and positive ion cores. The cohesion of a metallic crystal is due to the attraction of the positive nuclei and the valence electrons passing between them. The delocalisation of the valence electrons leads to a decrease in both kinetic and potential energy and it is this energy decrease that is responsible for metallic bonding.

**Examples :** Sodium, Copper, Gold, Silver, Aluminium.

**Properties**

1. Metallic bonds are responsible for holding the atoms together in metals and their alloys.
2. This type of bonding is weaker than Ionic and covalent bonds which are called saturated bonds but stronger than Van der Waals' type.
3. Metallic solids have crystalline structure. Unlike other type of crystals, metallic crystals can be deformed without fracture since the electron gas behaves as a lubricant which permits the atoms to slide fast one another.
4. Metallic crystals possess a high degree of crystal symmetry due to symmetrical arrangements of positive ions.

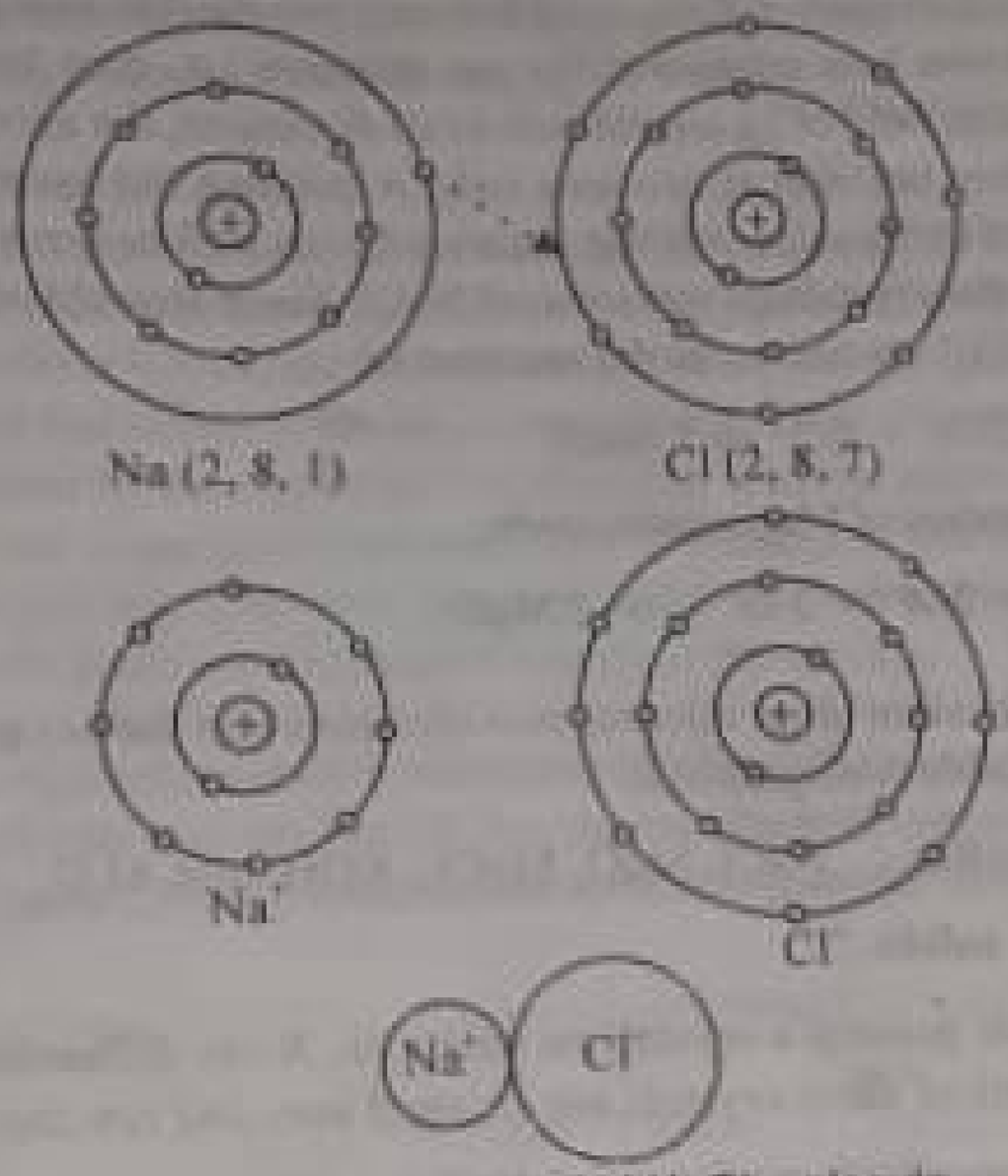



**Figure 2.2** Formation of NaCl molecule

As shown in figure 2.2, sodium has the following electronic configuration.

I orbit (K shell) contains 2 electrons
II orbit (L shell) contains 8 electrons
III orbit (M shell) contains 1 electron

So the first two shells of sodium are complete, but the third is incomplete. In the case of chlorine,

I orbit (K shell) contains 2 electrons
II orbit (L shell) contains 8 electrons
III orbit (M shell) contains 7 electrons

Suppose a chlorine atom and a sodium atom approach one another, Sodium atom can release one electron to get stable configuration and at the same time chlorine atom can accept one electron so as to form a complete electronic configuration in its M shell. The work required to release an electron from the outer shell of sodium is 5.1 eV/atom which is relatively small. The electron affinity of chlorine atom is 3.8 eV/atom.

This process of adding an extra electron to the chlorine atom is accompanied by the appreciable decrease in the potential energy. The energy lost will appear in the form of heat and light during the reaction or formation of NaCl. When sodium atom loses one electron it becomes a positive ion. (i.e. anion) and as chlorine atom gains one electron, it becomes a negative ion (i.e. cation). The ions attract each other with coulombic forces which lead to the

When the distance of separation is $r_0$, the attractive and repulsive forces exactly balance each other and the net force F is zero. This distance corresponds to stable equilibrium with a minimum in the potential energy '$U_0$'. The magnitude of the minimum energy '$U_0$' is called the bond energy. When two atoms form bond, the electrons in the outermost incomplete shell rearrange the nselves so as to reach a stable state by acquiring minimum potential energy. The strength of the bond between two atoms depends upon the energy lost in the process. Bond energy or bonding energy or cohesive energy is defined as the energy of the formation of 1 k mole of a substance from its atoms or ions. It can be calculated as the energy of the atoms or ions at the equilibrium spacing in the crystal structure using the state of infinite separation of the atoms or ions as the zero of potential. Bonding energy is equal but opposite in sign to the energy of dissociation of the substance. The strength of a bond is best measured by the energy required to break it, that is, the amount of heat which must be supplied to vaporize the solid (infinite separation) and hence separate the constituent atoms. Generally the stronger the bond, the higher are the melting and boiling points of the solids. The energy of a bond is usually expressed in electron volt per bond.

## 2.3 Different types of chemical bonds

According to bond strength, chemical bonds can be grouped into primary and secondary bonds. Primary bonds have strengths in the range of 1 to 5 eV and an interatomic separation of 1 to 2 Å. Covalent, metallic and ionic bonds are all primary bonds. Among these, covalent and ionic bonds are stronger than metallic bonds. Secondary bonds have strengths in the range of 0.02 to 0.5 eV and the interatomic distance of separation is larger in the range of 2 to 5 Å These are also called molecular bonds or Vander Waals bonds. Dispersion bonds, Dipole bonds and Hydrogen bonds are good examples for these Vander Waals bonds. Secondary bonds are formed by the forces that are hold the molecules together to form a solid. These are weaker than atomic bonds and do not involve transfer or sharing of electrons between atoms. Usually few materials have pure bonds of one type or the other. But generally we can see mixed bonds. So it is useful to classify materials according to the bond type that is dominant in a given material.

### Ionic or Electrovalent bond

The bond formed between two different atoms, one of which has low ionization energy and the other has high electron affinity, by the transfer of valence electrons from one atom to the other is called Ionic bond. Such bonds are mainly formed in inorganic compounds like NaCl and KOH, etc. and never in pure elements. This bond is naturally the attractive electrostatic force existing between a positive and negative ion when they are brought into a closer distance; these ions are formed when the atoms involved lose or gain electron in order to stablize or complete their outer shell electronic configuration.

Consider the formation of ionic bond in NaCl.

6. Ionic bonds are non-directional so that in an ionic crystal, a cation tends to surround itself by as many anions as possible and vice versa.

## b) Covalent bond or Homopolar bond

A covalent bond is formed when two or more similar or dissimilar atoms achieve stability by sharing valence electrons between themselves. This kind of bonding is possible whenever such sharing results in a lowering of the potential energy of the system. If we take Helium atom ($Z = 2$) which has stable noble gas configuration, there is no decrease in the potential energy of the system by sharing its two 1s electrons with the electrons of another Helium atom. So the Helium atom is monoatomic. But if we take atoms of incompleted quantum states like Hydrogen and Chlorine, they can share electrons among themselves forming their molecules with decrease in potential energy of the system.

Let us examine the origin of covalent bond between the hydrogen atoms in a hydrogen molecule where ionic bond can play no part. If the shared electrons circulate around the hydrogen nuclei as in the figure 2.3, they spent more time on the average between the nuclei.

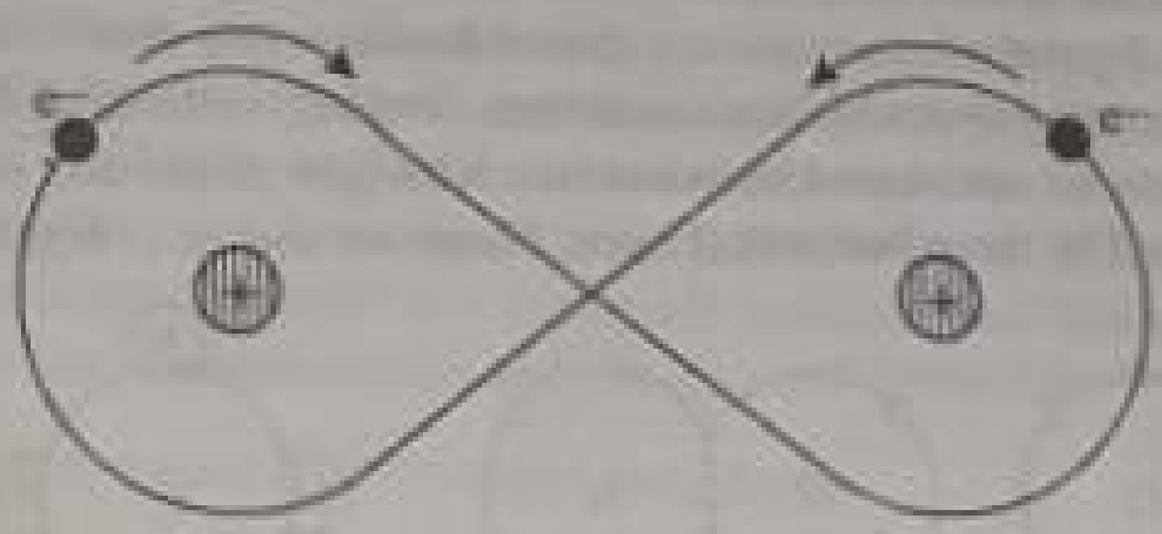


**Figure 2.3** Formation of hydrogen molecule

This is because during the formation of molecule the density of electron distribution increases at points between the nuclei along the internuclear axis. So there is an effective negative charge between the positive charge of nuclei of two hydrogen atoms. This effective negative charge exerts an attractive force on the nuclei which is more than enough to counter balance the direct repulsion between the two nuclei. If the nuclei are too close together however their repulsion becomes dominant and the molecule is not stable. The balance between attractive and repulsive force occurs at a separation of 0.74 Å and hence the covalent bond exists with decrease in potential energy of the system. Hence some energy must be spent to break the covalent bond of hydrogen molecule into hydrogen atoms. Actually 4.5 eV is required to break one H-H bond.

i.e. $$H_2 + 4.5\ eV \rightarrow H + H$$

The number of covalent bonds that can be formed by an element is determined by the number of electrons that can be added to the valence shell without exceeding 8. Therefore the maximum number of covalent bonds is $(8 - N)$ where N is the number of valence electrons.

The hydrogen molecule is represented as

$$H - H \rightarrow H_2$$

Here the horizontal single line between two hydrogen atoms indicates that one electron comes from each atom. In the case of chlorine, each atom has seven electrons in the outer shell. When two chlorine atoms combine to form a molecule, one electron from each atom is shared with the other atom. Thus

$$Cl - Cl \rightarrow Cl_2$$

The formation of Hydrogen Chloride gas can be written as

$$H - H + Cl - Cl \rightarrow H - Cl + H - Cl \rightarrow 2HCl$$

Here one hydrogen atom and one chlorine atom combine and form a hydrogen chloride molecule with decrease in potential energy of the molecule by sharing one electron from each atom. Let us see some other examples where two or more electrons are shared between two or more similar or dissimilar atoms. When more than one pair of electrons is shared between two atoms a double (or) triple covalent bond is said to be formed. In the case of oxygen molecule 2 pairs of electrons are shared between two atoms and so it has double bond which is represented by double horizontal lines. Similarly in the case of Nitrogen molecule, three pairs of electrons are shared between two Nitrogen atoms and so it has triple bond which is represented by three horizontal lines. These are shown in figure 2.4.

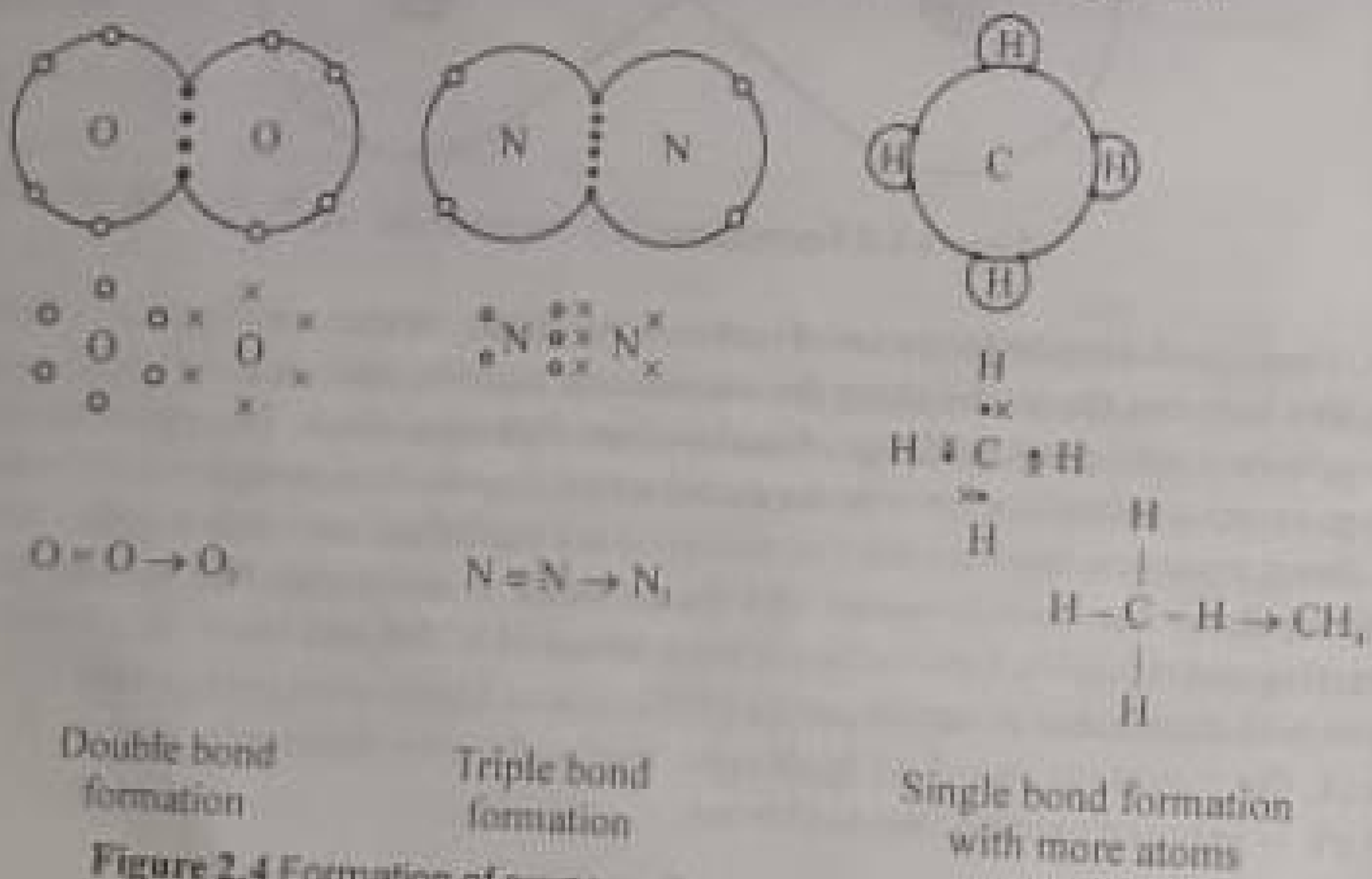



**Figure 2.4** Formation of oxygen, nitrogen and methane molecules

The bonding of methane ($CH_4$) molecule is also shown in figure 2.4. Carbon has 4 valence electrons. Each of these electrons forms an electron pair with the 1s electrons of the four surrounding hydrogen atoms. Diamond is another example of crystal structure in which carbon atoms are linked by covalent bonds. Each carbon atom shares its four valence electrons

with those of neighbouring atoms thus forming single valence bonds with each of them. Following additional points about covalent bond formation are worth nothing:-

i. attainment of noble gas or octet configuration is not essential in such a bond.

ii. the essential feature of such a bond is the fact that it involves the pairing of two electrons with opposite spin.

iii. a covalent bond may be either polar or non polar depending on the fact whether the electron pair is shared unequally or equally between the two atoms.

**Examples of covalent substances :**

Gases : Hydrogen, Carbon di oxide, Nitrogen
Liquid : Carbontetrachloride
Solids : Diamond, Germanium, Silicon, Tin

***Properties of covalent substances***

1. The covalent crystals of different materials have very large difference in their physical properties due to their bonding types. For example, carbon in the diamond structure is the hardest known substance having a high melting point (3280 K). (But the hardness and melting point then decrease as we proceed to other elements in column IV of the periodic table from silicon to lead). But tin is very soft and has a low melting point. Similarly Diamond is a very good insulator. But Silicon and Germanium are well known semiconductors and Tin is a good conductor.

2. The covalent crystals are of three types

i. those in which molecules are small and held together by weak forces. Such crystals are soft and easily fusible.

**Examples :** Sulphur and Iodine.

ii. those in which each atom is united with the other by covalent links resulting in the formation of giant molecules.

**Examples :** Diamond and Silicon Carbide.

In diamond, each atom is united by covalent bonds with four neighbouring carbon atoms held at the corners of a regular tetrahedron.

iii. those which consist of separate layers such as graphite. Here carbon atoms are arranged in regular hexagons in flat parallel layers, such that each atom is linked by the neighbouring atoms. However there is no strong bonding between different layers, which are therefore easily separable from each other. This is the cause of softness and lubricating action of graphite.

3. Based on the number of electrons sharing, the bond length and bond energy also change in their values. When the number of electrons shared is more, the bond length between the bond is decreased and at the same time the bond energy is increased.

formation of an electrovalent or ionic bond between two neighbouring Na and Cl atoms. At the same time, the two ions achieve noble gas structure i.e., they have their shells filled. Since the electrostatic field of an ion extends in all directions, the above process of $Na^+$ ion attracting Cl ion does not stop at two ions only. A positive Na ion will be surrounded by negative Cl ions and in the same way the negative Cl ion will be surrounded by positive Na ions. This leads to the crystalline structure of NaCl. Since free chlorine exists only in the form of molecule '$Cl_2$' we can write the reaction as

$$2Na + Cl_2 + 2Na^+ + 2Cl^- \rightarrow 2\,NaCl$$

Similarly in the formation of Magnesium oxide,

$$2\,Mg + O_2 \rightarrow 2M^{++} + 2\,O^{--} \rightarrow 2\,MgO$$

Here the Magnesium atom releases two electrons and the oxygen atom accepts two electrons to form a stable configuration.

**Examples of ionic solids :** NaCl, MgO, $MgCl_2$, KOH, and $Al_2O_3$

**Properties of ionic solids**

1. All ionic solids possess a crystalline structure. X-ray diffraction studies show that the constituents of these crystals are charged ions and not atoms.
2. Ionic solids have high melting and boiling points (above 300°C). It is because considerable external energy is required to overcome the electrostatic forces existing between the ions in such a solid.
3. Ionic solids are hard and brittle.
4. Pure and dry ionic solids are good insulators because all the electrons are tightly bound with the ions involved in the bond formation. However such solids show electrical conductivity when heated or dissolved in solvents like water. At high temperatures, the electrostatic forces between the ions are greatly reduced so that some of the ions themselves transport the charge in the material. In other words, ions are the charge carriers (not electrons as is the case with metals). Since the ionic mobility increases with temperature, the electrical conductivity of ionic solids also increases with temperature. Similarly when an ionic solid is dissolved in water, the electrostatic forces are considerably weakened due to high permittivity of water. The result is that the ions become free and wander about in the solution. If now a potential difference is applied, these ions will themselves carry the charge in the solution. This is known as electrolysis.
5. Ionic solids are soluble in polar solvents like water and liquid ammonia. This is because the molecules of the polar solvent interact stroogly with the ions so as to reduce the attraction between the ions. Also, the polar solvent possesses high dielectric constant, for example, water has a high dielectric constant of 80. i.e. water will reduce the electrostatic force of attraction between the ions to 1/80 of the original value. Ionic solids are insoluble in nor polar solvents like benzene and carbon tetrachloride because their dielectric constants are very low.


**Figure 2.5** (b) Polar molecules : $H_2O$ and $NH_3$

5. Covalent bonds are always directional and thus a change in the direction of the bond will result in the formation of a different substance.
6. Covalent substances are soluble in non polar solvents like benzene and carbon di sulphide, etc. This is because of the covalent nature of the solvent. However covalent bonds with giant molecules are not soluble in any solvent because of the large size of the molecules.
7. The melting and boiling points of covalent solids are usually low as compared to those of ionic compounds. This is because the covalent bond is not so strong as the ionic bond and also the electrons are less powerfully attracted towards each other.
8. Most of the pure covalent solids are good insulators. This is because all the valence electrons are tightly held in the covalent bonds. However when certain impurities are added to such solids, they become semiconductors.
9. Covalent compounds may be solids, liquids or gases. Generally those substances which have high molecular weights exist as solids. Covalent solids are hard as well as brittle and possess crystalline structure.

**Difference between Ionic and Covalent bonds**

| Ionic Bond | Covalent Bond |
|---|---|
| 1. Ionic bond is formed between two atoms by transfer of electrons from one atom to other atom. | Covalent bond is formed between two atoms when they share one or more pair of electrons between them. |
| 2. These bonds are non directional. | These bonds are directional. |
| 3. Ionic compounds are soluble in polar solvents. | Covalent compounds are soluble in nonpolar solvents. |
| 4. Ionic compounds are existing only in the form of solids. | Covalent compounds are existing in solids, liquids and gases. |
| 5. All ionic compounds are existing in crystalline structure. | Only the covalent solids are existing in crystalline structure. |
| 6. Electrical conductivity is increased when they are dissolved in polar solvents. | Electrical conductivity is increased by suitable doping of impurities. |

| Bond | Bond length Å | Bond energy kJ/k mole × $10^3$ |
|---|---|---|
| H – H | 0.74 | 437.6 |
| Cl – Cl | 2 | 243.6 |
| C – C | 1.5 | 349 |
| C = C | 1.3 | 613.2 |
| C ≡ C | 1.2 | 817 |
| C – O | 1.5 | 352.8 |
| C = O | 1.2 | 751.8 |

4. Due to bond formation, dipole moment arises. For example in the covalent bonded hydrogen chloride molecule the net effect of the electron sharing process is to give the chlorine atom has a slight negative charge while the hydrogen atom has a corresponding slight positive charge. The charges are actually small being of $0.272 \times 10^{-19}$ coulomb compared with $1.6 \times 10^{-19}$ coulomb for a single electron. The spacing of the atoms in that molecule is 1.27 Å resulting a dipole moment of $0.343 \times 10^{-29}$ coulomb metre or 1.03 Debye unit. 1 Debye unit $= \frac{1}{3} \times 10^{-29}$ coulomb metre.

A molecule may contain dipoles but it may produce zero dipole moment if the bonds are distributed symmetrically so that the individual dipoles cancel each other. Such a molecule is called a nonpolar molecule. Carbon di oxide and carbon tetrachloride are examples for the nonpolar molecules.


Zero dipole moment in $CO_2$ Zero dipole moment in $CCl_4$

**Figure 2.5** (a) Non polar molecules : $CO_2$ and $CCl_4$

In the case of carbon di oxide molecule, due to symmetrical arrangement of carbon atom with oxygen atoms, the resultant dipole moment in that molecule is zero. Similarly in Carbon tetrachloride molecule the resultant dipole moment is zero because carbon atom is symmetrically surrounded by the chlorine atoms. But in polar molecules which have non symmetrical distribution of bonds like $H_2O$ and $NH_3$ there is a resultant dipole moment in each molecule.

In an atom or molecule the centres of positive charges and negative charges coincide with each other as shown in figure 2.6(a). But it has been observed that at certain times, i.e., when the inert gas is cooled and solidified, the distribution of electrons in the atom or molecule is not symmetrical around the nucleus. This results in the displacement of the centres of positive and negative charges as shown in figure 2.6(b). The electronic imbalance of the charges in an atom or molecule is known as polarisation. This polarisation is of the fluctuating nature and is known as dispersion effect. Due to this effect, there exists a weak force of attraction between the two atoms of the same element and a bond called dispersion bond is formed between them. For example, if we take a noble gas like Helium, it has stable electronic configuration in its outermost shell. In such a stable condition, the primary bonds cannot be formed because they all require adjustment of valence electrons which is not possible in the case of noble gas. Consequently Helium gas remains monoatomic under ordinary temperature and pressure conditions. Helium gas condenses only at extremely low temperatures when the thermal agitation of its atoms is considerably reduced. Obviously this condensation could not have taken place if there were no interatomic forces. So helium gas condenses into liquid at extremely low temperatures due to weak interatomic forces called Van der Waals' forces. This will be true for all inert gases like neon and argon. Thus the molecules of noble gases which consist of single atoms are held together by dispersion bonds when they are solidified at very low temperatures.

**Properties**

1. Molecular solids may be crystalline or non crystalline. Their structural units are molecules. Moreover as these crystals are formed of elements with low atomic numbers, they have low densities.
2. Because of weak molecular bonds arising out of Van der Waals' forces, such solids have low melting points. For example, the melting point of solid neon is –249°C. Its bond length is equal to 3.2 Å and its bond energy is equal to $7.8 \times 10^3$ kJ/k mole. Therefore these type of bonds are very weak.
3. Because in such solids no valence electrons are available, they are good insulators.
4. They are usually transparent to light.
5. They are soluble in both polar and non polar liquids.
6. Dispersion bonds are non directional.

**b) Dipole bond**

Dipole bond is formed between molecules having permanent electric dipoles. The permanent dipoles are arising due to unequal sharing of electrons between the two atoms. Let us consider the formation of hydrogen fluoride molecule by electron sharing. The hydrogen atom has only one electron in its outermost energy level and the fluorine atom has 7 electrons in its outermost energy level. The hydrogen atom requires one more electron to acquire stable configuration and fluorine atom also requires one more electron to acquire stable

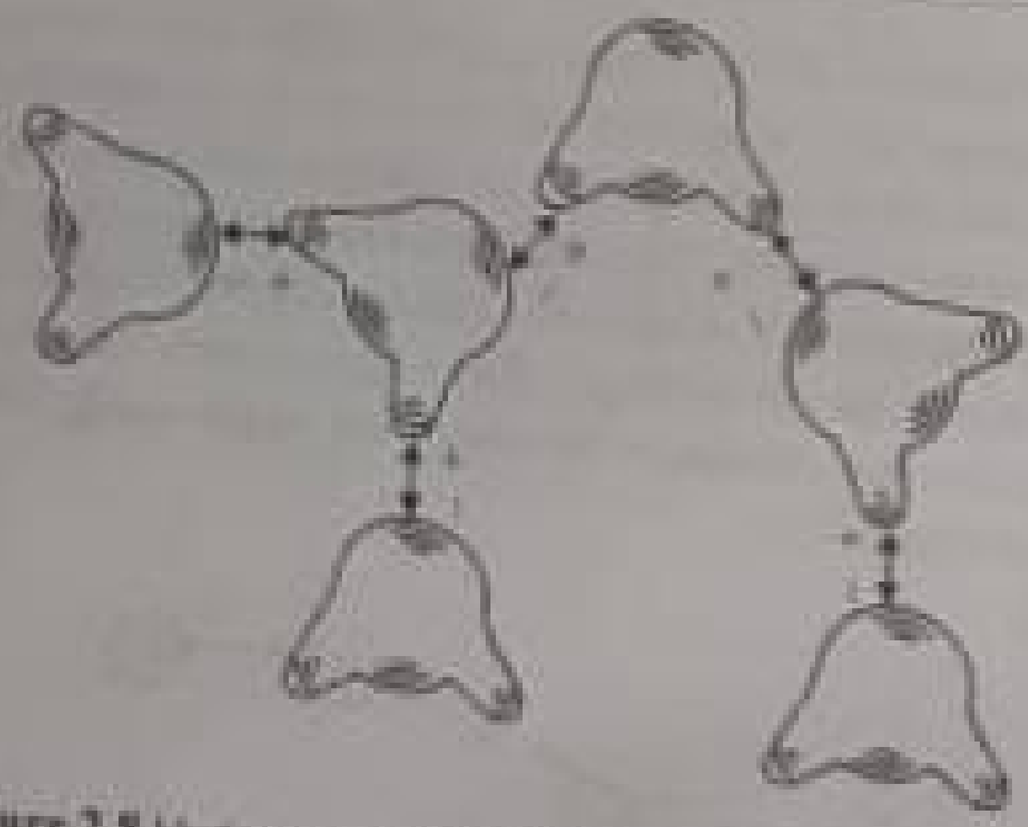


**Figure 2.8** Hydrogen bond between water (ice) molecules

The bond that is formed between ice or water molecules due to attraction between the positively charged hydrogen end of a molecule and the negatively charged Oxygen end of another molecule is called the hydrogen bond. It is also one of the molecular bonds. We can see this type of bond in ammonia molecules also.

**Properties**

1. The bond between water molecules is strong enough to persist in the liquid state. It is responsible for the unusual properties of ice and water. For example, the relatively open network of hydrogen bonds in ice as shown in figure 2.6 collapses to a more closely packed liquid, accounting for the anamalous increase in density on melting.
2. The hydrogen bonds are directional.
3. Hydrogen bonded solids have low melting points. We know that the melting point of ice is 0°C.
4. Because in such solids no valence electrons are available they are good insulators.
5. They are transparent to light since there are no free electrons.
6. They are soluble in both polar and non polar solvents.
7. Such solids may be crystalline or non crystalline. Moreover as these solids are formed of elements of low atomic numbers, they have low densities.
8. These bonds are stronger than dispersion bonds but are weaker than primary bonds. Thus these bonds have enough strength to exist in liquid and gaseous states.

**Lattice energy of ionic crystals**

The binding energy of a crystal will give the information about the mechanical and other properties. To calculate the binding energy of a crystal, we must know the different types of forces acting between the elements which create the lattice. One can calculate the binding energy of an ionic crystal using simple ideas. Let us calculate the binding energy of

configuration. Therefore both the hydrogen and fluorine atoms share a pair of electrons to acquire stable configuration. This leads to the formation of covalent bond and the resultant molecule formed is called hydrogen fluorine. In this covalent bond, the fluorine atom has a high affinity than the hydrogen atom. Thus the shared electron pair shifts towards the fluorine atom. This shifting of electron pair produces an electric dipole. Similar dipoles are formed in adjacent molecules also. Adjacent hydrogen fluoride molecules therefore attract each other by means of the electrostatic attraction between their oppositively charged ends and the dipole bond is formed (figure 2.7).

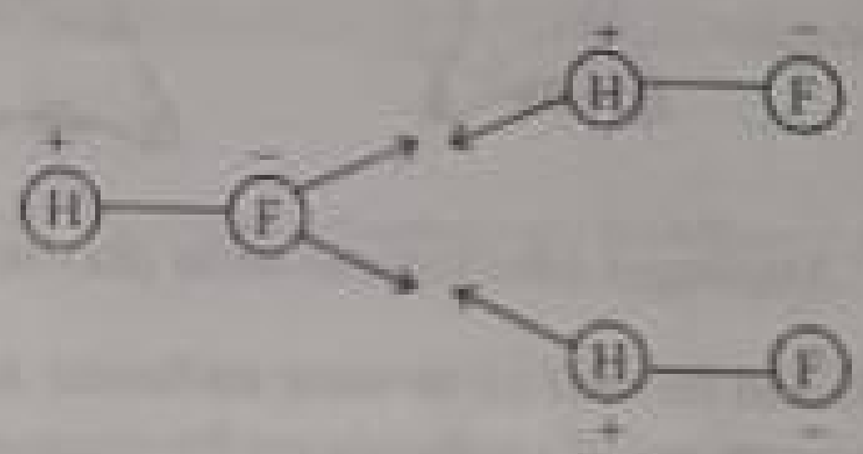



**Figure 2.7** Formation of dipole bond

We can see the dipole bond in HCl, $SO_2$ and HBr.

**Properties**

1. Dipole bonds are much weaker than primary bonds but that are stronger than dispersion bonds.
2. These are directional.
3. Because in such solids no valence electrons are available they are good insulators.

**c) Hydrogen bond**

A hydrogen bond is a particular type of dipole bond in which one of the atom is a hydrogen atom. The other atom has a high affinity to attract electron from the hydrogen atom. Thus it is a special type of dipole bond made between similar molecules, each molecule having one end as a hydrogen atom converted into a positive ion by a strongly electronegative adjacent atom in the same molecule. Hydrogen bond is formed by a hydrogen ion located between two anions. Since hydrogen has only one electron it can lose it to either of the two adjoining ions with the result that there is an equal probability of finding the electron on either ion. The positive hydrogen ion tends to draw the two anions more closely together than their normal separation in crystals so that such a shortening of their interatomic separation serves to indicate the presence of a hydrogen bond.

5. Metallic bond is non directional since this bond can exist only when there is large aggregate of metallic atoms.
6. Since the metallic bonds are weak, the melting point and boiling point are lower than the Ionic and Covalent compounds.
7. Since there are enormous number of free electrons, these type of materials have high thermal and electrical conductivity.
8. Metals are opaque to light since the light energy is absorbed by the free electrons.

## Secondary bonds

Now let us see the different types of secondary bonds or molecular bonds.

### a) Dispersion bond

Dispersion bond occurs between molecules when there is a formation of oscillating dipoles on them. Thus it is one of the molecular bonds. This bonding occurs for those elements or compounds whose electron configuration is such that little electron transfer takes place between their atoms. Consequently in their case, the three primary bonds considered above cannot be formed.

This type of bonding results from the momentary fluctuations in the spherical charge distribution around the nucleus. Even though the time averaged electron probability distribution is spherically symmetric, the electronic charge at any instant of time is concentrated locally resulting in a weak fluctuating dipole within the atom. The electric field of this imbalance in charge can induce a dipole moment in a neighbouring atom, in such a way as to attract it. The dipole in the second atom can then induce a dipole in the third atom and so on. This dipole induced dipole interaction energy varies as the reciprocal of the sixth power of the distance between the two atoms. But when the atoms are close enough, then there is a repulsion between the atoms. So the variation of potential energy during the bond formation is

$$W = -\frac{A}{r^6} + \frac{B}{r^{12}}$$

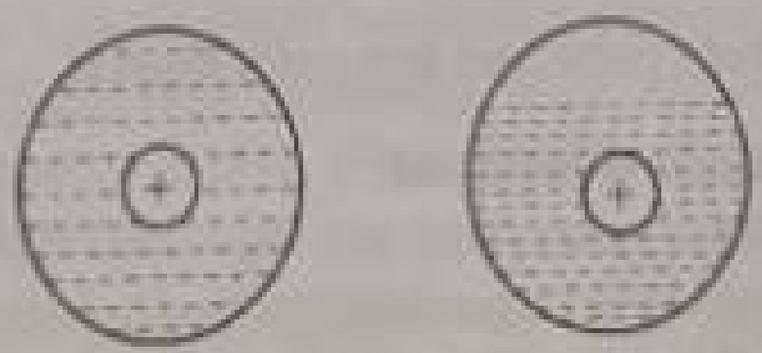



**Figure 2.6** Dispersion bond formation
(a). Same centre for +ve nuclear and negative electron cloud
(b). Different centres for +ve nucleus and negative electron cloud

# 7. Crystal Physics

**Single crystalline, polycrystalline and amorphous materials – Single crystals unit cell, crystal systems, Bravais lattices, directions and planes in a crystal, Miller indices – interplaner distances – coordination number and packing factor for SC, BCC, FCC, HCP and diamond structures – crystal imperfections point defects, line defects – Burger vectors, stacking faults – role of imperfection in plastic deformation – growth of single crystals solution and melt growth techniques.**

## Introduction

Materials differ from one another in their properties. Some solids are brittle, some are ductile, some are malleable, some are strong, some are weak, some are good conductors of heat and electricity, some are bad-conductors of heat and electricity, some are magnetic, some are non-magnetic and so on.

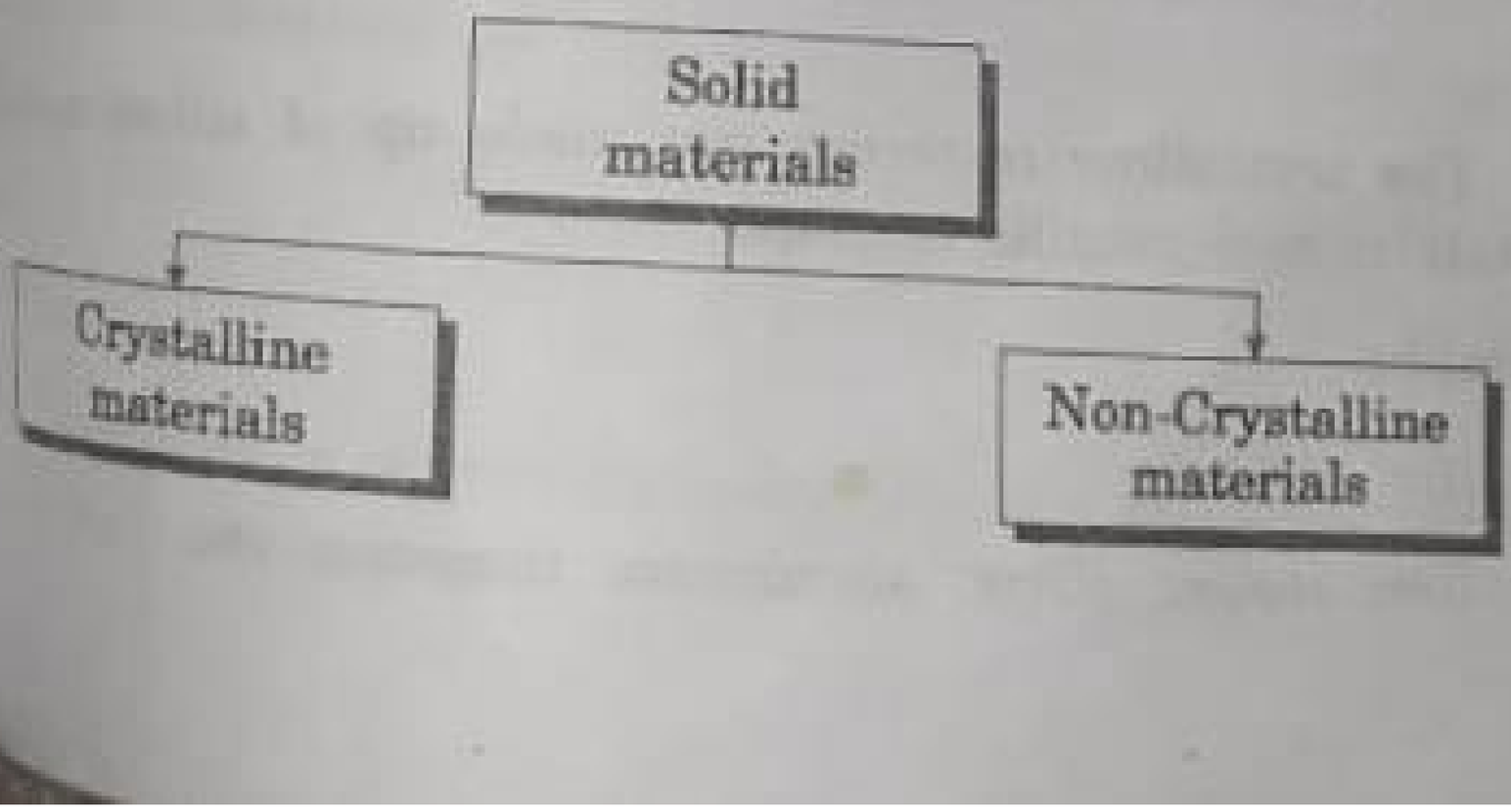
The differences in the properties of the various solids are due to their structures. The behaviour of a solid material is related to its crystal structure.

## Classification of Solids

From the crystal structure point of view, the solid materials are broadly classified as

(i) **Crystalline materials** and

(ii) **Non - Crystalline or Amorphous materials**



**(i) Crystalline materials**

**The materials in which the atoms are arranged in a systematic pattern (regular pattern) are known as crystalline materials.**

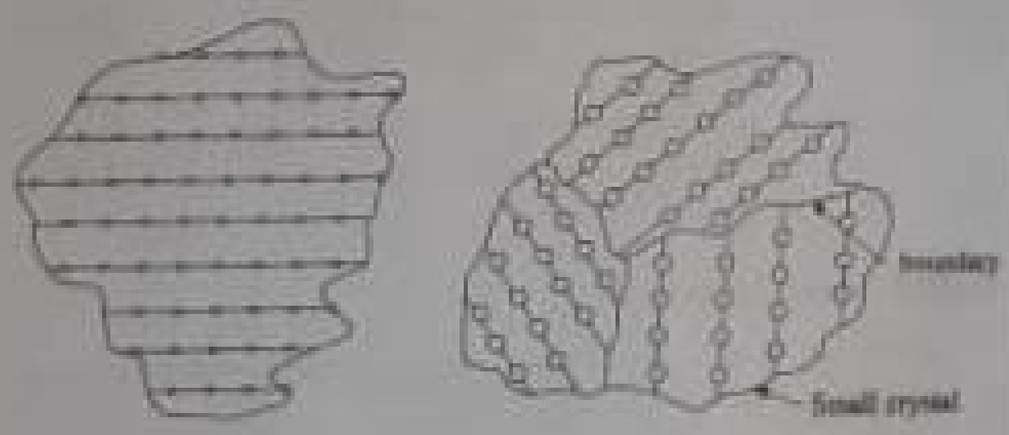
*In these materials, the arrangement of atoms is in a periodically repeating pattern.*

## 7.1 SINGLE AND POLY CRYSTALLINE MATERIALS

The crystalline material is either a **single crystal** or **poly - crystal**. In single crystal, the entire material consists of only one crystal. (Fig. 7.1 (a))

In poly - crystal material, a collection of many small crystals is separated by well-defined boundaries. (Fig. 7.1 (b))

The atomic arrangements of single crystal and poly - crystal are shown in fig 7.1 (a) and (b)




(a) (b)

**Fig. 7.1 Atomic arrangement**
**(a) single crystal (b) poly - crystal**

The crystalline materials are made up of either metallic crystals or non-metallic crystals.

**Example**

**Metallic crystals**

*Iron, copper, silver, aluminium, tungsten, etc.*



**...metallic crystals**

*Crystalline carbon, germanium, silicon, crystallised ..., etc.*

## (ii) NON-CRYSTALLINE OR AMORPHOUS MATERIALS

**Amorphous means without form.**

**The materials in which atoms are arranged in an ...(random) fashion are known as non-crystalline ...amorphous materials.**

**...ple**

*Glass, rubber and plastics*

**The arrangement of atoms in non - crystalline materials is ...ressions is shown in fig. 7.2.**

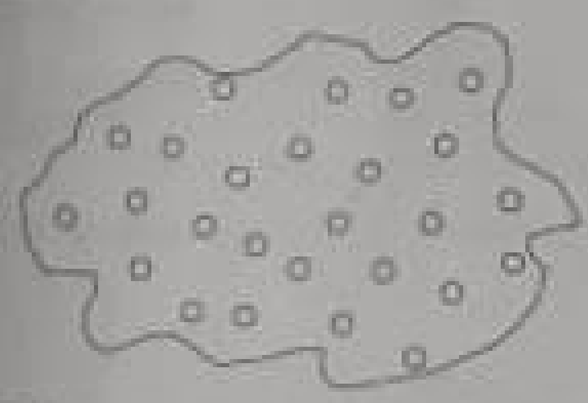


**Fig. 7.2 Non - crystalline or Amorphous material**

**...llographic terms**

*...et us understand some of the important crystallographic ...*

**...al**

***...rystal is a three-dimensional solid which consists ...eriodic arrangement of atoms.***

## Crystal structure

***The arrangement of atoms in a crystal is known as crystal structure. It is the basis for understanding the properties of materials.***

## Crystallography or Crystal physics

***The branch of physics which deals with the internal structure, properties, external or internal symmetries in a crystal is known as crystallography or crystal physics.***

## Space Lattice

A crystal is an array of atoms in three dimensions. As a matter of convenience, these atoms can be associated with a set of imaginary points in space.

These points are arranged in such a way that every point has an identical surrounding as any other point in three dimensions and it is known as a **space lattice or simply lattice**.

Lattice is an imaginary geometrical concept. It is a large assembly of points in which each point represents the position and orientation of an atom in the crystal.

**Note:** In 2 dimensions, the arrangement of points is only in 2D (X & Y).

### Definition

**Space lattice is an array of points in space to represent atoms in a crystal in which the environment about each point is the same i.e., every point has identical surroundings as that of every other point in the array.**

### Explanation

The collection of points in two dimensions is shown in fig. 7.3 (a) and (b).

It is found that in fig 7.3 (a) the environment (position of neighbouring points) about any two points is same. Hence, it is a 2D lattice.





The mathematical representation of a 2D lattice is $\vec{T} = l\vec{a} + m\vec{b}$ where $l$ and $m$ are integers, $\vec{a}$ and $\vec{b}$ are the translation vectors in X and Y directions.

For example $\vec{T} = \vec{AB} = 2\vec{a} + 2\vec{b}$ as shown in fig 7.3 (a).

On the other hand, in fig. 7.3 (b) the environment about any two points is not the same. So, it is not a proper lattice.

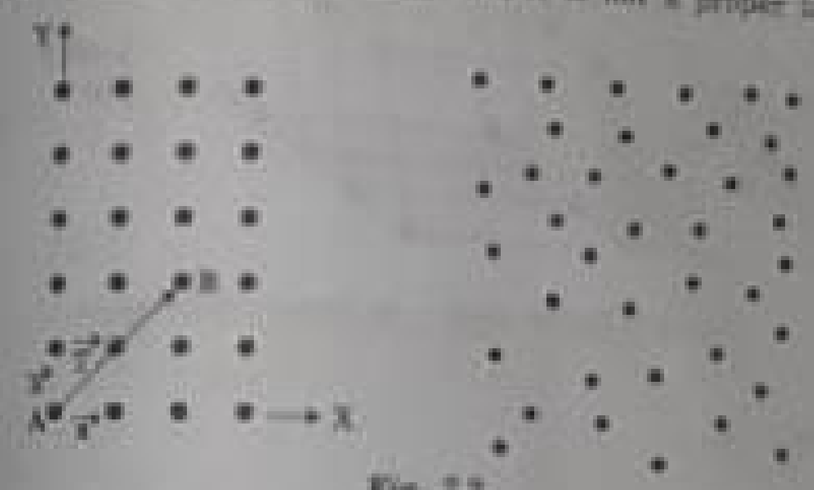



Fig. 7.3

**(a) Two-dimensional lattice** **(b) Two-dimensional collection of points but not a space lattice**

A similar argument is extended to three-dimensional space also. For 3D, $\vec{T} = l\vec{a} + m\vec{b} + n\vec{c}$ such that $\vec{a}$, $\vec{b}$ and $\vec{c}$ are the translation vectors.

### ...ice points

...points in a space lattice are called **lattice points** (Fig. 7.4)

### ...ice lines

The lattice points are joined with lines as shown in fig. These lines are known as **lattice lines**.

### ...ice plane

A plane containing lattice points is known as **lattice ...** (Fig. 7.4)

In fig 7.8, the axial lengths OA = a, OB = b and OC = c are known as intercepts a, b and c along three axes.

**Interfacial angles**

**The angles between three intercepts ($\alpha$, $\beta$ and $\gamma$) are called interfacial angles.**

**The three intercepts and three interfacial angles are the lattice parameters of the unit cell. They determine the actual size and shape of the unit cell:**

**(a, b, c) – axial lengths, ($\alpha$, $\beta$, $\gamma$) – interfacial angles**

## 7.4 CRYSTAL SYSTEMS

**There are '7' types of crystal systems. They are**

1. **Cubic**
2. **Tetragonal**
3. **Orthorhombic**
4. **Monoclinic**
5. **Triclinic**
6. **Rhombohedral**
7. **Hexagonal**

### 1. Cubic system

In this crystal system, all the three axial lengths of the unit cell are equal and they are perpendicular to each other (fig. 7.9 [a])

i.e., $a = b = c$ and

$\alpha = \beta = \gamma = 90°$



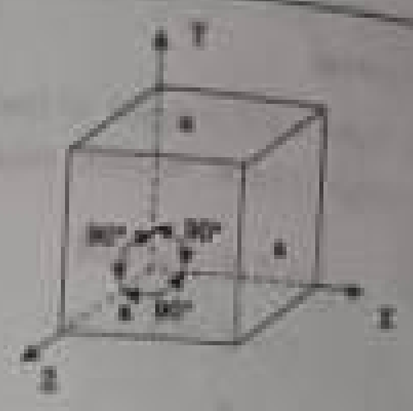



**Fig. 7.9 (a) Cubic**

ample: Iron, Copper, Sodium Chloride (NaCl), Calcium Fluoride ($CaF_2$).

### Tetragonal system

In this system, two axial lengths of the unit cell are equal third axial length is either longer or shorter (fig. 7.9 [b]) the three axes are perpendicular to each other.

i.e., $a = b \neq c$ and

$\alpha = \beta = \gamma = 90°$

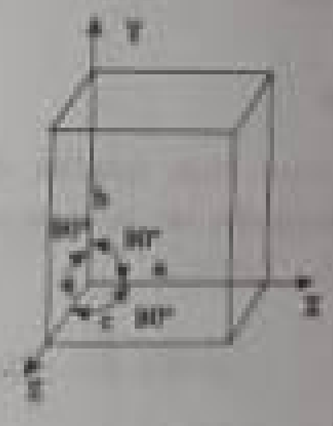



**Fig. 7.9 (b) Tetragonal**

ample: White tin, Indium

**The region ABCD is known as unit cell. $\vec{a}$ and $\vec{b}$ are basis vectors.**

The choice of the unit cell is not unique. It can be constructed in a number of ways like A' B'C'D' or A" B" C"D" without affecting the symmetry of the crystal (fig. 7.6).

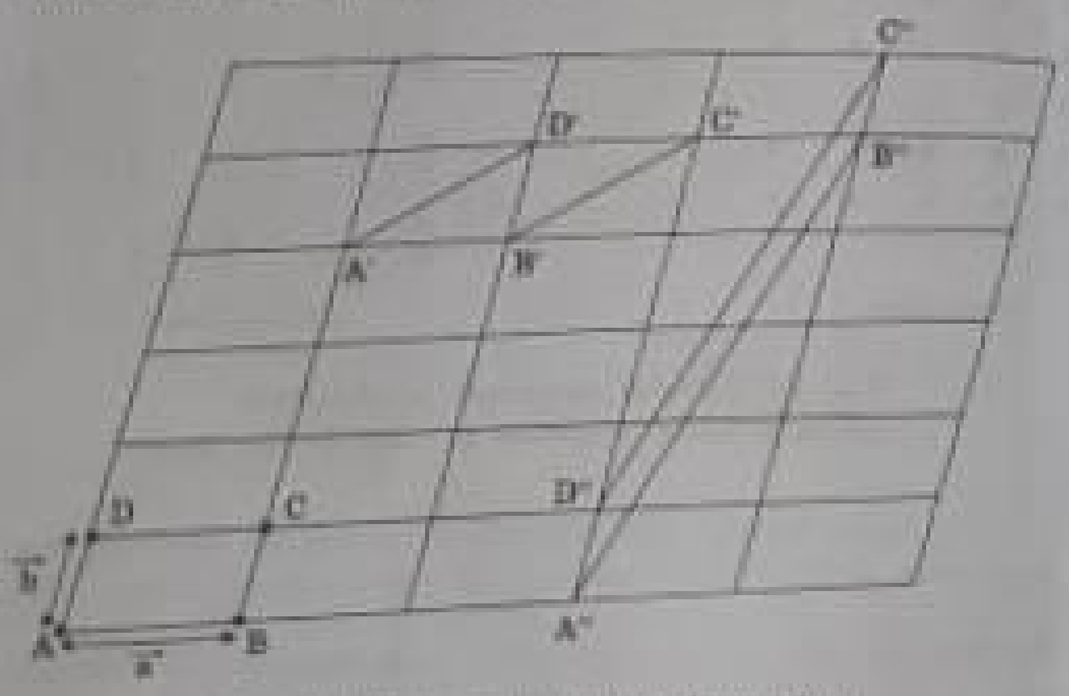



**Fig. 7.6 Unit cell in two-dimension**

**Definition**

**The unit cell is defined as the smallest geometric figure which is repeated in three dimensions to derive the actual crystal structure.**

The unit cell fully represents the characteristics of the entire crystal.

The same principle is extended for a three-dimensional case. A unit cell in three-dimensions is shown fig. 7.7.

**It is also defined as the smallest volume of a solid from which the entire crystal structure is constructed by translational repetition in three-dimensions**



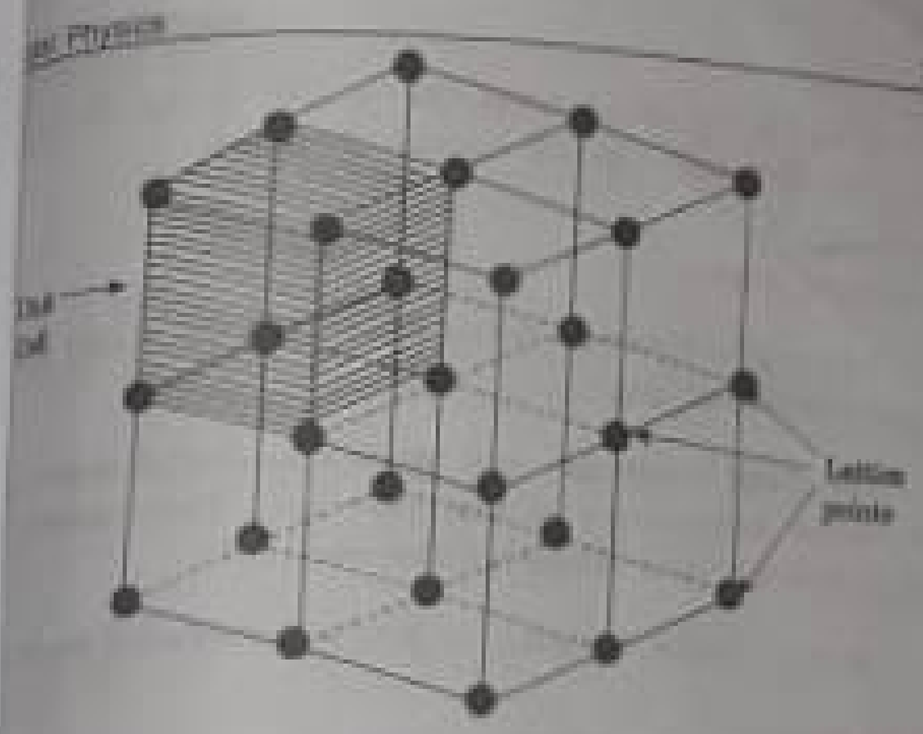
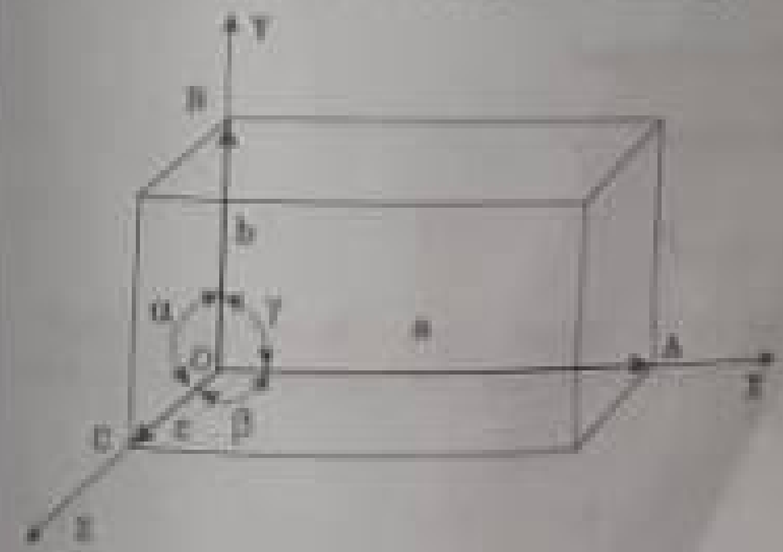



**Fig. 7.7 Unit cell in three-dimensions**

*ice parameters of the unit cell*

e unit cell is constructed if the distance between two ghbouring lattice points along three directions and angles ween them are known.

The distance between two neighbouring lattice points is the of the unit cell. The lengths OA, OB, OC in three axes OY and OZ are the **axial lengths or intercepts** (Fig. 7.8)



**(ii) Body - centred tetragonal lattice**

It has lattice points at all 8 corners of the unit cell and one lattice point at the body centre as shown in fig. 7.10 (b).

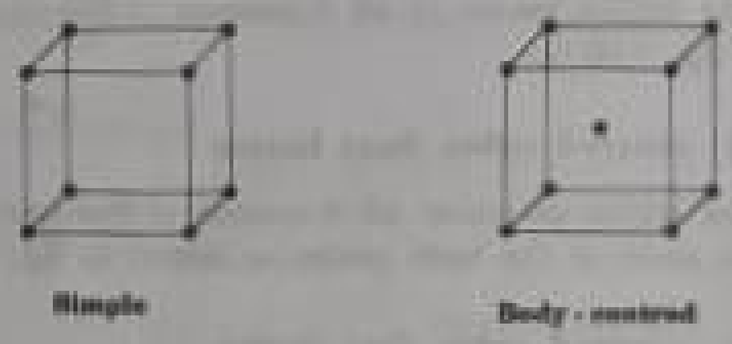



**Fig. 7.10 (b) Tetragonal lattice**

**3. Orthorhombic lattice**

It has four possible types of lattices.

**(i) Simple orthorhombic lattice**

It has lattice points at all 8 corners of the unit cell as shown in fig. 7.10 (c).

**(ii) Body - centred orthorhombic lattice**

It has lattice points at all 8 corners of the unit cell and one lattice point at the body centre as shown in fig. 7.10 (c).

**(iii) Face - centred orthorhombic lattice**

It has lattice points at all 8 corners of the unit cell and one lattice point at the each face centre of the 6 faces of the unit cell as shown in fig. 7.10 (c).

**(iv) Base - centred orthorhombic lattice**

It has lattice points at all 8 corners of the unit cell and 2 lattice points each at the centre of two faces (base) opposite to each other as shown in fig. 7.10 (c).



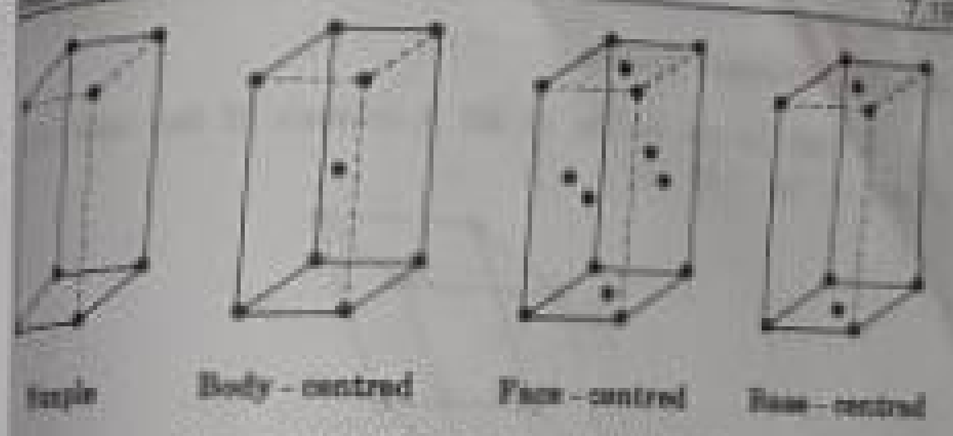



**Fig. 7.10 (c) Orthorhombic lattice**

**...noclinic lattice**

It has two possible space lattices.

**Simple monoclinic lattice**

It has lattice points at all 8 corners of the unit cell as ...es in fig. 7.10 (d).

**Base - centred monoclinic lattice**

It has lattice points at all 8 corners of the unit cell and ...attice points each at the centre of two faces (faces of the ...e opposite to each other as shown in fig. 7.10 (d).

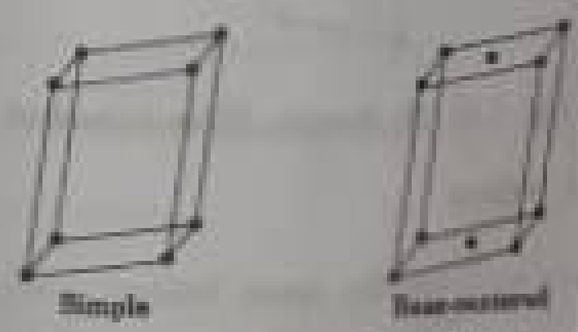



**Fig. 7.10 (d) Monoclinic lattice**

**Triclinic lattice**

It has only one possible space lattice.

### 6. Rhombohedral system (Trigonal)

In this system, three axial lengths of the unit cell are equal. They are equally inclined to each other at an angle other than 90° (Fig. 7.9 (f)).

i.e., $a = b = c$ and

$\alpha = \beta = \gamma \neq 90°$

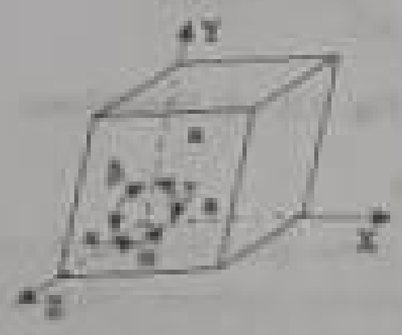



Fig. 7.9 (f) Rhombohedral

**Example:** Calcite.

### 7. Hexagonal system

In this system, two axial lengths of unit cell (say horizontal) are equal and lying in one plane at angle 120° with each other. (fig. 7.9 (g)).

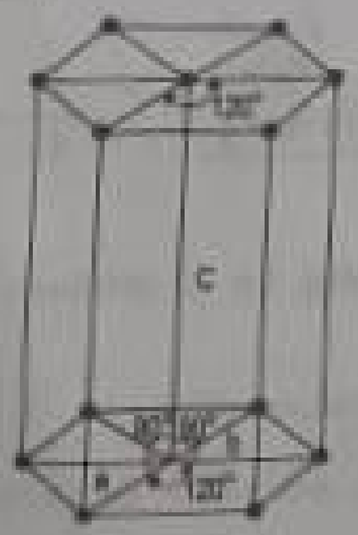



Fig. 7.9 (g) Hexagonal



The third axial length (say vertical) is either longer or ...ger than other two and it is perpendicular to this plane.

i.e., $a = b \neq c$ and

$\alpha = \beta = 90°, \quad \gamma = 120°$

...mple: Quartz, Tourmaline.

**Table 7.1**

**Seven Crystal Systems**

| Crystal system | Axial lengths (a, b, c) | Interfacial angles ($\alpha, \beta, \gamma$) | Example |
|---|---|---|---|
| Cubic | $a = b = c$ | $\alpha = \beta = \gamma = 90°$ | Iron, Copper, $CaF_2$, NaCl. |
| Tetragonal | $a = b \neq c$ | $\alpha = \beta = \gamma = 90°$ | Ordinary white tin, Indium |
| Orthorhombic | $a \neq b \neq c$ | $\alpha = \beta = \gamma = 90°$ | Sulphur, Topaz |
| Monoclinic | $a \neq b \neq c$ | $\alpha = \beta = 90°$, $\gamma \neq 90°$ | $Na_2SO_4$, $FeSO_4$ |
| Triclinic | $a = b \neq c$ | $\alpha \neq \beta \neq \gamma \neq 90°$ | $CuSO_4$, $K_2Cr_2Cl_7$ |
| Rhombohedral | $a = b = c$ | $\alpha = \beta = \gamma \neq 90°$ | Calcite |
| Hexagonal | $a = b \neq c$ | $\alpha = \beta = 90°$, $\gamma = 120°$ | Quartz, Tourmaline |

## 3) BRAVAIS LATTICE

**Bravais showed that there are only 14 possible ways arranging points in space such that the environment the same from each point.**

Thus, there are only 14 types of space lattices which are ...ly developed from 7 crystal systems.

These 14 types of space lattices are known as Bravais ... The lattice can be primitive or non-primitive.

**Simple Triclinic lattice**

It has lattice points at all 8 corners of the unit cell as shown in fig. 7.10 (e).

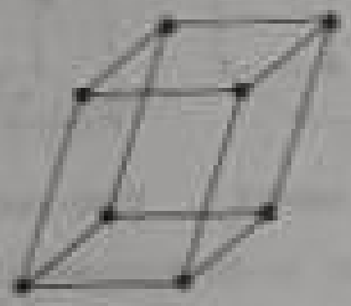


**Fig. 7.10 (e) Simple Triclinic**

**6. Rhombohedral lattice**

It has only one possible space lattice.

**Simple Rhombohedral lattice**

It has lattice points at all 8 corners of the unit cell as shown in fig. 7.10 (f).

**Fig. 7.10 (f) Simple Rhombohedral**

**7. Hexagonal lattice**

It has only one possible space lattice.

**Simple Hexagonal lattice**

It has lattice points at all 12 corners of the hexagonal unit cell and 2 lattice points each at the centre of two hexagonal faces of the unit cell (top and bottom) as shown in fig. 7.10 (g).



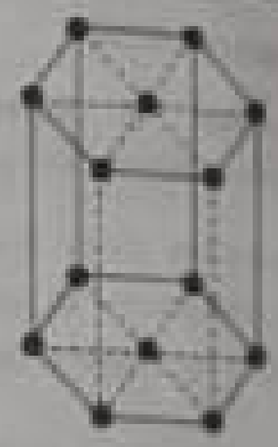


**Fig. 7.10 (g) Simple Hexagonal**

In fact, it is proved mathematically that there are only 14 pendent ways of arranging points in three dimensional space h that each arrangement confirms to the definition of space tice.

**Characteristics of the unit cell**

The unit cell is characterized by the following parameters (assuming one atom to one lattice point)

(i) ***Number of atoms per unit cell***

(ii) ***Coordination number***

(iii) ***Nearest neighbouring distance***

(iv) ***Atomic radius***

(v) ***Packing factor***

**Number of atoms per unit cell**

**It is the number of atoms possessed by the unit cell.** It is determined by the arrangement of atoms in the unit

### Primitive cell

A primitive cell is the simplest type of unit cell which contains only one lattice point per unit cell (contains lattice points only at the corners of unit cell).

Example: Simple Cubic (SC), Simple Tetragonal

### Non - primitive cell

The unit cell which contains more than one lattice point is called non - primitive cell.

Example: BCC, FCC and HCP contains more than one lattice point per unit cell.

If the number of lattice points per unit cell is two (BCC), three and four (FCC), then the unit cell is called **doubly primitive, triply primitive** and **quadruply primitive** respectively.

**Table 7.2**

**Bravais lattices**

| S. No. | Crystal system | Number of possible types | |
|---|---|---|---|
| 1. | Cubic | 3 | Simple, Body - centred and Face centred |
| 2. | Tetragonal | 2 | Simple and Body - centred |
| 3. | Orthorhombic | 4 | Simple, Base - centred, Body - centred and Face - centred |
| 4. | Monoclinic | 2 | Simple and Base - centred |
| 5. | Triclinic | 1 | Simple |
| 6. | Rhombohedral (Trigonal) | 1 | Simple |
| 7. | Hexagonal | 1 | Simple |



### 1. Cubic lattice

It has 3 possible types of arrangements of lattice points

(i) **Simple (or primitive) cubic lattice (SC)**

It has lattice points at all 8 corners of the unit cell as shown in fig. 7.10 (a).

(ii) **Body - centred cubic (bcc) lattice**

It has lattice points at all 8 corners of the unit cell and one lattice point at the body centre as shown in fig. 7.10 (a).

(iii) **Face - centred cubic (fcc) lattice**

It has lattice points at all 8 corners of the unit cell and one lattice point at each face centre of 6 faces of the cube as shown in fig. 7.10 (a).

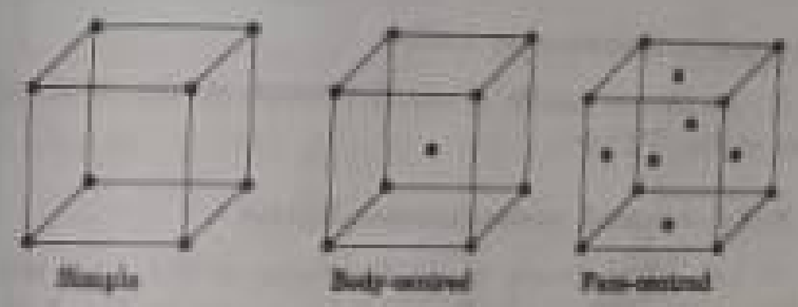



**Fig. 7.10 (a) Cubic lattice**

### 2. Tetragonal lattice

It has two possible types of lattices.

(i) **Simple tetragonal lattice**

It has lattice points at all 8 corners of the unit cell as

**1. Number of atoms per unit cell**

The unit cell of the BCC structure is shown in fig. 7.17

Each corner atom is shared by 8 surrounding unit cells

Hence, the share of one unit cell $= \frac{1}{8}$ of corner atoms.

There are '8' corner atoms.

Contribution of all corner atoms $= \frac{1}{8} \times 8 = 1$ atom

There is one atom at the body centre of each unit cell

Total number of atoms in one unit cell

$= 1 + 1 = 2$ atoms

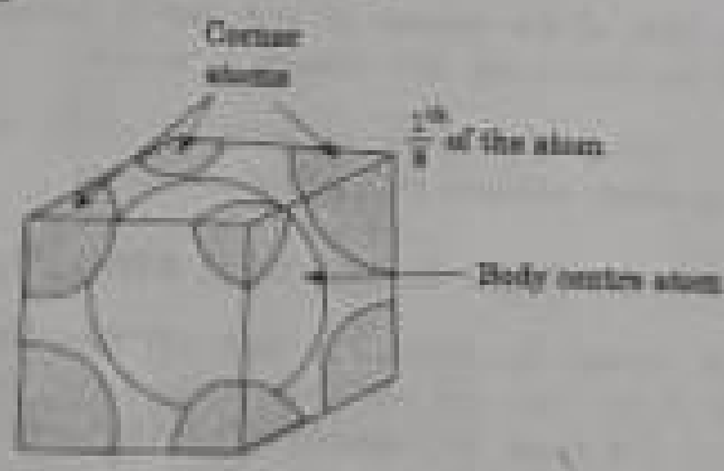



Fig. 7.17 BCC unit cell

**Coordination number**

In the unit cell of BCC structure, there is one atom (say atom X) at the body centre of the unit cell. There are '8' atoms at the 8 corners of the unit cell as shown in fig. 7.18

The corner atoms do not touch each other. But all the eight corner atoms touch the body centre atom along the body diagonal. Thus, for body centre atom 'X', there are 8 nearest neighbours (ie., 8 corner atoms).



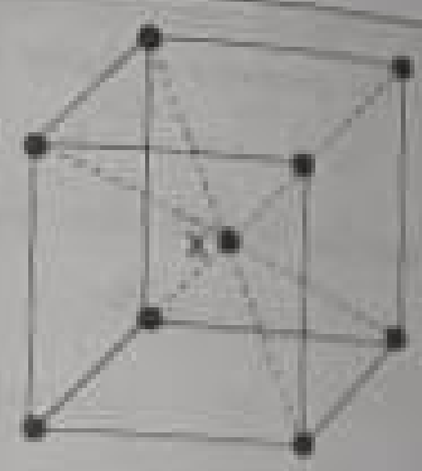


Fig. 7.18

Hence, the coordination number of body centred structure is 8.

The coordination number can also be determined in another way by taking the corner atom as reference atom.

In a BCC structure, each corner atom is surrounded by '8' body centred unit cells. Therefore, the nearest adjacent neighbours of any corner atom are the '8' body centred atoms of the surrounding '8' unit cells.

**Thus, the coordination number is 8.**

**Atomic radius**

The corner atoms do not touch each other. However, each corner atom touches the body centre atom. The unit cell of BCC is shown in fig. 7.19. The side of the unit cell is 'a'.

Consider the atoms at A, G and at the centre of the unit cell.

It is clear from fig. 7.19 that the corner atoms A and G are the nearest neighbouring atoms to the body centre atom G.

These atoms lie in a straight line along the body diagonal of the cube.

### (iii) Coordination Number (CN)

**It is the number of nearest atoms directly surrounding a particular atom in a crystal.**

The coordination number gives the information about the packing of atoms in a structure. It tells whether the crystal structure is closely packed or loosely packed.

If the coordination number is high, then the structure is more closely packed. If it is low, then the structure is loosely packed.

### (iii) Nearest neighbouring distance (2r)

**It is the distance between the centres of two nearest neighbouring atoms.**

It is expressed in terms of the length of edge of the unit cell 'a' and it is 2r in simple cubic. (Fig. 7.11)

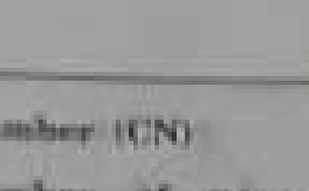



**Fig. 7.11 Nearest neighbouring distances atomic radius**

### (iv) Atomic radius (r)

It is half of the distance between two nearest neighbouring atoms in a crystal. It is denoted by 'r'. It is usually expressed in terms of cube edge 'a' (lattice parameter)

For a simple cubic unit cell, the atomic radius (Fig. 7.11)

$$r = \frac{a}{2}$$



### ...) Packing Factor (Pf)

**It is defined as the ratio of total volume occupied ... the atoms in a unit cell to the total volume of a unit ...**

...king factor

$$\frac{\text{Total volume occupied by the atoms in a unit cell (v)}}{\text{Total volume of the unit cell (V)}} = \frac{v}{V}$$

$$\frac{\text{Number of atoms per unit cell} \times \text{Volume of one atom}}{\text{Total volume of the unit cell}}$$

It is also known as **density of packing**.

The packing factor tells us how closely the atoms are ...ked in the unit cell. A high packing factor indicates that ...ms are very closely packed and therefore there is very little ...upied space.

On the other hand, a less packing factor indicates loose ...ing of atoms and hence there is relatively more unoccupied ...e.

## ...RDINATION NUMBER AND PACKING FACTOR FOR ...TAL STRUCTURES – SC, BCC, FCC and HCP

It is noted that a large number of metallic crystal ...ures have hcp, fcc and bcc structures. Simple Cubic (SC) ...ure is very rare in metals.

The alkali metals Li, Na, K etc., have bcc structures, some ...sition elements and rare earths have fcc structures, elements ...second group have hcp structures.

### ...) SIMPLE CUBIC (SC) STRUCTURE

The simple cubic structure is the simplest and easiest ...l structure. In this structure, there is one atom at each ...e 8 corners of unit cell. These atoms touch each other ...ng cube edges. (fig. 7.12).

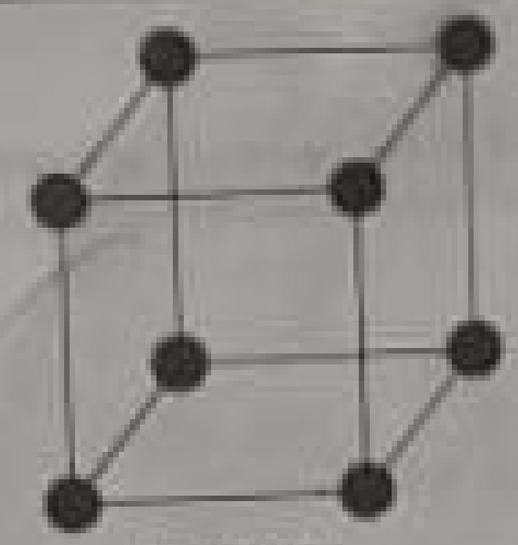


Fig. 7.12 (a)

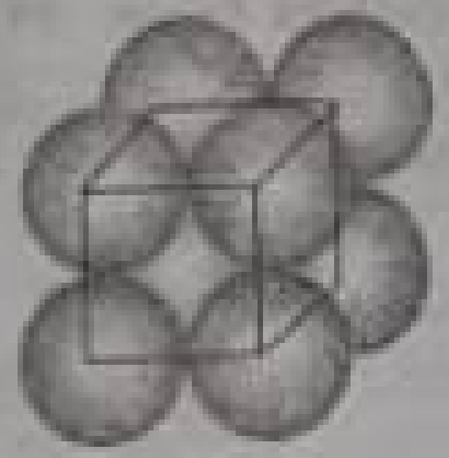


Fig. 7.12 (b)

**Fig. 7.12 Simple cubic - unit cell**

### 1. Number of atoms per unit cell

The unit cell of a simple cubic structure is shown in fig 7.12. The representative arrangement is drawn in fig 7.12 (a). The actual way of arrangement is shown in Fig 7.12 (b).

There are 8 atoms, one atom at each corner of unit cell. Each corner atom is shared by 8 adjacent unit cells (Fig 7.13)

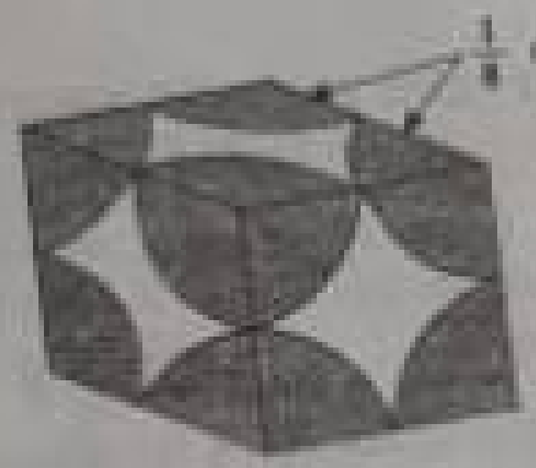



**Fig. 7.13 Simple cubic - unit cell**

$$\therefore \text{Share of each unit cell} = \frac{1}{8} \text{ of corner atoms}$$

$$= \frac{1}{8} \times 8 = 1$$

Total number of atoms in one unit cell = 1 atom



### Coordination number

Simple cubic unit cell has 8 corner atoms. Let us consider of the corner atoms (say X). It is shared by 8 adjacent unit as shown in fig 7.14.

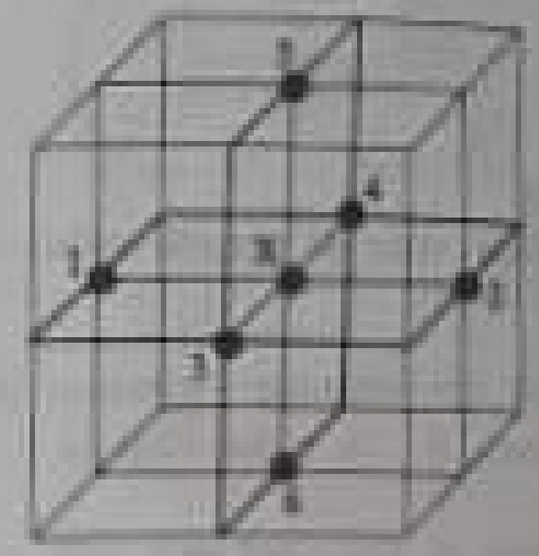



**Fig 7.14**

There are 4 nearest neighbouring atoms to this particular X which are shown by 1, 2, 3, and 4 in a plane **zontal plane**). Further, there are 2 more nearest atoms directly above (atom 5) and the other one directly below the atom X.

Thus, there are only six (4 + 2) nearest neighbours for the X

**Hence, coordination number for simple cubic is 6.**

> Similarly if we consider any corner atom, the total number of nearest neighbours i.e., the co-ordination number is the same.

### radius

Consider a face of unit cell of a simple cubic structure (fig The atoms touch each other along the edges of the cube

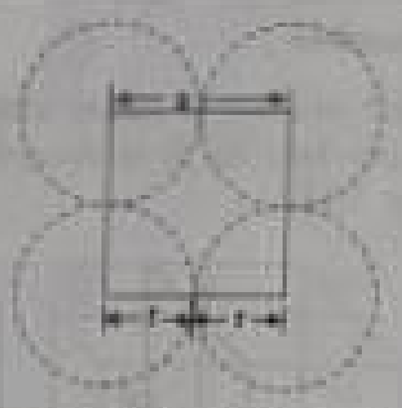


Fig. 7.15 Face view of simple cubic - unit cell

It is clear that the distance between the centres of two nearest atoms is equal to the cube edge a.

If 'a' is the side of the unit cell and $r$ its radius, then from fig. 7.15,

$$2r = a$$

$$\boxed{r = \frac{a}{2}}$$

**4. Packing factor**

Number of atoms per unit cell = 1

Volume of the atoms in the unit cell, $v = 1 \times \frac{4}{3}\pi r^3$

Atomic radius $r = \frac{a}{2}$

Total volume of the unit cell, $V = a^3$

We know that packing factor = $\frac{v}{V}$

Substituting for $v$ and $V$, we have



$$\text{...king Factor} = \frac{\frac{4}{3}\pi r^3}{a^3}$$

Substituting for $r$, we have

$$= \frac{\frac{4}{3}\pi\left[\frac{a}{2}\right]^3}{a^3} = \frac{\frac{4}{3}\pi\frac{a^3}{2^3}}{a^3} = \frac{\frac{4}{3}\pi\frac{a^3}{8}}{a^3}$$

$$= \frac{\pi}{6} = \frac{3.14}{6} = 0.52$$

...king factor = $0.52 \times 100\ \%$

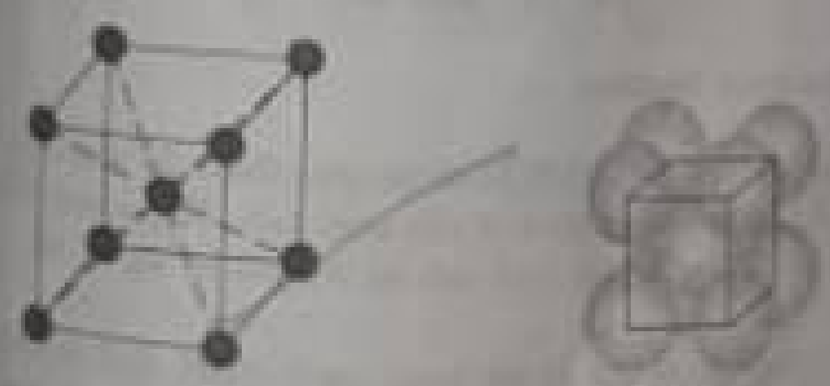
$$\boxed{PF = 52\%}$$

Thus, 52% of the volume of unit cell is occupied by ... and the remaining 48% volume is vacant.

...mple: Only one element polonium ($P_o$) at certain ...perature range exhibits this crystal structure.

**3. BODY - CENTRED CUBIC (BCC) STRUCTURE**

In this crystal structure, the unit cell has one atom at ...corner of the cube and one atom at the body centre of the ...7.16 (a). The atoms represented as hard spheres are shown ...7.16 (b).



(a) Unit cell - BCC (b) Hard sphere model

Fig. 7.16 Body - centred cubic cell

From the geometry of figure 7.19,

$$AG = r + 2r + r = 4r$$

on squaring on both sides, we get

$$AG^2 = (4r)^2$$

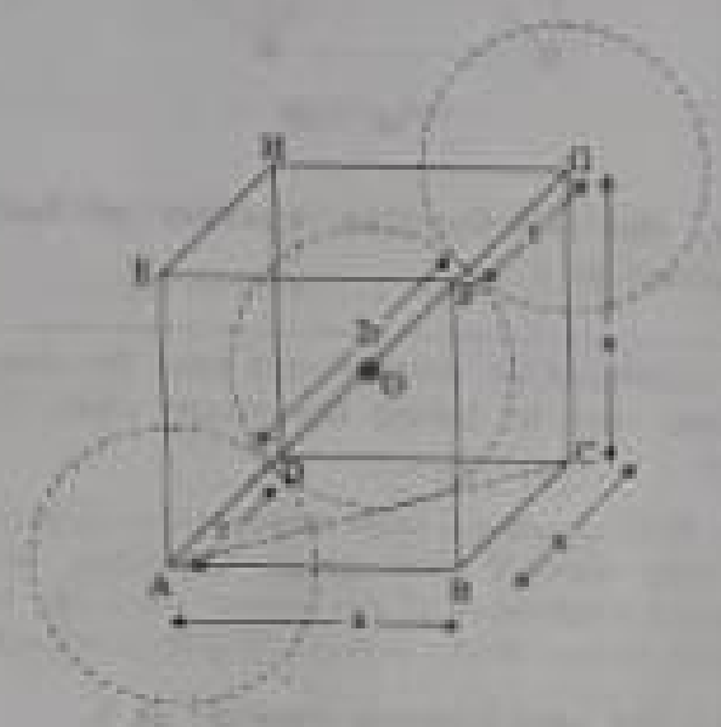



Fig. 7.19 Unit cell of BCC

From the right angled $\triangle$ ABC,

$$AC^2 = AB^2 + BC^2$$

substituting for AB and BC from the fig 7.18, we have

$$AC^2 = a^2 + a^2$$

$$AC^2 = 2a^2$$



From the right angled $\triangle$ ACG,

$$AG^2 = AC^2 + CG^2$$

Substituting for $AG^2$, $AC^2$ and $CG^2$, we have

$$(4r)^2 = 2a^2 + a^2 + a^2$$

$$4^2 r^2 = 3a^2$$

$$\text{or } r^2 = \frac{3a^2}{4^2}$$

Taking square root on both sides, we have

$$\sqrt{r^2} = \sqrt{\frac{3a^2}{4^2}}$$

$$\sqrt{r^2} = \frac{\sqrt{3}\sqrt{a^2}}{\sqrt{4^2}}$$

$$\boxed{r = \frac{\sqrt{3}\,a}{4}}$$

**Packing factor**

Number of atoms per unit cell = 2

Volume of 2 atoms in the unit cell, $v = 2 \times \frac{4}{3}\pi r^3$

$$\text{Atomic radius } r = \frac{\sqrt{3}\,a}{4}$$

Volume of the unit cell, $V = a^3$

$$\text{Packing factor} = \frac{v}{V}$$

Share of each unit cell = $\frac{1}{8}$ of corner atoms

Number of atoms per unit cell from the contribution of corner atoms = $\frac{1}{8} \times 8 = 1$ atom

In addition, there are 6 atoms at the 6 face centres of the cube. Each face-centred atom is shared by 2 adjacent unit cells

Hence, the share of each unit cell = $\frac{1}{2}$ of face-centred atoms

Number of atoms in the unit cell from the contribution of face-centered atom

$$= \frac{1}{2} \times 6 = 3 \text{ atoms}$$

Total number of atoms per unit cell

$$= 1 + 3 = 4 \text{ atoms}$$

**2. Coordination number**

In FCC structure, there are 8 corner atoms and 6 face centred atoms one at the centre of each face of the unit cell

Consider a corner atom (X) of a unit cell as shown in fig 7.22. There are three mutually perpendicular planes with a common point of intersection on the atom X.

In plane I, it has 4 face centred atoms (1, 2, 3, 4) as nearest neighbours

In plane II, it has 4 more face centred atoms (5, 6, 7, 8) as nearest neighbours for the corner atom X.



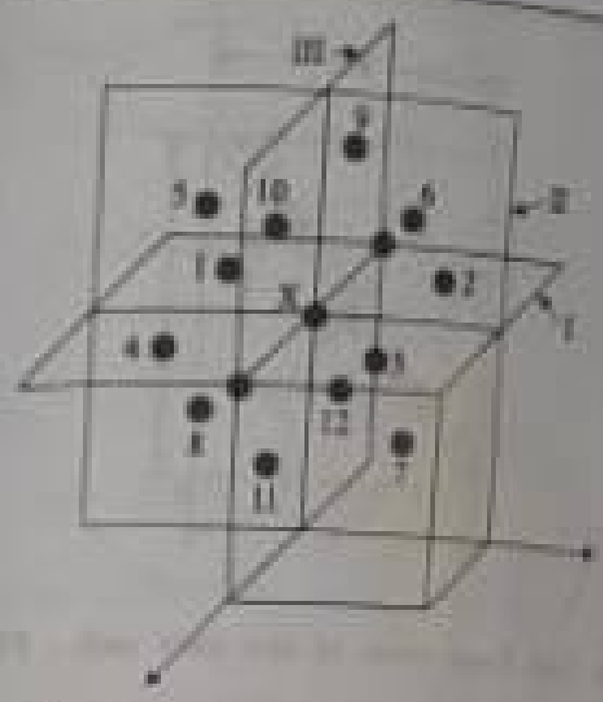



**Fig. 7.22 Calculation of coordination number**

Similarly, plane III has 4 more face centred atoms (9, 10, 11, 12) as nearest neighbours to the corner atom X.

Therefore, total number of nearest atoms to any corner atom is 4 + 4 + 4 = 12

**Hence, coordination number is 12.**

> The coordination number can also be found by using face centred atom as the reference atom, nearest neighbouring atoms are corner atoms. It is found to be the 12.

**Atomic radius**

Consider the atoms at A and C in a face of unit cell of [illegible]. These atoms lie in a straight line along the face diagonal

The atoms touch each other along the face diagonal of the [illegible]. The length of the face diagonal AC = r + 2r + r = 4r (Fig 7.23).

In right angled Δ ABC

$$AC^2 = AB^2 + BC^2$$

Substituting for r and V, we have

$$PF = \frac{2 \times \frac{4}{3}\pi r^3}{a^3}$$

Substituting for r, we have

$$PF = \frac{2 \times \frac{4}{3}\pi\left(\frac{\sqrt{3}\,a}{4}\right)^3}{a^3}$$

$$= \frac{\frac{8}{3}\pi\frac{(\sqrt{3})^3 a^3}{4^3}}{a^3}$$

$$= \frac{\pi}{3} \times \frac{\sqrt{3} \times \sqrt{3} \times \sqrt{3}}{4 \times 4 \times 4}$$

$$= \frac{\pi}{3} \times \frac{3\sqrt{3}}{64}$$

$$PF = \frac{\pi\sqrt{3}}{8}$$

$$PF = \frac{3.14 \times \sqrt{3}}{8} = 0.68$$

or $= 0.68 \times 100\ \%$

$PF = 68\%$

Thus, packing factor is 68% ie., 68% of the volume of unit cell is occupied by atoms and the remaining 32% volume is vacant.

**Common examples of this type of structure**

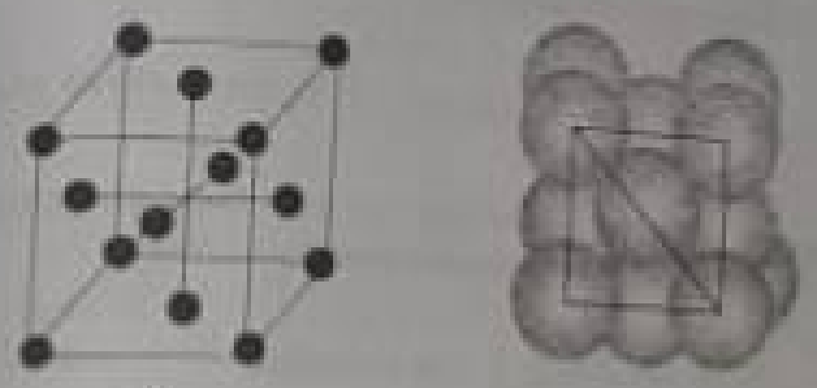
Tungsten, Chromium and Molybdenum



## 7.9 FACE-CENTRED CUBIC (FCC) STRUCTURE

In this type of crystal structure, the unit cell has one atom at each corner of the cube and one atom at the centre of each face. (fig. 7.20).

This structure is close-packed because each atom has 12 nearest neighbours. This type of structure is more common in metals.



(a) (b)

Fig. 7.20 Face-centred cube - Unit cell

**1. Number of atoms per unit cell**

A unit cell of a face-centred cube structure is shown in fig 7.21. There are 8 corner atoms, one at each of its 8 corners. Each corner atom is shared by 8 surrounding unit cells.

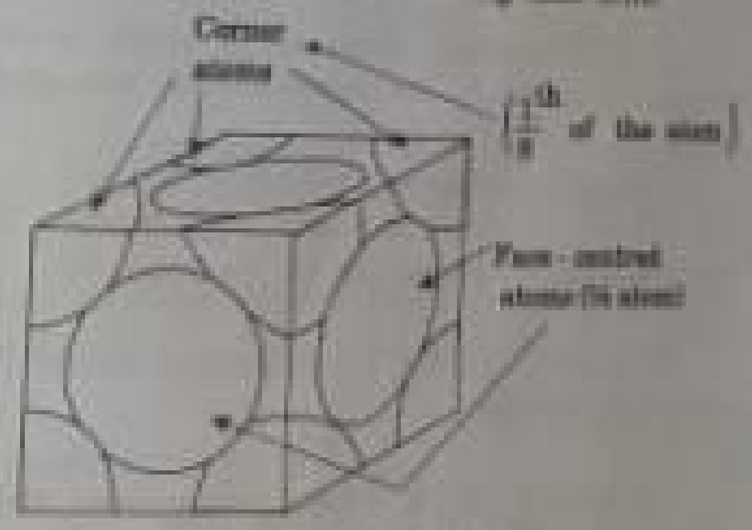



Fig. 7.21 FCC unit cell

**(ii) Number of face centred atoms per unit cell**

Each face centred atom is shared by 2 unit cells. We have 6 face centred atoms.

∴ Number of face centred atom per unit cell

$$= \frac{1}{2} \times 6 = 3 \text{ atoms}$$

**(iii) Number of atoms inside unit cell**

Inside the unit cell, we have 4 atoms represented by 1, 2, 3, 4 in fig. T.26 which are not shared by any other surrounding unit cells.

∴ **Total number of atoms per unit cell** $= 1 + 3 + 4 = 8$

**E. Atomic radius**

The corner atoms do not touch each other. Similarly the face centred atoms also do not touch each other.

But both face centred atoms and corner atoms touch with the atoms (1, 2, 3, 4) situated inside the unit cell as shown in fig. T.26.

For example, the nearest two neighbours which have direct contact (shown by double line) are atoms 'X' and 'Y' as shown in fig. T.26.

A perpendicular is drawn to Y atom which meets the unit cell at a point 'Z' as shown in fig. T.26 which is at a distance of a/4.


Fig. T.26



From fig. T.26,

$$XY^2 = XZ^2 + ZY^2$$

$$XY^2 = XT^2 + TZ^2 + ZY^2 \qquad \because XZ^2 = XT^2 + TZ^2$$

Substituting for XT, TZ and ZY, we have

$$XY^2 = \left(\frac{a}{4}\right)^2 + \left(\frac{a}{4}\right)^2 + \left(\frac{a}{4}\right)^2$$

$$= \frac{a^2}{4^2} + \frac{a^2}{4^2} + \frac{a^2}{4^2}$$

$$= \frac{a^2}{16} + \frac{a^2}{16} + \frac{a^2}{16}$$

$$XY^2 = \frac{3a^2}{16}$$

Taking square root on both sides, we have

$$\sqrt{XY^2} = \sqrt{\frac{3a^2}{16}} = \frac{\sqrt{3}\sqrt{a^2}}{\sqrt{16}}$$

$$XY = \frac{\sqrt{3}\,a}{4}$$

Since XY = 2r, we have

$$2r = \frac{\sqrt{3}}{4}a$$

$$r = \frac{\sqrt{3}\,a}{4 \times 2}$$

$$r = \frac{\sqrt{3}\,a}{8}$$

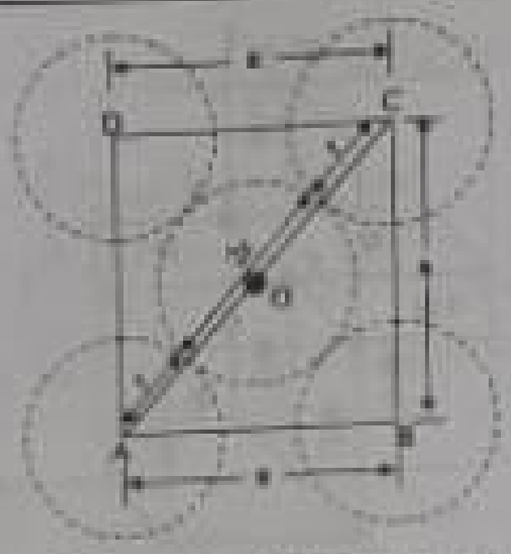



**Fig. 7.23 Face view of the unit cell - FCC**

Substituting for $AC^2$, $AB^2$ and $BC^2$ from fig 7.23, we have

$$(r + 2r + r)^2 = a^2 + a^2 \qquad \because AC = 4r$$

$$(4r)^2 = a^2 + a^2$$

$$4^2 r^2 = 2a^2$$

$$r^2 = \frac{2a^2}{4^2}$$

Taking square root on both sides, we have

$$\sqrt{r^2} = \sqrt{\frac{2a^2}{4^2}} = \frac{\sqrt{2a^2}}{\sqrt{4^2}} = \frac{\sqrt{2}\sqrt{a^2}}{4}$$

$$\boxed{r = \frac{\sqrt{2}\,a}{4}}$$



**3. Packing factor**

Number of atoms per unit cell = 4

Volume of 4 atoms, $v = 4 \times \frac{4}{3}\pi r^3$

Atomic radius $r = \frac{\sqrt{2}\,a}{4}$

Side of the unit cell $= a$

Volume of the unit cell $V = a^3$

Packing factor $= \frac{v}{V}$

Substituting for $v$, $V$ and $r$, we have

$$PF = \frac{4 \times \frac{4}{3}\pi r^3}{a^3} = \frac{4 \times \frac{4}{3} \times \pi\left[\frac{\sqrt{2}\,a}{4}\right]^3}{a^3}$$

$$= \frac{4 \times \frac{4}{3} \times \frac{\pi (\sqrt{2})^3 a^3}{4^3}}{a^3} = \frac{4 \times \frac{4}{3} \times \frac{\pi \times \sqrt{2} \times \sqrt{2} \times \sqrt{2} \times a^3}{4 \times 4 \times 4}}{a^3}$$

$$= \frac{\pi \times 2\sqrt{2}}{3 \times 4}$$

$$PF = \frac{\pi\sqrt{2}}{6}$$

$$= \frac{3.14 \times \sqrt{2}}{6} = 0.74$$

$$= 0.74 \times 100\,\%$$

$$\boxed{PF = 74\%}$$

### Some special cubic crystal structures

In addition to SC, BCC, FCC and HCP, there are some special cubic structures. Some of these structures are derivatives from or combination of the basic structures described above.

## 7.10 DIAMOND CUBIC (DC) STRUCTURE

The diamond cubic structure is a very important crystal structure. Besides diamond, the elemental semiconductors silicon and germanium also have this structure. The unit cell of diamond cubic structure is shown in fig 7.26.

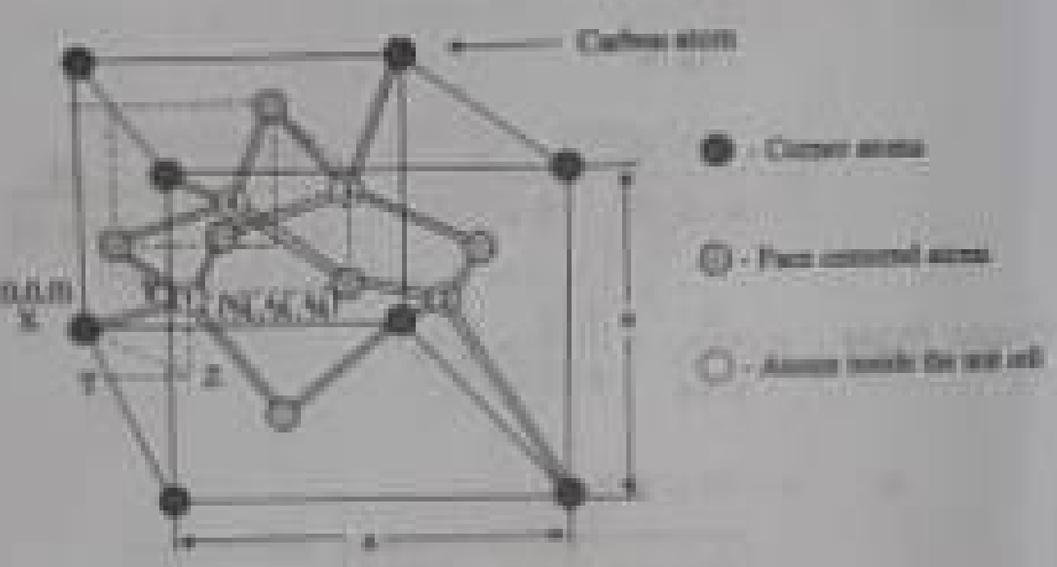



**Fig. 7.26 Unit cell of diamond cubic structure**

This structure is a combination of two interpenetrating face - centred - cubic (FCC) sub lattices.

One sub - lattice has its origin at (0, 0, 0) (atom X). The other sub - lattice has its origin (atom Y) quarter of the way along the body diagonal i.e., at the point $\left(\frac{a}{4}, \frac{a}{4}, \frac{a}{4}\right)$.

It is loosely packed structure since each atom has only four nearest neighbours (ie., coordination number is 4).



### Number of atoms per unit cell

In the unit cell of diamond, the carbon atoms are present in three different positions of the unit cell as shown in fig 7.26

(i) Corner atoms represented by 'C'

(ii) Face centred atoms represented by 'F'

(iii) Four atoms present fully inside the unit cell represented as 1, 2, 3 and 4.

The positions of atoms projected on a cube face is as shown in fig 7.27

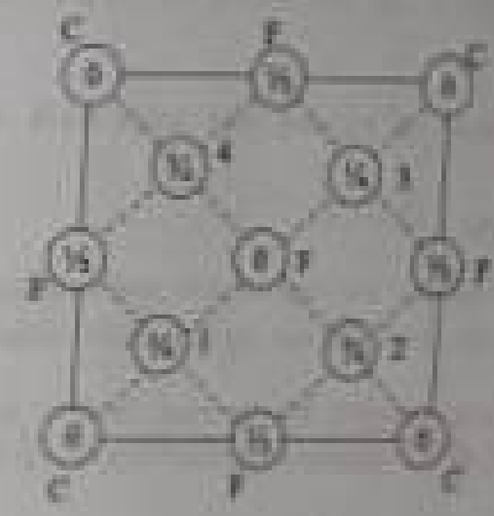



**Fig. 7.27 Diamond structure**
**Atomic position projected on a cube face**

### Number of corner atoms per unit cell

Each corner atom is shared by 8 unit cells. There are 8 corner atoms in the unit cell.

Therefore, the number of atoms due to corner atoms per unit cell

$$= \frac{1}{8} \times 8$$

$$= 1 \text{ atom}$$

$$\therefore \text{Atomic radius } r = \frac{\sqrt{3}\,a}{8}$$

### 3. Coordination number

From fig. 7.26 the number of nearest atoms (shown by double line) for Y atom is 4. Therefore, the coordination number for diamond is 4.

**Coordination number for diamond = 4**

**Note:** The coordination number is found to be same even if it is calculated with respect to atoms say (2), (3), (4), corner (or) face centred atoms.

### 4. Packing factor

We know that Packing factor (PF)

$$= \frac{\text{Volume occupied by the atoms per unit cell (v)}}{\text{Volume of the unit cell (V)}} \quad \ldots (1)$$

Volume occupied by 1 atom

$$= \frac{4}{3}\pi r^3$$

In diamond, we have 8 atoms per unit cell

∴ Volume occupied by all the '8' atoms per unit cell

$$(v) = 8 \times \frac{4}{3}\pi r^3$$

We know that atomic radius for diamond structure

$$r = \frac{\sqrt{3}\,a}{8}$$

∴ Volume occupied by the atoms per unit cell

$$v = 8 \times \frac{4}{3}\pi\left(\frac{\sqrt{3}\,a}{8}\right)^3$$



$$v = 8 \times \frac{4}{3}\pi\frac{a^3(\sqrt{3})^3}{8^3}$$

$$v = 8 \times \frac{4}{3}\pi\frac{a^3\sqrt{3}\times\sqrt{3}\times\sqrt{3}}{8\times8\times8}$$

$$v = \frac{\pi a^3\sqrt{3}}{2\times8}$$

Volume occupied by the atoms per unit cell

$$v = \frac{\pi a^3\sqrt{3}}{16} \quad \ldots (2)$$

Now diamond has cubic structure, the volume of the unit

$$V = a^3 \quad \ldots (3)$$

Substituting the eqns (2) and (3) in (1) we get

$$PF = \frac{v}{V} = \frac{\frac{\pi a^3\sqrt{3}}{16}}{a^3} = \frac{\pi a^3\sqrt{3}}{16a^3}$$

$$\therefore PF = \frac{\pi\sqrt{3}}{16} = \frac{3.14\times\sqrt{3}}{16}$$

Packing factor = 0.34

= 0.34 × 100 %

∴ Packing factor = 34%

*Thus only 34% volume of the unit cell in diamond cubic lattice is occupied by atoms and the remaining 66% volume is empty.*